

CRANFIELD UNIVERSITY

BLESSING EKPE

MODELLING FIRESIDE CORROSION OF SUPERHEATERS AND
REHEATERS FOLLOWING COAL AND BIOMASS COMBUSTION

SCHOOL OF WATER, ENERGY AND ENVIRONMENT

PhD

Academic Years: 2015 - 2019

Supervisor: Dr Joy Sumner
Associate Supervisor: Prof Nigel Simms
April 2019

CRANFIELD UNIVERSITY

SCHOOL OF WATER, ENERGY AND ENVIRONMENT

PhD

Academic Years 2015 - 2019

BLESSING EKPE

MODELLING FIRESIDE CORROSION OF SUPERHEATERS AND
REHEATERS FOLLOWING COAL AND BIOMASS COMBUSTION

Supervisor: Dr Joy Sumner
Associate Supervisor: Prof Nigel Simms
April 2019

This thesis is submitted in partial fulfilment of the requirements for the
degree of Doctor of Philosophy

© Cranfield University 2019. All rights reserved. No part of this
publication may be reproduced without the written permission of the
copyright owner.

ABSTRACT

Specific data analysis methods Principal Component Analysis (PCA) and Partial Least Squares (PLS) have been employed to develop a novel series of fireside corrosion models showing different rates for coal vs biomass, and the UK, US and world-traded coals with different controlling factors. The results from the analysis reveal the potential influence of corrosion resistant alloying elements and fuel contaminants on the fireside corrosion rates which are subsequently employed for fireside corrosion model building. Achieving this aim has involved two key steps i.e. (1) Fireside corrosion data from various plant investigations have been collated for this modelling work, (2) Fireside corrosion model development using PCA and PLS.

The results from UK coal fireside corrosion data indicate that the fireside corrosion rate, while requiring the presence of S, is dependent on the fuel's Cl, Na, and K levels as S is present in excess. The results from the UK woody biomass-fired data show the fireside corrosion rate dependent mainly on K, Ca, and Cl levels from the fuel. Co-firing of coal/biomass highlights slightly different fuel species including Cl, K, Mg, S and P. Data subsets based on probe investigations in the US following coal combustion depends on different variables for modelling when compared to UK coals and thus the fireside corrosion damage is attributed to mainly the fuel's chemistry. High performances of prediction models featuring austenitic tubes under coal/biomass, and ferritic/nickel-based tubes under biomass firing were achieved. However, the predictive performances of the ferritic and nickel-based metals under coal have been the least successful. The PLS method is best suited for prediction as it uses the input data (alloy/fuel elements, metal temperature) to find the most critical variables that have maximum covariance with the dependent variable; i.e. the corrosion rate, as opposed to PCA which only maximises variability in the input data.

Keywords:

Principal Component Analysis, Partial Least Squares, Co-firing, Fuel impurities

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to my sponsors, Biomass and Fossil Fuel Research Alliance (BF2RA), and Niger Delta Development Commission (NDDC) for affording me the opportunity to undertake this research. I thank the project partners (Doosan, EPRI) for supplying plant data that is the mainstay of this research. I am most grateful and indebted to my supervisors, Dr Joy Sumner and Professor Nigel Simms, for their invaluable advice, guidance and patience with me from start to finish.

I also wish to thank my family; my long-suffering mother for her inspiration and encouragements; my sisters, Sandra and Mayen, my nephews for putting up with me as they have complained I have been in school for all their lives, and special gratitude to my cousin, Mary Udo and her family. I would also like to thank my friends, Chiara Riccio, Dominika Orlicka, and Chioma Vivian Osuji, for their unwavering support and confidence in me. I also acknowledge Kim Vercrussye for her valuable advice on the statistical technique employed in this research.

I acknowledge and appreciate my colleagues; Jon, Justin, Andrew, Toyin, Victor, Shurooq, Kalu, Hisham, Talib; and other acquaintances (SWEE) for their support, contributions, and shared experiences.

TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS	iii
LIST OF TABLES	xi
LIST OF EQUATIONS.....	xx
LIST OF ABBREVIATIONS	xxiii
1 INTRODUCTION.....	1
1.1 Current Energy Overview.....	1
1.2 Coal Imports to the UK: World Traded Coals.....	3
1.3 Coal / Biomass Combustion	4
1.3.1 Pulverised Coal Combustion	4
1.3.2 Biomass Combustion.....	6
1.3.3 Co-firing Coal with Biomass.....	7
1.4 Research Overview, Aim and Objectives.....	8
1.4.1 Aim.....	9
1.4.2 Objectives	9
1.5 Thesis Structure	9
1.6 Research Presentations and Publication	10
2 LITERATURE REVIEW	13
2.1 Overview of Fireside Corrosion Issues in Power Plants	13
2.2 Superheaters and Reheaters	15
2.2.1 Material Selection and Alloy Grades	17
2.3 Fuels.....	19
2.3.1 Coal Chemistry.....	19
2.3.2 Biomass Chemistry.....	24
2.4 Comparison of Coal Properties from Different Regions	26
2.5 Mineral Matter Transformation during Coal and Biomass Combustion.....	34
2.5.1 Impact of Coal Chemistry in Combustion (UK vs the US).....	35
2.5.2 Impact of Biomass Chemistry in Combustion.....	37
2.6 Factors that Affect Deposition Rate and Composition.....	37
2.6.1 Deposit Composition	37
2.6.2 The Effect of Temperature	38
2.6.3 The Effect of SO ₃	39
2.6.4 The Effect of Chlorine on Corrosion.....	39
2.6.5 The Effect of Alkali Metals on Corrosion	40
2.6.6 The Effect of Alloy Materials.....	41
2.6.7 The Effect of Co-firing Coal and Biomass.....	41
2.7 Fireside Corrosion Mechanism.....	42
2.8 Review of Previous Fireside Corrosion Models.....	44
2.8.1 Research Gap in Fireside Corrosion Model Development.....	51

2.9 Statistical Technique Employed to Analyse Fireside Corrosion Data and Build Fireside Corrosion Prediction Models	52
2.9.1 Principal Component Analysis - Overview	52
2.9.2 Partial Least Squares - Overview	53
2.9.3 The difference between PCA and PLS	53
2.9.4 Concluding Remarks on the use of Statistical Techniques for Fireside Corrosion Modelling	54
3 METHODOLOGY	55
3.1 Data Collection and Gathering	55
3.1.1 CEGB PE-8 UK Dataset: Field Investigations on UK Utility Boilers Burning UK Coal.....	56
3.1.2 US Coal Data: Field Investigations on US Utility Boilers Burning US Coal.....	60
3.1.3 UK Data on Austenitic Materials: Field Investigation on UK Utility Boilers Burning Eastern European Coal.....	67
3.1.4 UK Data on Coating Materials: Field Investigation on UK Utility Boiler Burning UK and World -Traded Coals	69
3.1.5 Biomass Dataset: Field Investigations on UK Utility Boilers Burning Biomass	71
3.1.6 Co-firing Data: Field Investigations on UK Utility Boilers Co-firing Coal and Biomass.....	76
3.1.7 Data Gathering and Collection Concluding Remarks	77
3.2 Multivariate Statistical Analysis.....	80
3.2.1 Descriptive Statistics and Data Visualisation.....	80
3.2.2 Principal Component Analysis	80
3.2.3 Partial Least Squares	93
3.3 Fireside Corrosion Model Structure	101
3.4 Fireside Corrosion Model Development Flow Chart/Summary.....	102
4 RESULTS AND DISCUSSION: MODEL DEVELOPMENT.....	105
4.1 Corrosion Dataset	105
4.1.1 Limitations in Dataset Construction.....	106
4.2 Fireside Corrosion Model Development	109
4.2.1 Fireside Corrosion Framework Models.....	109
4.2.2 Variables Selected (Input Parameters) for Model Building	113
4.3 Coal Models.....	119
4.3.1 Austenitic Leading Tubes/UK Coal (PCA/PLS Models 1A and 1B).....	119
4.3.2 Discussion on PCA Coal Model 1A and PLS Coal Model 1B Results.....	127
4.3.3 Discussion on PCA/PLS Coal Corrosion Models 2-9.....	132
4.4 Biomass Models (Corrosion Models 10-13)	138
4.5 Co-firing Models (Corrosion Models 14-16)	142
4.6 Summary of PCA, PLS Fireside Corrosion Models.....	144
5 VARIATION IN CORROSION MODEL BUILDING	147

5.1 Variations in Model Structure	147
5.1.1 Change in Model Parameters Represented as Framework Model C: Metal Temperature (K) and Gas Temperature (K)	147
5.2 PCA Using Combined Variables from Loadings Plot.....	149
5.3 PCA/PLS Interaction (Fireside Corrosion) Models.....	157
5.3.1 PCA/PLS Interaction Model for Data Subset 1.....	158
5.3.2 PCA/PLS Interaction Model for Data Subset 5.....	160
5.3.3 PCA/PLS Interaction Model for Data Subset 10.....	161
5.3.4 Summary of Interaction Models	162
5.4 Corrosion Data Sensitivity Analysis.....	163
5.4.1 PLS Model 1B with Modified Cr Content	163
6 MODEL PERFORMANCE AND VALIDATION.....	167
6.1 Assessment of Model Performance	167
6.2 Summary and Discussion of Model Predictive Performances for PCA vs PLS	172
6.3 Model Adequacy and Validation.....	172
6.3.1 Graphical Residual Testing	177
6.4 Comparison between PCA, PLS and PE-8 Models for PE-8 Data (UK Data subset 1) and US Data	181
6.4.1 PE-8 vs PCA, PLS Models (UK data subset 1).....	181
6.4.2 PE-8 vs PCA, PLS Models (US data subset 5)	183
6.5 Applicability of PCA/PLS Fireside Corrosion Models	185
7 CONCLUSIONS	187
8 RECOMMENDATIONS FOR FUTURE WORK.....	191
REFERENCES	193
APPENDICES	213
Appendix A Fuel Data	213
Appendix B Correlation Matrix.....	223
Appendix C Variable Selection Criteria (Framework Model F)	241
Appendix D Framework Model A-E Results	269
Appendix E Model Performance Summary (Frameworks A-F)	293
Appendix F Corrosion Data Sensitivity (PCA Model).....	299
Appendix G Notes on the PCA/PLS Modelling Approach	301

LIST OF FIGURES

Figure 1-1: Global energy-related carbon dioxide (CO ₂) emissions by source (International Energy Agency, 2019).....	1
Figure 1-2: Top coal producing countries (in million tonnes of oil equivalent) (McGrath, 2015)	3
Figure 1-3: Imports of coal to the United Kingdom between 2002 and 2017 (UK Department for Business, 2018).....	4
Figure 1-4: Schematic of a pulverised coal-fired plant (Peltier, 2013)	5
Figure 2-1: Location of superheaters and reheaters in a subcritical boiler (Babcock and Wilcox Energy Solutions, 2018).....	14
Figure 2-2: Location of radiant (pendant) and low-temperature convective superheaters (ATC-CES, 2018)	15
Figure 2-3: The ideal reheat Rankine cycle (Mechanical Engineering Lectures, 2017)	16
Figure 2-4: Stainless steel alloy grades (Schade <i>et al.</i> , 2008)	18
Figure 2-5: 10 ⁵ hours rupture strength as a function of stress and temperature for various steel and nickel-based materials. Ni-based have been circled for clarity (Modified from Shingledecker, 2012).....	19
Figure 2-6: Classification of coal based on organic and inorganic components (Modified from Jones, 2005)	21
Figure 2-7: Major coalfields of the British Isles (English, Scottish, Welsh and Northern Ireland coalfields) (Northern Mine Research Society, 2016)	27
Figure 2-8: Major coalfields of the United States (Energy Information Administration, 1999)	29
Figure 2-9: Schematic diagram showing the transformation of mineral matter during coal combustion (CoalTech Pty Ltd, 2007)	35
Figure 2-10: Broad spread in sulphur and chlorine levels in UK coals delivered to two UK power stations over the period 1992-1994. The striped region shows the mean value for UK stations (Wright and Krause, 1997b)	36
Figure 2-11: Corrosion dependence on temperature (Simms <i>et al.</i> , 2007).....	38
Figure 2-12: Schematic illustration of the deposit formed on the upstream side of the superheater tube (Wright and Kung, 2018).....	43
Figure 2-13: Comparison of reactive species for a range of coals with calculated RCP values (Wright and Shingledecker, 2015).....	48
Figure 2-14: Neural prediction of fireside corrosion rate as a function of sulphur content in a typical thermal Indian coal (Kumari <i>et al.</i> , 2017).....	50

Figure 2-15: Neural prediction of fireside corrosion rate as a function of SO _x content in the flue gas (Kumari <i>et al.</i> , 2017)	50
Figure 2-16: Transformation of input data using PCA; the blue arrows show the derived principal components. The horizontal axis on the graph at the right is PC 1, and the vertical axis is PC 2 (University of Illinois, 2000)	53
Figure 3-1: Block chart of data subsets analysed classified according to the fuel type .	56
Figure 3-2: Summary of steps in principal component analysis (steps represented in blue are via the PCA module in STATISTICA and brown portion represents computation in MS Excel)	83
Figure 3-3: An example of a loadings plot of PC 1 vs PC 2 constructed using independent input values of PC 1 and PC 2 from the loadings table in Table 3-21. The loadings plot shows the correlation between the variables and the PCs and the correlation (positive or negative) between the variables.	88
Figure 3-4: Summary of steps of partial least squares (blue section implemented using PLS application in STATISTICA and brown portion computed in MS Excel)	95
Figure 3-5: Average R ² values of the predictor (red) and dependent variable (blue) versus the number of PLS components.....	98
Figure 3-6: Flow chart adapted from Shardt (2015) summarising the PCA/PLS fireside corrosion model building	102
Figure 4-1: A screenshot of detailed result from Coalqual database for US coal. The sample description (LHS) can be used to filter the search field (Palmer; et al., 2015)	107
Figure 4-2: Variables selected and retained in PCA model 1A plotted using standardised regression coefficients (the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	122
Figure 4-3: Box and whisker plot showing the median, range and 25th-75th percentile for the Cl and S content (in the fuel) from data subset 1	129
Figure 4-4: PCA loadings plot (PC 1 vs PC 2) for data subset 1 showing the PC-variable relationship and the correlation between the predictor variables (fuel elements are in symbols and the alloy elements in full; circled region indicates fuel elements Ti and Si)	131
Figure 4-5: PCA loadings plot (PC 1 vs PC 2) for data subset 3 showing the PC-variable correlation and the relationship between the predictor variables (circled portion shows the highly correlated alloy elements)	134
Figure 4-6: Average R ² values of Y, the corrosion rate (blue) and X, input data (red) plotted against the number of PLS components (PLS model 6B)	136
Figure 4-7: Plot of corrosion rates measured against metal temperature, US coal data subset 6.....	137

Figure 4-8: Box and whisker plot showing the median, range and 25th-75th percentile of data for metal and gas temperatures (in degrees C) for biomass data subset 12	141
Figure 5-1: Loadings plot for PC 1 vs PC 2 from PE-8 data subset 1 showing highly correlated variables combined for re-analysis (circled regions). Fuel elements are indicated with symbols; alloy elements are written in full. The supplementary variables are in red.	150
Figure 5-2: Loadings plot for PC 1 vs PC 2 from biomass data subset 10 showing correlated fuel variables	155
Figure 5-3: Loadings plot for PC 1 vs PC 2 from biomass data subset 11 (Ni-based tubes) showing correlated variables (focus is on the circled region; silicon from the alloy and S from the fuel; iron from the alloy and K from the fuel).....	155
Figure 5-4: Loadings plot for PC5 vs PC6 from data subset 3 showing correlated variables	157
Figure 5-5: Comparison of measured corrosion rates and predicted (PLS) corrosion rates using original Cr values and modified Cr values for data subset 1.....	165
Figure 6-1: Scatterplot of the PCA models against the measured corrosion rates for data subsets 1A-16A	170
Figure 6-2: Scatterplot of the PLS models against the measured corrosion rates for data subsets 1B-16B	171
Figure 6-3: Scatterplot showing the predicted corrosion rates versus the measured corrosion rates and the R^2 value for the test data (data subset 1B).....	176
Figure 6-4: Residual plots for PCA models 1A-16A	178
Figure 6-5: Residual plots for PLS models 1B-16B.....	179
Figure 6-6: Residual plot for modified PLS model 7B (v2) excluding the supercritical portion of the corrosion data (US coatings data with coal).....	181
Figure 6-7: Comparison of measured corrosion rate with predicted rates from PE-8 model, PCA model 1A, and PLS model 1B (PE-8 UK data subset 1).....	183
Figure 6-8: Comparison of measured corrosion rate with predicted rates from PE-8 model, PCA model 5A, and PLS model 5B (US data subset 5)	184
Figure F-1: Comparison of measured corrosion rates and predicted (PCA) corrosion rates using original Cr values and modified Cr values for data subset 1	299

LIST OF TABLES

Table 1-1: List of conferences, other events and paper submitted for review.....	11
Table 2-1: Coal classification based on rank (dry mineral matter free) (Toporov, 2014)	20
Table 2-2: Common coal minerals (Riley, 2007)	23
Table 2-3: General classification of biomass varieties (Vassilev <i>et al.</i> , 2010)	25
Table 2-4: Chemical analysis of coals from different mines (UK) (Wigley and Williamson, 1993; Energieonderzoek Centrum Nederland (ECN) Phyllis2, 2012)	28
Table 2-5: Chemical Analysis of Various Coals (US) (*Smith and Smoot, 1990; **Laumb, 2008).....	31
Table 2-6: Chemical Analysis of Selected World Traded Coals: Russia, Indonesia (Energieonderzoek Centrum Nederland (ECN) Phyllis2, 2012)	33
Table 2-7: Total Cl, S, and ash content from three selected coals (British coal, high-Cl Illinois (US) coal and low-Cl Illinois coal (US)) (Chou <i>et al.</i> , 1999)	36
Table 3-1: Ashed fuel analyses (excluding Na ₂ O) and ash and sulphur contents of Midlands and North Eastern region coals (UK) (Wright and Krause, 1997b)	58
Table 3-2: Nominal alloy compositions (for austenitic tubes) for data subsets 1 and 2.	60
Table 3-3: Nominal alloy compositions (for ferritic tubes) for data subsets 3 and 4.....	60
Table 3-4: Ashed fuel analyses (expressed as highest oxides), Cl and S for US coal from data subsets 5-7	62
Table 3-5: Nominal alloy composition of austenitic tubes for data subset 5 (Blough, Seitz and Girshik, 1998; Blough <i>et al.</i> , 2000; Purgert <i>et al.</i> , 2015).....	64
Table 3-6: Nominal alloy compositions of nickel-based metals for data subset 6 (Blough <i>et al.</i> , 2000; Purgert <i>et al.</i> , 2015)	65
Table 3-7: Nominal coating compositions for data subset 7 (Blough, Seitz and Girshik, 1998; Blough <i>et al.</i> , 2000; Purgert <i>et al.</i> , 2015).....	66
Table 3-8: The average ashed fuel analyses (expressed as highest oxides) values for data subset 8 (Doosan Babcock, 2011).....	68
Table 3-9: Nominal alloy compositions of austenitic tubes for data subset 8 (Doosan Babcock, 2011)	68
Table 3-10: Fuel analyses covering the UK and World Traded Coals for data subset 9	70
Table 3-11: Coating analyses determined via X-ray elemental analysis for data subset 9 (Uniper Technologies, 2016c)	70

Table 3-12: Ashed fuel analysis (expressed as highest oxides) for biomass (woody) fuels from data subsets 10-13 (E.ON Technologies, 2015b; Uniper Technologies, 2016a)	72
Table 3-13: Nominal alloy compositions (for austenitic tubes) for data subset 10 (E.ON Technologies, 2015b; Uniper Technologies, 2016a)	73
Table 3-14: Nominal alloy compositions (for nickel-base tubes) for data subset 11 (E.ON Technologies, 2015b; Uniper Technologies, 2016a).....	74
Table 3-15: Nominal alloy compositions (for ferritic tubes) for data subset 12 (E.ON Technologies, 2015b; Uniper Technologies, 2016a)	74
Table 3-16: Nominal coatings' compositions for data subset 13 (E.ON Technologies, 2015b; Uniper Technologies, 2016a).....	75
Table 3-17: Ashed fuel analyses (expressed as highest oxides) of Daw Mill coal, wood and CCP for data subsets 14-16 (Powergen, 2004)	76
Table 3-18: Nominal alloy compositions for tube materials (austenitic and ferritic) for data subsets 14, 15 and 16 (Powergen, 2004)	77
Table 3-19: Metal and gas temperatures and alloys analysed within the 16 data subsets	78
Table 3-20: Eigenvalues of the correlation matrix (PCA) for data subset 1 – shaded cells are the eigenvalues greater than 0.5 (selection criteria).....	86
Table 3-21: Factor-variable correlations (loadings) that describe the weight of importance of each independent input variable to the PCs. The alloy elements are written in full, and the fuel elements are shown in symbols. Marked loadings (in red) are > 0.5	87
Table 3-22: Example of varimax rotated loadings plot showing the correlations between the independent input variables and the PCs. The alloy elements are written in full, and the fuel elements are shown in symbols.....	89
Table 3-23: The average R^2 values and increase in average R^2 values for the predictor (X) and dependent (Y) variables	97
Table 3-24: The average R^2 values and increase in average R^2 values for the predictor (X) and dependent (Y) variables obtained via cross-validation. A total of 9 out of 16 PLS components in red text are suggested following the PRESS statistic in the last column (the procedure stops at the smallest PRESS value hence components 10-16 were not indicated)	99
Table 4-1: Model suite derived from PCA (designated A) and PLS (designated B). Tube positions not specified are assumed to be in the leading position	112
Table 4-2: Estimated standardised regression coefficients for the predictor variables in PCA models 1A-16A. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant.	115

Table 4-3: Estimated standardised regression coefficients for the predictor variables in PLS models 1B-16B. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant.	117
Table 4-4: Correlation matrix for selected variables in data subset 1 (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the element in full is from the metal/alloy).....	120
Table 4-5: The best (PC) subset stepwise regression module highlighting the PCs retained for model building (data subset 1)	121
Table 4-6: PC/variable correlation (varimax rotated loadings table). Highlighted (yellow) PCs are used for fireside corrosion model building. Variables with loadings > 0.5 are marked in red and selected for model building (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy).....	121
Table 4-7: The increase in R^2 values and average R^2 values for the predictor (X) and dependent (Y) variables (data subset 1).....	123
Table 4-8: The X scores (1-9) corresponds to the number of PLS components selected. The X scores 1-6 are statistically significant at $p < 0.05$ (numbers in red) and thus 6 PLS components were used to build the corrosion model for data subset 1.....	124
Table 4-9: Predictor weights corresponding to the number of PLS components used for variable selection and model building	125
Table 4-10: Variable importance in projection (VIP) scores (red text indicates variables above a threshold of 0.8 and selected for inclusion in the PLS fireside corrosion model 1B; the fuel elements are in symbols, alloy elements are written in full)..	126
Table 4-11: Standardised regression coefficients for the predictor variables in data subset 1 derived from PCA and PLS (shaded cells indicate predictor variables not selected for model building; the fuel elements are in symbols, alloy elements are written in full)	127
Table 4-12: Standardised regression coefficients of Cl and S (fuel) depending on the number of PLS components selected for analysis (PLS model 5B)	135
Table 4-13: Correlation matrix for selected variables in data subset 10 (red text indicates significant correlation judged from reliability index i.e. $p < 0.05$; elements in symbols are the fuel elements).....	138
Table 4-14: Correlation matrix for selected variables in data subset 14 (red text indicates significant correlation judged from reliability index i.e. $p < 0.05$; elements in symbols are the fuel elements).....	143
Table 5-1: Estimated standardised regression coefficients for the predictor variables in PCA and PLS models for equation framework C. The shaded cells signify variables not selected for model building (elements in symbols are the fuel elements and the elements in full are from the metal/alloy; <i>fc</i> is short for 'framework C').....	148

Table 5-2: Results showing the standardised regression estimates from the PCA model using combined variables from the loading plots (elements in symbols are the fuel elements and the elements in full are from the metal/alloy)	152
Table 5-3: Performance statistics (R^2) from the combined variables PCA version (PCA model 1A combined) and the initial PCA derived model (PCA model 1A).....	152
Table 5-4: Results showing the standardised regression estimates from PLS analysis using combined variables from the loading plots (elements in symbols are the fuel elements and the elements in full are from the metal/alloy)	153
Table 5-5: Performance statistics (R^2) from the PLS derived model (PLS model 1B), the revised versions of PLS model 1B (combined) and PCA model 1A (combined)	154
Table 5-6: Standardised regression coefficients for the predictor variables including an interaction term for data subset 1 (shaded cells were excluded from model building; the fuel elements are in symbols, alloy elements written in full)	159
Table 5-7: Standardised regression coefficients for the predictor variables including an interaction term for data subset 5 (shaded cells indicate predictor variables excluded from model building; the fuel elements are in symbols, alloy elements written in full)	160
Table 5-8: Standardised regression coefficients for the predictor variables including an interaction term for data subset 10 (shaded cells indicate predictor variables excluded from model building; the fuel elements are in symbols, alloy elements written in full)	162
Table 5-9: Regression coefficients for the PLS model using original Cr values and modified Cr data (alloy compositions written in full, fuel in symbols; all variables in <i>ln</i> form)	164
Table 6-1: Comparison of PCA/PLS RMSE values for data subsets 1-16 (framework model F).....	169
Table 6-2: Variable importance in projection (VIP) scores (red text indicates variables above a threshold of 0.8 and selected for inclusion in the PLS corrosion model; the fuel elements are in symbols, alloy elements are written in full)	174
Table 6-3: Estimated regression coefficients for the training data (data subset 1; the fuel elements are in symbols, alloy elements are written in full).....	174
Table 6-4: Measured and predicted corrosion rates from the training data and test data obtained via cross-validation (data subset 1)	175
Table A-1: UK Coal Data.....	214
Table A-2: Fuel elements, Si, Ti, calculated from oxides	216
Table A-3: Co-firing Fuel Blend (Coal/Biomass)	219
Table A-4: Co-firing fuel blend calculation; biomass was fired at 20% and 10% on a thermal basis (CCP refers to cereal co-product)	220

Table A-5: Ash data for coal, wood, CCP, and coal/wood/CCP blend.....	221
Table B-1: Correlation matrix UK coal data subset 1, austenitic leading tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	224
Table B-2: Correlation matrix for UK coal data subset 2, austenitic non-leading tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	225
Table B-3: Correlation matrix for UK coal data subset 3, ferritic leading tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	226
Table B-4: Correlation matrix for UK coal data subset 4, ferritic non-leading tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	227
Table B-5: Correlation matrix for US coal data subset 5, austenitic tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	228
Table B-6: Correlation matrix for US coal data subset 6, nickel-based tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	229
Table B-7: Correlation matrix for US coal data subset 7, coatings (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	230
Table B-8: Correlation matrix for world traded coal data subset 8, austenitic tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	231
Table B-9: Correlation matrix for world traded coal data subset 9, coatings (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	232
Table B-10: Correlation matrix for biomass data subset 10, austenitic tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	233
Table B-11: Correlation matrix for biomass data subset 11, nickel-based tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	234
Table B-12: Correlation matrix for biomass data subset 12, ferritic tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	235

Table B-13: Correlation matrix for biomass data subset 13, coatings (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	236
Table B-14: Correlation matrix for co-firing data subset 14, austenitic tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	237
Table B-15: Correlation matrix for co-firing data subset 15, TP316 (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	238
Table B-16: Correlation matrix for co-firing data subset 16, T22 (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)	239
Table C-1: Description of data subsets	241
Table C-2: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 1)	242
Table C-3: Varimax rotated loadings table for data subset 1 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)	242
Table C-4: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 2). Note: eigenvalue criterion reduced to 0.2 to retain metal temperature	244
Table C-5: Varimax rotated loadings table for data subset 2 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)	244
Table C-6: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 3)	245
Table C-7: Varimax rotated loadings table for data subset 3 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)	245
Table C-8: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 4)	246
Table C-9: Varimax rotated loadings table for data subset 4 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)	246
Table C-10: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 5)	247
Table C-11: Varimax rotated loadings table for data subset 5 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)	248
Table C-12: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 6). Forced stepwise regression to include PCs that have high loading(s) with the metal temperature	250

Table C-13: Varimax rotated loadings table for data subset 6 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy).....	250
Table C-14: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 7)	251
Table C-15: Varimax rotated loadings table for data subset 7 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy).....	252
Table C-16: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 8)	254
Table C-17: Varimax rotated loadings table for data subset 8 (here the elements in symbols are from the metal/alloy)	254
Table C-18: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 9)	255
Table C-19: Varimax rotated loadings table for data subset 9 (here the elements in symbols are from the metal/alloy)	255
Table C-20: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 10)	256
Table C-21: Varimax rotated loadings table for data subset 10 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy).....	256
Table C-22: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 11)	257
Table C-23: Varimax rotated loadings table for data subset 11 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy).....	258
Table C-24: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 12)	259
Table C-25: Varimax rotated loadings table for data subset 12 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy).....	259
Table C-26: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 13)	260
Table C-27: Varimax rotated loadings table for data subset 13 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy).....	261
Table C-28: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 14). Forced stepwise regression to include PC that have high loading(s) with metal temperature.....	263
Table C-29: Varimax rotated loadings table for data subset 14 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy).....	263

Table C-30: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 15). Forced stepwise regression to include PC that have high loading(s) with metal temperature.....	264
Table C-31: Varimax rotated loadings table for data subset 15 (elements in symbols are the fuel elements).....	264
Table C-32: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 16)	265
Table C-33: Varimax rotated loadings table for data subset 16 (elements in symbols are the fuel elements).....	265
Table C-34: VIP scores calculated for the predictor variables for data subsets 1B-16B (B indicates PLS models; shaded cells indicate the variables not present in the data subset; red text indicate variables with VIP score > 0.8 threshold).....	267
Table D-1: Number of principal components used for model building (i.e. PCA corrosion framework models A-F; shaded cells were not analysed)	270
Table D-2: Number of PLS components used for model building (i.e. PLS corrosion framework models A-F; shaded cells were not analysed)	271
Table D-3: PCA framework model A: Estimated standardised regression coefficients for the predictor variables in PCA models 1A-16A for framework A. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant.....	273
Table D-4: PLS framework model A: Estimated standardised regression coefficients for the predictor variables in PLS models 1B-16B for framework A. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant.	275
Table D-5: PCA framework model B: Estimated standardised regression coefficients for the predictor variables in PCA models 1A, 5A and 10A for framework B. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant	278
Table D-6: PLS framework model B: Estimated standardised regression coefficients for the predictor variables in PLS models 1B, 2B, 5B and 10B for framework B. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant	280
Table D-7: PCA framework models C (LHS) and D (RHS): Estimated standardised regression coefficients for the predictor variables in PCA models 1A, 3A and 6A. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant	283
Table D-8: PLS framework models C (LHS) and D (RHS): Estimated standardised regression coefficients for the predictor variables in PLS models 1B, 3B and 6B. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant	285

Table D-9: PCA framework model E: Estimated standardised regression coefficients for the predictor variables in PCA models 1A, 5A, and 10A. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant	288
Table D-10: PLS framework model E: Estimated standardised regression coefficients for the predictor variables in PCA models 1B, 5B, and 10B. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant	290
Table E-1: R^2 values for PCA fireside corrosion models 1A-16A (framework models A-F; shaded cells not analysed)	294
Table E-2: R^2 values for PLS fireside corrosion models 1B-16B (framework models A-F; shaded cells not analysed)	295
Table E-3: RMSE values for PCA fireside corrosion models 1A-16A (framework models A-F; shaded cells not analysed).....	296
Table E-4: RMSE values for PLS fireside corrosion models 1B-16B (framework models A-F; shaded cells not analysed)	297

LIST OF EQUATIONS

2-140

2-240

2-341

2-441

2-5 42

2-6 42

2-7 42

2-8 44

2-9 45

2-10..... 46

2-11..... 47

2-12..... 47

3-1 81

3-2 83

3-3 84

3-4 84

3-5 85

3-6 87

3-7 89

3-8 91

3-9 91

3-10..... 91

3-11..... 92

3-12..... 92

3-13..... 92

3-14..... 93

3-15..... 93

3-16..... 93

3-17.....	93
3-18.....	94
3-19.....	95
3-20.....	96
3-21.....	96
3-22.....	96
3-23.....	96
3-24.....	100
3-25.....	101
3-26.....	102
4-1	109
4-2	110
4-3	110
4-4	110
4-5	110
4-6	110
4-7	110
4-8	130
5-1	147
5-2	149
5-3	164
6-1	167
6-2	168
6-3	181
6-4	182
6-5	182
6-6	184
6-7	184

LIST OF ABBREVIATIONS

AUSC	Advanced Ultra Supercritical
BCURA	British Coal Utilisation Research Association
CEGB	Central Electricity Generating Board
DECC	Department of Energy and Climate Change
DOE	Department of Energy
GCV	Gross Calorific Value
GHG	Greenhouse Gas
HELE	High Efficiency Low Emission
HP	High Pressure
HVOF	High Velocity Oxy-Fuel
IEA	International Energy Agency
IP	Intermediate Pressure
LP	Low Pressure
MSEP	Mean Squared Error of Prediction
NIPALS	Non-Linear Iterative Partial Least Squares
PC	Pulverised Combustion
PCs'	Principal Components
PCA	Principal Component Analysis
PCC	Pulverised Coal Combustion
PCR	Principal Component Regression
PLS	Partial Least Squares
PRB	Powder River Basin
PRESS	Predicted Residual Error Sum of Squares
QSAR	Quantitative Structure Activity Relationship
QSPR	Quantitative Structure Property Relationship
RCP	Relative Corrosion Potential
RMSE	Root Mean Square Error
SEM	Scanning Electron Microscopy
SI	Sensitivity Index
UK	United Kingdom
US	United States
USGS	United States Geological Survey
VIP	Variable Importance in Projection

1 INTRODUCTION

1.1 Current Energy Overview

One of the main factors driving energy policy is climate change, a result of global energy-related carbon dioxide (CO₂) emissions which, according to the International Energy Agency (IEA), rose 1.7% in 2018 to hit a record high of 33.1 Gt CO₂ (Figure 1-1); this increase is 70% higher than the average recorded since 2010 (International Energy Agency, 2019). Although the emissions from all fossil fuels increased (Figure 1-1), the power sector accounted for nearly two-thirds of emissions growth (International Energy Agency, 2019). Coal use alone accounted for up to 10 Gt CO₂ (mostly in Asia) (International Energy Agency, 2019) thus, the utilisation of coal as a fuel for power generation has been contentious. The concern about increasing greenhouse gas (GHG) emissions has given rise to several directives such as the Large Combustion Plant Directive (European Commission, 2016) and the Kyoto Protocol (United Nations Climate Change, 2019). This has led to, as examples, the closure of many coal-fired plants in the United Kingdom (Toporov, 2014), the decline of coal utilisation in the United States (Mooney and Dennis, 2019), and mounting pressure on companies to divest from coal in France (Baxter *et al.*, 2018).

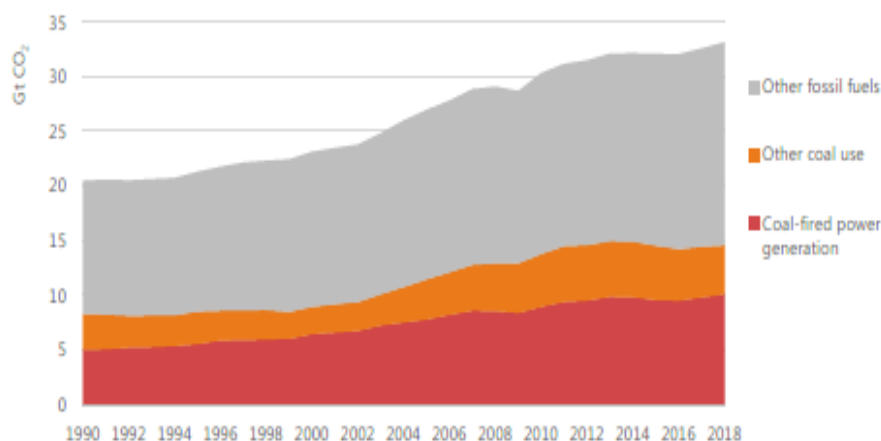


Figure 1-1: Global energy-related carbon dioxide (CO₂) emissions by source (International Energy Agency, 2019)

In 2016, there was a 50% drop in power generated by coal in the UK as reported by the Department of Energy and Climate Change (DECC; now part of Department for Business, Energy and Industrial Strategy, UK; Grimwood, 2016). Similarly, worldwide; reports from the 2018 World Energy Outlook predicts a 3.7% compound annual decline in the global thermal coal trade (Roker, 2018a). The International Energy Agency (IEA), in its '*sustainable development scenario*' cited by Roker (2018a), forecasts an 80% decrease in coal consumption in the global power sector, down to 732 million tonnes in 2040 (Roker, 2018a), with more coal forecasts downgrade expected in 2019.

The same report acknowledges, however, the increasing role of emerging economies on the expansion of new coal builds to match the growing energy demands. India, for instance, has been projected as the biggest coal growth market globally (Roker, 2018a). There is also an increase in the demand for coal, particularly in South-East Asia, Africa and South America (e.g. China, Brazil, India, Indonesia, Mexico, South Africa) (Power Technology, 2017; International Energy Agency, 2018a). Over 60% of India's electricity (as an example) is produced from coal, and in South Africa, 82% of electricity is generated from coal (International Energy Agency, 2018b).

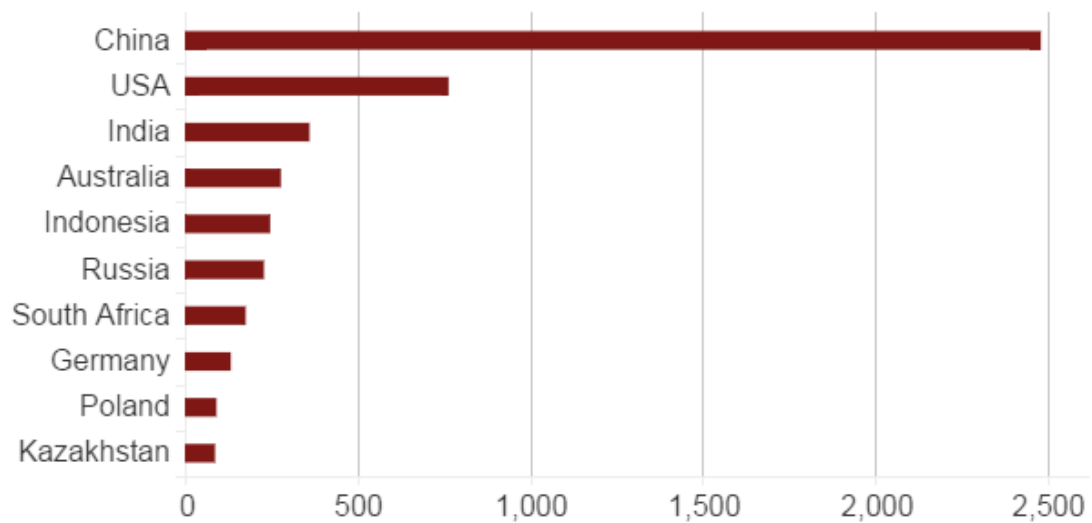
Due to the long-term impact of coal-fired power generation on the environment and contribution to global warming, different approaches have been adopted to significantly reduce CO₂ emissions, such as co-firing coal with biomass or a complete switch to renewables and other sustainable fuels (Simms, 2011b). Also, there have been ambitious undertakings to improve the overall efficiency of thermal-based power plants by increasing steam parameters (temperature, pressure) which have the added benefit of a reduction in carbon footprint. Countries such as China and Japan have sought to construct new power plants prioritising the development of High-Efficiency Low Emission (HELE) coal technology in Southeast Asia (Roker, 2018b). Hence it is very likely that coal will continue to play a role in power generation on a global scale, with an estimated 36% of the energy mix forecasted to be coal-generated by 2021 (Power Technology, 2017).

1.2 Coal Imports to the UK: World Traded Coals

Major coal producers include China, the United States, India, Indonesia, Australia, Russia and South Africa (Figure 1-2) (McGrath, 2015; World Energy Council, 2019). Major coal imports to the UK are from Russia, China, Australia, South Africa, Colombia and the United States (Figure 1-3) (Bains and Robinson, 2016).

Top coal producing countries

In million tonnes of oil equivalent



Source: World Energy Council

BBC

Figure 1-2: Top coal producing countries (in million tonnes of oil equivalent) (McGrath, 2015)

Despite 600 million tons of coal reserves being available in deep mines or shallow deposits in the UK (World Energy Council, 2013; The Carbon Brief, 2015), coal production output in the UK has been on the decline since the mid-1960s, falling to less than 100 million tons per year by 1990 (World Energy Council, 2013). Coal imports, however, reached a peak in 2012, i.e. at about 44.8 million tonnes (World Energy Council, 2013). In 2013, the volume of coal imports to the UK was about three times the coal produced (indigenous production was at 16.8 million tonnes) (World Energy Council, 2013). One of the drivers for coal imports is the need to utilise high-quality

coal, which is determined by the amount and composition of the ash, sulphur content, and calorific value (Speight, 2013). However, the drive to decarbonise power generation has significantly reduced coal consumption as current EU legislation has led to the closure of many coal-fired plants in the UK (Ambrose, 2015).

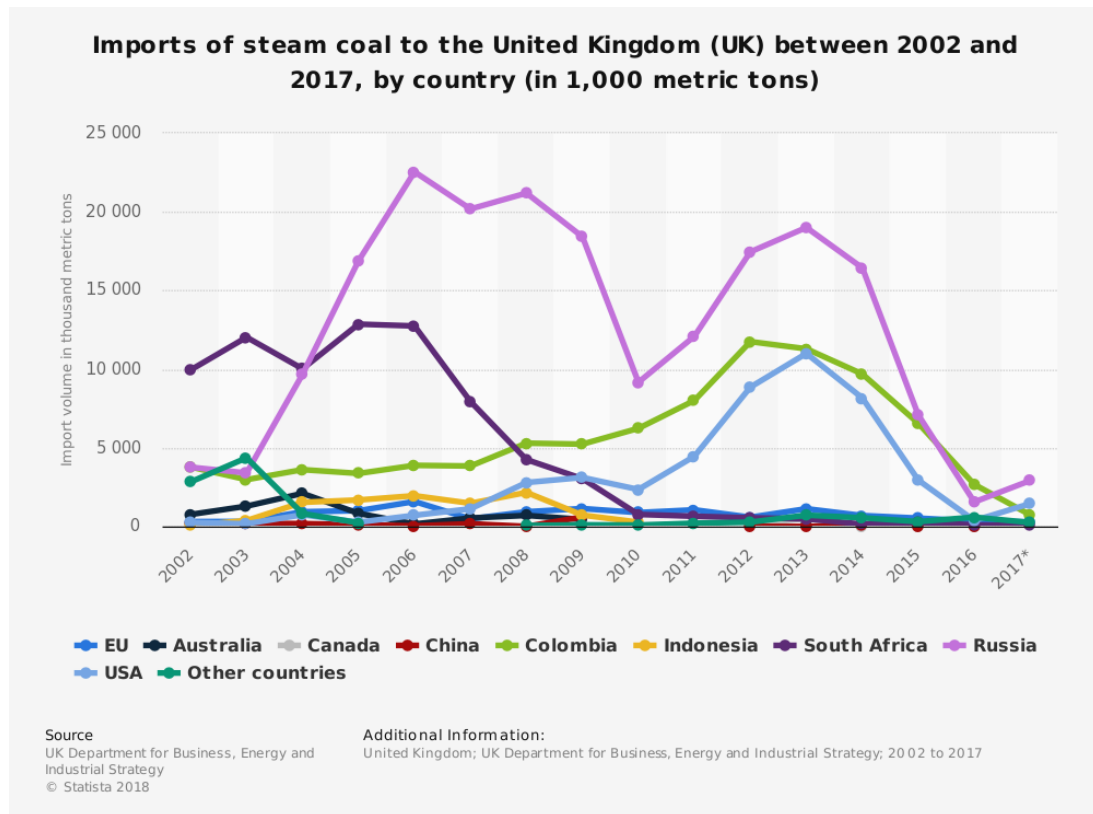


Figure 1-3: Imports of coal to the United Kingdom between 2002 and 2017 (UK Department for Business, 2018)

1.3 Coal / Biomass Combustion

1.3.1 Pulverised Coal Combustion

Pulverised Coal Combustion (PCC) is one of the conventional combustion technologies that has been in place since the 1920s when increasing electricity demands required larger steam capacities than were available (Beér, 2007). A wide variety of coal types (lignite, peat, anthracite, bituminous coal) can be used in pulverised coal combustion. Before its use in boilers, coal is crushed to a fine powdery form with a particle size set such that, for bituminous coal, less than 2% of the powder is over 300 μm and 70-75% is below 75 μm (IEA Clean Coal Centre, 2010).

The pulverised coal particles are mixed with heated (primary) combustion air and blown into the firebox of the boiler (Figure 1-4) through a set of burners (Zhang and Lu, 2010), and then mixed with secondary air at the burner exit to establish the right combustion conditions (Williams *et al.*, 2001). The furnace walls are surrounded by evaporation heating surfaces that boil and partially vaporise the feed water. The heated steam/water mixture flows into a steam drum which separates the generated steam from the hot water. The steam is sent to the superheater located at the furnace roof (i.e. SH; Figure 1-4) where it is heated to temperatures $> 500\text{ }^{\circ}\text{C}$ and pressures up to 165 bar before it is piped to the high pressure (HP) turbine where it is expanded, pushing against the turbine blades, and turns the generator shaft. Exhaust steam from the HP turbine is routed to the reheaters (i.e. RH; Figure 1-4) where it is heated back to the superheat temperature and flows to the intermediate pressure (IP) turbine. The exhaust from this IP turbine is low pressure steam that flows to the low pressure (LP) turbine to turn the generator shaft connected to the turbine.

Modern pulverised coal combustion boilers now operate with increased steam parameters (pressure, temperature) to improve overall efficiency and reduce CO_2/MWh from coal-fired plants. Supercritical and ultra-supercritical (USC) PC-fired boilers are gradually replacing conventional subcritical boilers. Supercritical boilers work with steam operating pressures and temperatures higher than the critical pressure ($> 22\text{ MPa}$) and temperature.

Figure 1-4 shows the schematic of a PC fired plant (Peltier, 2013).

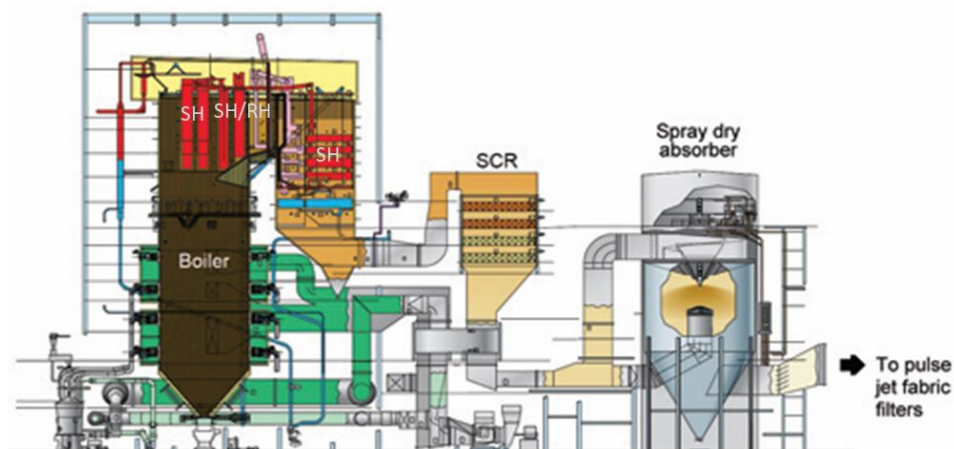


Figure 1-4: Schematic of a pulverised coal-fired plant (Peltier, 2013)

1.3.2 Biomass Combustion

The IEA's assessment on the impact of fossil fuel use determined that CO₂ emitted from coal combustion was responsible for an increase in over 0.3 °C in global average annual surface temperatures, marking coal as the largest source of global temperature increase (International Energy Agency, 2019; Mooney and Dennis, 2019). Thus there has been considerable investment in renewable energy resources to combat this problem (Roni *et al.*, 2017). Biomass combustion is gradually gaining popularity as an alternative to coal-firing following climate change concerns, although research and uptake are somewhat intermittent and depend on government policies (The Department for Business, Energy and Industrial Strategy (BEIS), 2012). The range of biomass fuel species employed as fuel for power generation includes wood pellets, olive cake and pellets, palm kernel expellers, citrus pulp expellers, sunflower husk, sawdust, energy crops (e.g. willow, poplar, miscanthus, straws and grasses) and sewage sludge (Vassilev *et al.*, 2010; The Biomass Energy Centre, 2011).

Biomass is regarded as inherently low carbon given that plants absorb an amount of carbon equivalent to that released to the atmosphere when biomass fuels are burnt (The National Council for Air and Stream Improvement, 2015). Biomass, however, is less energy dense than coal and would require a significant land mass to grow the amount needed to replace coal completely. As an example, the US Department of Energy's (DOE) 2016 billion-ton model (BT16) (Langholtz *et al.*, 2016) states that for the commercialisation of biomass to energy crops, the maximum eligible pastureland required is about 47 million acres (or 11% of pastureland). More specifically, a report from Partnership for Policy Integrity (2016), citing the aforementioned DOE's billion-ton model, states that forest harvesting will require clear-cutting up to 4.7 million acres per year to produce a 100 million dry tons of (forest) biomass for the production of wood pellets. Blakeslee (2009) projected that about 1.6 billion tons of biomass per year are required to replace a billion tons of coal.

There are three main combustion techniques employed to burn biomass fuels: grate-fired, fluidised bed (bubbling and circulating) and pulverised units (Rosendahl, 2013). Grate firing is the oldest technique for burning biomass and is suitable for coarser and uneven biomass material. Pulverised fuel method is more efficient and ideal for large-

scale firing, particularly for coal-fired boilers that have been converted to burn biomass (Rosendahl, 2013). Fluidized (circulating) bed combustion is the most efficient method of directly burning biomass as it is designed to cope with a wide range of fuels (UNEP-DTIE Energy Branch, 2003). All three types of biomass-firing employ superheaters and reheaters for the production of dry (superheated) steam which is delivered to the turbine for power generation.

One of the degradation mechanisms for critical components in power plants is fireside corrosion. Fireside corrosion of superheater and reheaters is more challenging in boilers burning pure biomass than for coal-fired boilers, as the flue gas contains corrosive gases and high concentrations of low melting alkali metals and chlorides that severely damage and reduce the life of boiler tube materials (discussed in more detail in chapter 2). Hence steam conditions in biomass-fired plants are generally lower than those of coal-fired plants if the boiler must continue its operation over an extended period (Simms, 2011a).

1.3.3 Co-firing Coal with Biomass

According to the definition posted by the Biomass Energy Centre (2011), co-firing is the process of replacing a portion of the fossil fuel supplied for combustion (usually coal) with a renewable alternative. Coal/biomass co-firing is a low-cost way of introducing biomass firing as existing coal-fired infrastructure can be utilised for co-firing (although only for very low levels of biomass), and the uncertainties regarding biomass feedstock supplies are minimised (Roni *et al.*, 2017). The process involves either co-milling a biomass constituent with coal following blending on or off-site, or providing a separate feed line for the biomass fuel and directly injecting both fuels into the furnace (direct co-firing) (Savolainen, 2003; The Biomass Energy Centre, 2011). Alternatively, a gasifier can be installed to convert biomass fuel into syngas (fuel gas) before injection into the furnace (indirect co-firing) (Roni *et al.*, 2017). Candidate biomass species considered for co-firing include woody products and wood waste, short rotation herbaceous crops (e.g. switchgrass), alfalfa stems, landfill gas and manure (Tillman, 2000).

Following numerous incentives and legislation introduced by the UK government to facilitate the move to renewable energy generation and achieve a low carbon economy,

the number of co-fired coal and biomass plants in the UK was increased. However, regulations changed (e.g. less subsidy for using biomass) and only about 8 major coal-fired UK power plants are currently co-firing coal with biomass as a secondary fuel source (Norfolk, 2005; Department of Energy and Climate Change, 2014; ECPK, 2016; Roni *et al.*, 2017). In other European countries, Germany is reported to have the largest number of co-firing units, about 30; while countries such as the Netherlands and Denmark face challenges from co-firing due to financing, efficiency concerns, availability of raw materials (notably Denmark) and government policies (Roni *et al.*, 2017). Although co-firing in North America (US, Canada) is mainly at commercial demonstration levels (Tillman, 2000; Agbor, Zhang and Kumar, 2014), there are 40 out of 560 coal-fired power plants in the US currently utilising co-firing technologies (Roni *et al.*, 2017).

1.4 Research Overview, Aim and Objectives

Fireside corrosion damage on superheaters and reheaters has been studied for many years, and the mechanisms of the degradation process under certain conditions have been established (Simms, 2011a; Wright and Shingledecker, 2015). Field investigations and previous research into this issue have revealed that the primary cause of this damage is the presence of molten deposits on the tube surfaces (Nelson and Cain, 1960; Reid, 1971; Stringer, 1983, 1995; Wright and Shingledecker, 2015). Hence, different approaches have been attempted in this thesis for modelling fireside corrosion by making use of this understanding. Previous attempts have included mechanistic models which have been applied with varying degrees of success. The main issue with many of these existing models has been that they are hard to extrapolate to other conditions, mainly because the range of input parameters that were used to derive the models were limited to specific fuel or alloy species (e.g. the fuel chlorine content or the chromium content etc.; discussed in detail in section 2.8). As such, this current research has covered an entirely different approach to modelling, and the input parameters expanded to include the alloy elements, fuel elements, and boiler operating conditions (metal and gas temperatures). This current research does not address individual corrosion reactions (of which several operate in parallel) but attempts to use statistical methods to find correlations between input parameters and degradation over a specific temperature/

operation range. The main objective is to reveal if additional input variables prove valuable in quantifying the extent of corrosion damage when subjected to specific corrosive environments.

The corrosion models developed will potentially enable plant lifetime extensions. This will be aided as conventional assumptions about factors affecting fireside corrosion can be identified. This will also allow for the assessment of the potential impacts of an increasingly wide range of fuels on superheater and reheater materials to be made based on their compositions. Key aspects of the fireside corrosion resistant materials can be identified which allows for the selection of alternative tube material that can be used in future plants or form the basis for the development of future protective coating systems

1.4.1 Aim

This research aimed to develop a suite of models to predict the degree of fireside corrosion damage experienced by superheaters and reheaters in coal, biomass and coal/biomass co-fired boilers. The focus has been relating fireside corrosion damage to fuels when using specific operating conditions.

1.4.2 Objectives

- Data collection and gathering: to review, collate and calculate additional information on historical and current fireside corrosion datasets gathered from various studies of material fireside corrosion performance in power plants.
- Data analysis through statistical methods, namely *Principal Component Analysis* and *Partial Least Squares*: to select fireside corrosion parameters for model building that allow for improved data analysis.
- Fireside corrosion model building: to develop regression models that predict the degree of fireside corrosion damage over a range of boiler operating conditions and fuels.
- Model validation: to compare the performance of the two statistical techniques in order to optimise the models' predictive capabilities.

1.5 Thesis Structure

This thesis contains eight chapters and an appendix section.

Chapter 2 includes an extensive literature review with a focus on previously proposed fireside corrosion models and their limitations.

Chapter 3 explains the methodology employed in this research which includes the corrosion data collected and the statistical techniques applied to analyse the datasets.

Chapter 4 covers the predictive models developed (using PCA and PLS) for different fuels and a discussion of the results.

Chapter 5 covers the different model variants explored (i.e. different framework models, loadings plot from PCA, data sensitivity).

Chapter 6 details the performance and validation of the fireside corrosion models.

Chapter 7 is a summary of the conclusions.

Chapter 8 outlines areas for further research.

1.6 Research Presentations and Publication

Table 1-1 outlines conferences attended, other (research-themed) events and paper submitted for publication relating to this research.

Table 1-1: List of conferences, other events and paper submitted for review

Event/Publication	Location	Date
Energy Science Lecture (Poster Presentation)	University of Leeds	20 Sep 2016
Female Researchers Network Biennial Lecture (Poster Presentation)	Cranfield University	19 June 2017
High Temperature Materials Degradation Workshop (Poster Presentation)	The Boiler House, Grantham	12 Sep 2017
Energy Science Lecture (Presentation)	Prince Philip House, London	02 Oct 2017
European Conference on Fuel and Energy Research (ECCRIA)	Cardiff University	5-7 Sep 2018
Modelling Fireside Corrosion of Superheaters and Reheaters following Coal and Biomass Combustion	Paper submitted to FUEL (Under review)	01 Mar 2019

2 LITERATURE REVIEW

This chapter reviews the current understanding of fireside corrosion, a degradation mechanism which affects the performance of boiler tube materials (section 2.1). There is a brief overview of the evolution of superheater and reheater materials used in large utility boilers (section 2.2). The influence of coal and biomass fuel chemistries on deposit formation is discussed, as it is the driving force behind fireside corrosion damage (section 2.3). The properties of UK coals and world-traded coals (US, Russia, Indonesia) are compared (section 2.4). The mineral matter transformation in coal and biomass combustion is outlined (section 2.5). Examples of deposits encountered in high-temperature coal-fired and biomass-fired environments are highlighted including the factors that influence the formation of deposits (section 2.6). The fireside corrosion mechanism as established in the literature is reviewed (section 2.7). Previous fireside corrosion models are also reviewed including the limitations (section 2.8), and lastly an overview of the statistical methods employed in this research to develop fireside prediction models (section 2.9).

2.1 Overview of Fireside Corrosion Issues in Power Plants

The operation of coal-fired plant boilers at high steam temperatures and pressures offers the potential for improved efficiency and a reduction of CO₂ emissions. As an example, projects sponsored by the U.S. Department of Energy and the Ohio Coal Development Office (Purgert *et al.*, 2008) have set 760°C (1400°F) and 345 bar (approximately 35 MPa) as target operating parameters for an ‘Advanced Ultra Super Critical’ (AUSC) boiler. It is projected that efficiency under these conditions will increase from 35% to about 46% (Purgert *et al.*, 2008). However, high-alloyed boiler materials for superheaters, reheaters, evaporators etc. with sufficient corrosion resistance and creep strength would have to be employed for extreme operating conditions (high temperatures and pressures). The aggressiveness of the combustion environment promotes fireside corrosion, an accelerated type of attack influenced by the vapourisation and condensation of impurities such as sodium (Na), potassium (K), sulphur (S) and chlorine (Cl). These impurities are present in the fuel and, following their condensation on to key boiler components ultimately leads to metal loss (Natesan *et al.*, 2003). Fireside corrosion can be defined as the corrosion of superheater and

reheater tube materials located in the hottest part of the boiler (Figure 2-1). It is the result of a complex interaction between the metallic material, the fuel combusted and the furnace operating conditions.

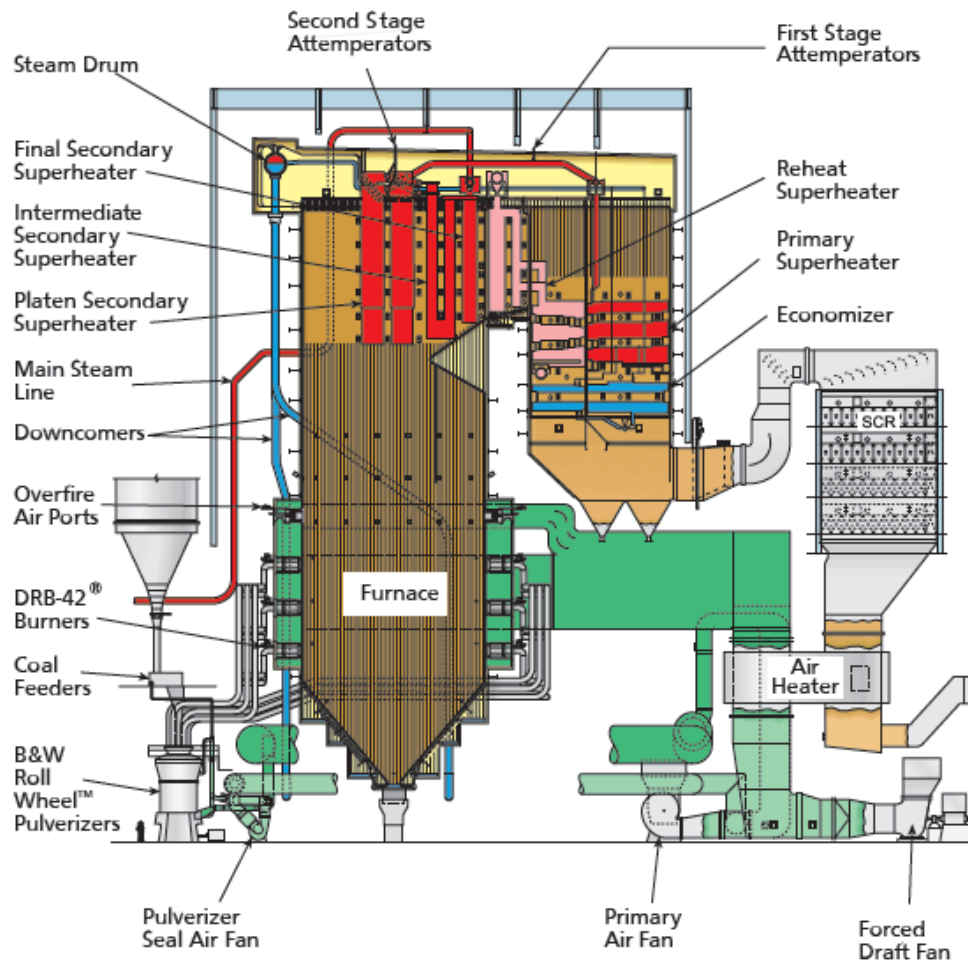


Figure 2-1: Location of superheaters and reheaters in a subcritical boiler (Babcock and Wilcox Energy Solutions, 2018)

Fuels from different sources are known to have varying impacts on heat exchanger surfaces due to the different levels of minor and trace impurities responsible for the fireside corrosion process (section 2.6) (Simms 2011a; Wright and Shingledecker, 2015). The resulting aggressive environments arising from these extreme conditions promote the degradation of the materials used in superheaters/reheaters over time thus

incurring excessive maintenance costs. Hence a scientific understanding of the mechanisms involved is vital.

2.2 Superheaters and Reheaters

The function of the superheaters and reheaters is to raise the steam temperature above the saturation temperature to produce dry, superheated steam for delivery to the turbine. There are two distinct types of superheaters depending on their location in the boiler; radiant and convective superheaters. The radiant superheaters are located in the combustion section of the furnace where the flue gas temperature is highest (Taler and Taler, 2009). The convective superheaters, also referred to as the primary superheaters, are located in the path of hot flue gases, usually above the economiser (Figure 2-1). Platen superheaters (usually positioned at the roof of the furnace) are designed as multiple pass heat exchangers that can absorb both radiant and convective heat (Figure 2-2) (Taler and Taler, 2009; Chattopadhyay, 2013).

Saturated steam from the steam drum (in sub-critical boilers) is routed to the roof superheaters. The superheated steam passes through an attemperator (Figure 2-1) where it is cooled and then routed to the pendant section (Figure 2-2), the low temperature (convective) section (Figure 2-2), and finally to the secondary superheaters before it is piped to the high pressure (HP) turbine (Chattopadhyay, 2013; ATC-CES, 2018).

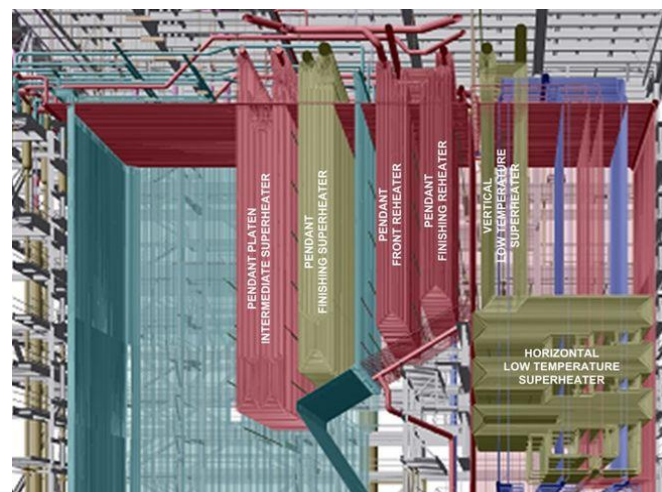


Figure 2-2: Location of radiant (pendant) and low-temperature convective superheaters (ATC-CES, 2018)

The exhaust steam from the HP turbine is then routed to the reheaters to raise its temperature before it is directed to the intermediate pressure (IP) turbine and finally to the low pressure (LP) turbine. The reheaters are necessary to reheat exhaust (wet) steam from the HP turbine producing drier steam, and also to improve the thermal efficiency (Kiameh, 2013). Figure 2-3 illustrates a Rankine reheat cycle (temperature-entropy; i.e. T-S) widely used for electric power generation. The cycle superheats the vapour from the steam drum to point 3 (see Figure 2-3) which is expanded in the HP turbine. The exhaust steam from the HP turbine (point 4) is returned to the boiler where it is reheated at constant pressure (ideally) (Kiameh, 2013) to a temperature at point 5 (Figure 2-3). Cycle thermal efficiency is increased because the heat flow up to points 3 and 5 occurs at a higher temperature; i.e. heat is added twice, from point 2 to 3 and then from point 4 to point 5 (Kiameh, 2013). An additional result is drier steam from the turbine exhaust at point 6 (Figure 2-3) which prevents erosion of the LP turbine blades (Kiameh, 2013).

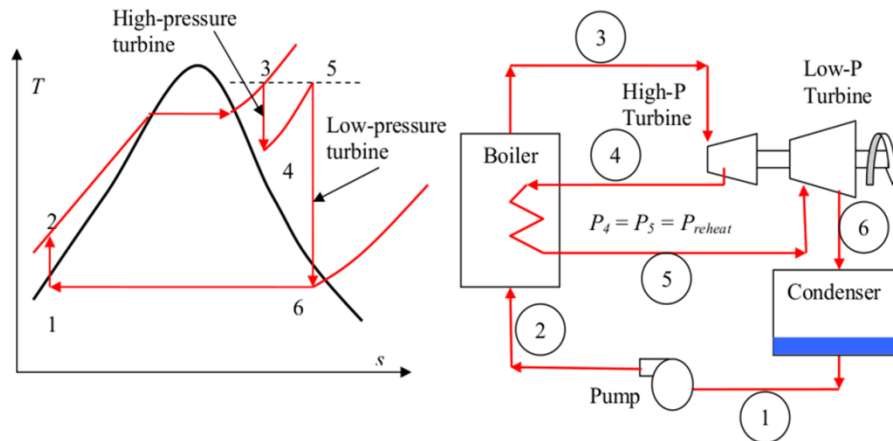


Figure 2-3: The ideal reheat Rankine cycle (Mechanical Engineering Lectures, 2017)

The internal diameter of convective superheaters ranges from 20 – 30 mm, and outside diameters from 38 – 76 mm for both superheaters and reheaters (Chattopadhyay, 2013). The reheater tubes, on the other hand, have maximum internal diameters of 50 mm since the reheater pressure is generally reported to be one-fifth of the operating pressure of other superheaters (Viswanathan, 1989; Chattopadhyay, 2013).

2.2.1 Material Selection and Alloy Grades

The superheaters and reheaters are used in aggressive combustion conditions (high temperatures, high pressures), and thus material requirements such as creep strength, corrosion resistance (fireside corrosion and steam side oxidation), weldability and low coefficients of thermal expansion are very stringent (Viswanathan, 1989). The superheater/reheater materials used in large utility boilers are specific types of ferritic and austenitic alloys. Material selection is based first on creep resistance, followed by high corrosion resistance; thus, austenitic tubes are favoured over ferritic tubes owing to the higher chromium (Cr) content, which significantly improves corrosion resistance. High Cr alloys are essential for the development of dense non-porous oxides on the tubes which resist fireside corrosion of the tube material. Austenitic steels are further classified with respect to their Cr levels; thus they fall into four categories, namely: 15% Cr; 18% Cr; 20 to 25% Cr, and >25% Cr stainless steels (Viswanathan *et al.*, 2005).

Several new alloy grades have been introduced following modifications to the composition of steel materials. This is to develop specialist alloys for use in applications requiring enhanced physical properties such as corrosion resistance, high creep resistance, thermal fatigue strength, weldability and machinability (Viswanathan *et al.*, 2005). Also, see Figure 2-4. Hence, the chemical composition of alloys is important in determining the material's properties and ultimately its performance particularly in high-temperature environments. The evolution of ferritic steels, for instance, involved the addition of molybdenum (Mo), vanadium (V) and niobium (Nb) to 9-12 Cr steels in the 1960s (Viswanathan *et al.*, 2005). The creep strength and oxidation resistance of conventional 18Cr-8Ni austenitic steels were improved by increasing the Cr and Ni content, and the addition of hardening and stabilising elements, titanium (Ti), V, Nb and Mo (Sourmail, 2004; Viswanathan *et al.*, 2005; Schade *et al.*, 2008) (Figure 2-4).

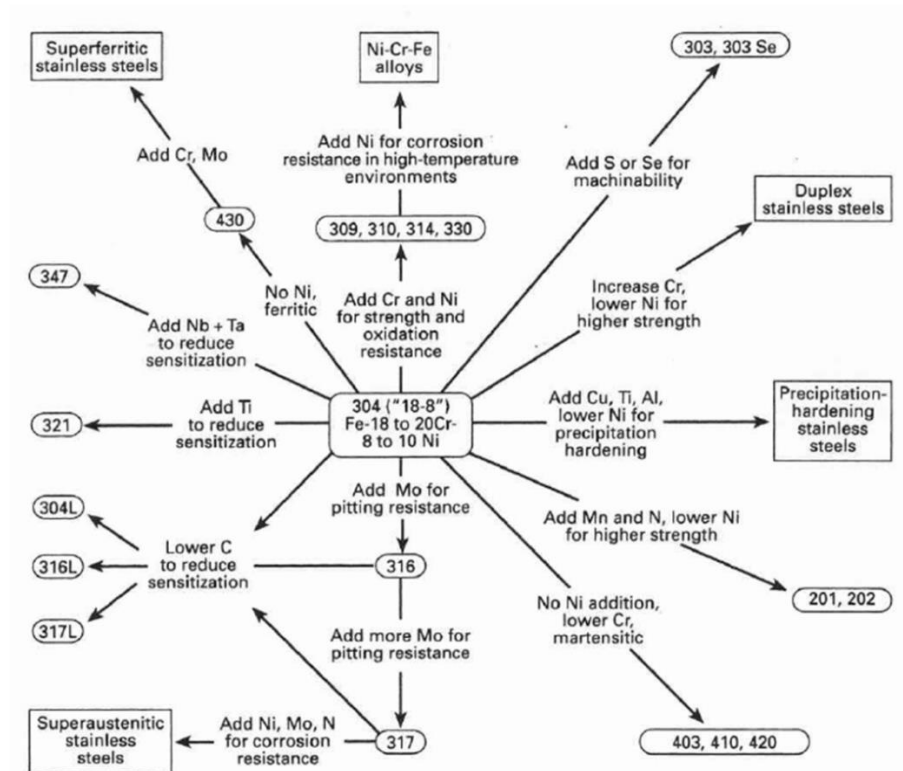


Figure 2-4: Stainless steel alloy grades (Schade *et al.* , 2008)

Stainless steel with nitrogen (N) additions improve the mechanical properties without affecting its corrosion resistance (e.g. HR3C), and the addition of tungsten (W) results in solid solution strengthening (e.g. 347W) (Viswanathan *et al.*, 2005). Titanium, tantalum (Ta), W and Nb are carbide forming alloying elements. The introduction of these elements prevents the loss of Cr as they inhibit Cr carbide precipitation (caused by the selective reaction of Cr and carbon) by forming different carbides (Weele, 1991). Nickel (Ni) stabilises austenite and improves the toughness of steels particularly in high-temperature environments (Figure 2-4), while manganese (Mn) is known to enhance the adherence of the protective oxide scale (Weele, 1991; Blough, et al., 1998).

Ni-based alloys (e.g. the highlighted (circled) alloys in Figure 2-5) can also be considered, as they are creep resistant at higher temperatures (up to 760 °C), however, they are costly. As such, high creep strength steel alloys, such as HR3C (i.e. 25Cr-20Ni grade with N additions up to 0.2 wt %) and NF709 (20Cr-25Ni grade with Nb, Mo, and Ti), have been developed as low-cost alternatives with effective corrosion resistance (Viswanathan, 1989; Viswanathan *et al.*, 2005).

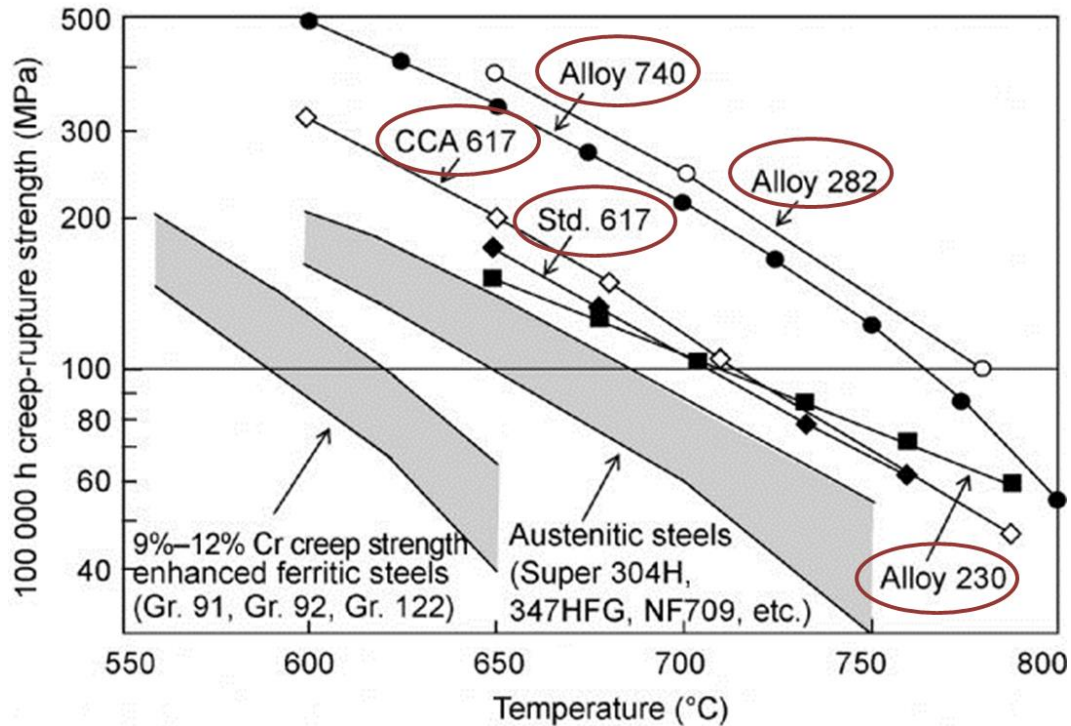


Figure 2-5: 10^5 hours rupture strength as a function of stress and temperature for various steel and nickel-based materials. Ni-based have been circled for clarity (Modified from Shingledecker, 2012)

2.3 Fuels

2.3.1 Coal Chemistry

Coal is a fossil fuel formed from the accumulation of buried plant debris that has been acted on by heat, pressure and temperature over millions of years. Coalification progresses with additional exposure to heat, pressure and temperature and eventually transforms the decomposed plant structures into peat, lignite, sub-bituminous coal, bituminous coal and finally anthracite (Osborne, 2013; Toporov, 2014). The carbon content and calorific value increases from peat to anthracite, and the oxygen content decrease through the series (Table 2-1).

Table 2-1: Coal classification based on rank (dry mineral matter free) (Toporov, 2014)

Coal Rank		Volatiles	C	H	O	S	GCV*
UN-ECE	USA (ASTM)	wt %	wt %	wt %	wt %	wt %	kJ/kg
<i>Lignite</i>	<i>Lignite</i>	≥ 45	≤ 75	6-5.8	34-17	0.5-3	≤ 22,100
<i>Sub bituminous</i>	<i>Sub bituminous</i>	≥ 45	≤ 75	6-5.8	34-17	0.5-3	≤ 28,470
<i>Bituminous</i>	<i>High volatile bituminous</i>	40-45	75-82	6-5.8	< 9.8	~ 1	≤ 32,870
	<i>Medium volatile bituminous</i>	28-35	85-87	5.6-5	7.3-4.5	~ 1	≤ 34,960
	<i>Low volatile bituminous</i>	14-19	89-90.5	4.5-4	3.2-2.8	~ 1	35,380
<i>Anthracite</i>	<i>Semi-anthracite</i>	10-14	90.5-91.5	4-3.7	2.8-2.5	~ 1	≤ 35,380
	<i>Anthracite</i>	7-12	< 91.5	< 3.7	< 2.5	~ 1	≤ 35,300

*GCV – Gross Calorific Value

Coal is composed of two principal parts: organic and inorganic materials (Figure 2-6). The micro-components and structures that make up the organic part are referred to as macerals and, in turn, consist of three forms: inertinite, vitrinite and liptinite (Riley, 2007). Vitrinite is the most abundant maceral formed in coal and is derived from woody tissues. Inertinite is derived from the partial carbonisation of the coal-forming materials by fire or degradation by microorganisms. Liptinite is derived from the spores, needles and leaf cuticles of plant materials (Riley, 2007).

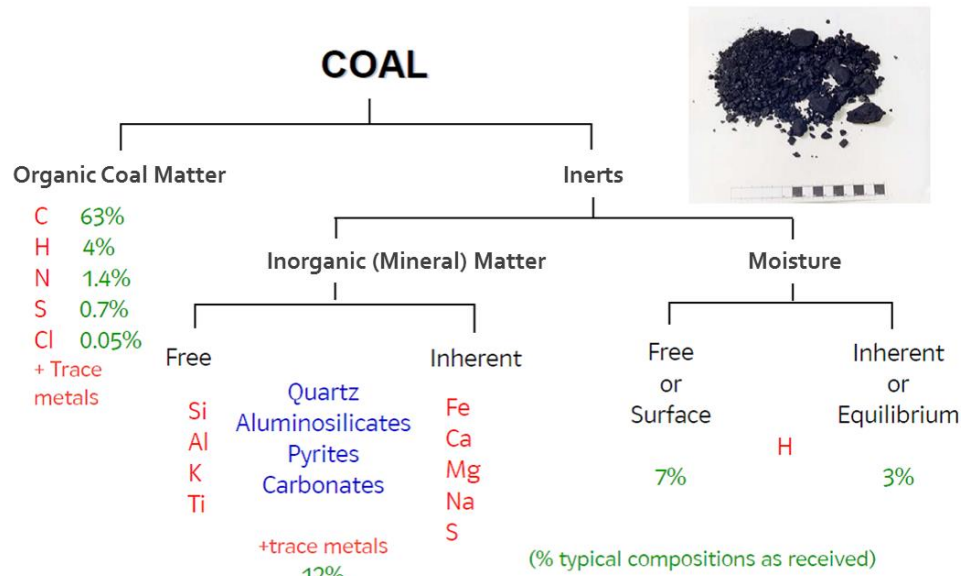


Figure 2-6: Classification of coal based on organic and inorganic components (Modified from Jones, 2005)

2.3.1.1 Overview of the mineralogy of coal

The mineral components of coal are a product of the physical, chemical and biological changes that occurred during the coalification process and, as such, are dependent on the local environment from where it originates (Riley, 2007). As depicted in Figure 2-6, the mineral matter could be inherent; that is, derived from the inorganic components within the peat forming plants (Speight, 2015), or free (extraneous) mineral particles; that is liberated from the coal during physical processing such as grinding (Sarofim and Helble, 1993). Further classification from Harvey and Ruch (1985) groups the mineral matter as adventitious (formed outside the peat swamp either during or after peat accumulation), detrital (transported into the peat swamp) or authigenic (formed within the environment and gathered during mining from surrounding rocks).

Clay is the most abundant mineral found in coal, comprising more than 50% of the minerals present in some cases. Kaolinite is the most common clay matter followed by illite and quartz in some seams (Osborne, 2013). The silicates originate in the shale, clay minerals, silts and sands (Riley, 2007). Pyrites, the principal source of iron oxide, and marcasite (two crystal forms of iron sulphide, FeS_2) are the most common iron minerals found, in varying extents, in all coals (Osborne, 2013). Ca and Mg oxides result from the decomposition of carbonate minerals, while sulphates are produced from the interaction between carbonates, pyrite and oxygen (Riley, 2007). Also present are inorganic elements bonded in various ways with the organic elements of coal. Together they make up the inherent mineral matter (Harvey and Ruch, 1985; Speight, 2015). These species vary considerably between coals in the mode of occurrence and abundance.

As shown in Figure 2-6, sulphur (S) occurs in two forms: organic and inorganic (inherent). The inorganic form of S occurs mainly as pyrites or marcasite (FeS_2), and inorganic sulphates (Speight, 2015). Sulphur from plant material has been established to be the primary source in low S coals, accounting for an excess of 50% of the total S content. Sulphates (mainly CaSO_4 and FeSO_4) rarely exceeds 0.1 wt % of the total S content (Speight, 2015). Chlorine in coal occurs predominantly as halides but can be associated with organic matter (Speight, 2015). The alkali metals can exist in the organic structure as exchangeable ions, or as salts contained in the coal or its moisture, and in included or excluded minerals (James *et al.*, 1997; Riley, 2007). In sub-bituminous and bituminous coals, K is mostly bound to the clay minerals, mainly as illite, with minor fractions bound to the organic structure as exchangeable ions. By contrast, a significant portion of Na is usually found as halite or exchangeable ions (Hurley *et al.*, 1993; Lind *et al.*, 1993).

Coal ash is the non-combustible inorganic residue that remains after complete combustion of the organic matter. The ash-forming constituents of coal are mainly minerals and are compounds of Si, Al, Fe, and Ca, with smaller quantities of Mg, Ti, Na and K (Figure 2-6). Although the mineral constituents of ash are reported in the literature as oxides, they occur in coal as a mixture of silicates, oxides, carbonates, sulphates etc. (Table 2-2) (Riley, 2007; Patra *et al.*, 2012). The reactions of the ash

Table 2-2: Common coal minerals (Riley, 2007)

Minerals		
Silicates	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
	Illite	$(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}$
	Chlorite	$(\text{MgFeAl})_6(\text{SiAl})_4\text{O}_{10}(\text{OH})_8$
	Quartz	SiO_2
Carbonates	Calcite	CaCO_3
	Dolomite	$\text{CaMg}(\text{CO}_3)_2$
	Ankerite	$\text{Ca}(\text{FeMg})\text{CO}_3$
	Siderite	FeCO_3
Disulphides	Pyrite	FeS_2 (cubic)
	Marcasite	FeS_2 (orthorhombic)
Sulphates	Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
	Szomolnokite	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
	Anhydrite	CaSO_4
	Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$
Feldspars	Plagioclase	$(\text{NaCa})\text{Al}(\text{AlSi})\text{Si}_2\text{O}_8$
	Orthoclase	KAlSi_3O_8
Sulfides	Sphalerite	ZnS
	Galena	PbS
	Pyrrhotite	FeS

particles can result in fouling of boiler tube surfaces (section 2.7); hence it is essential to determine the proportions of the mineral groups present in coal.

2.3.2 Biomass Chemistry

Biomass is a multifarious term covering a range of solid organic products, and to a lesser extent, inorganic matter, generated from natural and anthropogenic processes (Vassilev *et al.*, 2015). One way of classifying is by grouping into six groups based on the structure of the organic and inorganic constituent (Vassilev *et al.*, 2010; The Biomass Energy Centre, 2011; Hustad and Barrio, 2015) (see also Table 2-3):

- Wood residues (from forest residues, wood processing, arboriculture activities, and the paper and furniture industry).
- Agricultural residues (from crops, food processing and animals).
- Municipal waste/food waste.
- Industrial waste and co-products.
- Dedicated energy crops (high yield crops are grown specifically for energy applications).
- Biomass mixtures.

All biomass is made up of three main components: cellulose, hemicellulose and lignin. The organic part of biomass (mainly C, H, N and O) is present in the molecular structure of the cellulose, hemicellulose, and lignin component of biomass matter. The inorganic matter (0.1 – 46 wt % on a dry basis) is made up of various minor species from different mineral groups and classes such as phosphates, carbonates, silicates, chlorides, sulphates, oxyhydroxides, nitrates; as well as some amorphous inorganic phases (Vassilev *et al.*, 2010, 2013).

The identification of the chemical makeup of biomass fuels is of paramount importance as they offer potential replacements for fossil fuels. Similar to coal, biomass is a complex heterogeneous solid fuel containing various organic and inorganic or mineral matter. According to Vassilev *et al.* (2010), natural biomass systems are more straightforward to classify (Table 2-3) than their solid fossil fuel counterpart (i.e. coal) mainly due to the presence of lesser-known plant species and diagenetic processes

typical of coal and peat systems. The technogenic (processed and semi-processed) biomass system, on the other hand, is more complicated owing to the mixture of non-biomass materials during its processing.

Table 2-3: General classification of biomass varieties (Vassilev *et al.*, 2010)

Biomass Groups	Examples of Biomass Varieties and Species
<i>Wood and Woody Biomass</i>	Stems, branches, foliage, bark, chips, pellets, briquettes, sawdust, sawmill
<i>Herbaceous/Agricultural Biomass</i>	Grasses and flowers (bamboo, miscanthus, switchgrass etc.), straws (barley, oat, rice, rye), and other residues (shells, husks, grains, seeds, cobs, kernels, bagasse)
<i>Aquatic Biomass</i>	Marine or freshwater algae; seaweed, lake weed, water hyacinth
<i>Animal and Human Biomass Wastes</i>	Bones, chicken litter, manure, meat-bone meal
<i>Contaminated Biomass and Industrial Biomass Wastes</i>	Municipal solid waste, demolition wood, refuse-derived fuel, sewage sludge, plywood, waste papers, tannery waste
<i>Biomass Mixtures</i>	Blends from the above varieties

Although the literature on the chemical composition of different biomass varieties reveals similar contents of C, H and O (dry ash fuel basis), there are significant differences in the contents of N, ash-forming elements, and moisture. For instance, the wood-derived fuels show lower values of ash, Cl, K, N, S and Si, and higher concentrations of C and Ca. Straws and grasses, on the other hand, have a relatively high level of Cl, K, N, S, Na, S and Si (Vassilev *et al.*, 2010). Si and Cl content is high in herbaceous biomass relative to other classes of biomass fuels (Jenkins *et al.*, 1998).

The agricultural derived and contaminated biomass group shows the most significant difference in levels of ash, moisture, C, Cl, H, Na, N, S and occasionally Al, Fe, P and Ti. These distinctions are a result of their original geographic location and handling process (pesticides, harvesting and storage) (Vassilev *et al.*, 2010).

2.4 Comparison of Coal Properties from Different Regions

Ultimate analysis is used to determine the organic composition of coal, namely the C, H, O, N, trace elements, total S and Cl content, usually on a dry ash free basis (Chelgani *et al.*, 2010). Proximate analysis parameters such as fixed carbon (FC), volatile matter (VM), moisture and calorific value (Btu/lb) are rank-dependent (i.e. associated with the extent of coalification). However, Renton (1982) and Riley (2007) affirmed that other inorganic coal elements, including the N and S content are not rank dependent and are most likely derived forms of the original plant matter (Whitehurst *et al.*, 1980). This also explains the variation in the inorganic composition of coal sourced from different locations/regions; hence no two coals are alike; even coals within a distinct seam will exhibit slight variations (Osborne, 2013). Selected world-traded coals (mainly imports to the UK; also see section 1.2) will be discussed briefly in the following sections.

2.4.1.1 United Kingdom

The British Coal Utilisation Research Association (BCURA) coal sample bank contains a comprehensive record of seam samples considered representative of the major UK coalfields (The British Coal Utilisation Research Association, 2002) (Figure 2-7). A selection of UK coals and the corresponding ultimate and proximate analysis is presented in Table 2-4. UK coals show diverse chemistry depending on the original geographic location. However, routine analysis has been restricted to S/Cl levels, moisture content, ash content and calorific value. This is because the parameters; S, Cl, ash, were used to classify the slagging tendencies of coal, and the Cl content was convenient to use as a guide to determine the alkali levels in the coal that would be available to participate in deposit formation (James *et al.*, 1997). UK coals are usually characterised as having high Cl content (> 0.30 wt %) which is almost entirely water-soluble, and moderate to high S content ($\sim 1.4 - 2.4$ wt %; see Table 2-4). Studies in the 80s by British Coal on the mode of occurrence of Cl in UK-mined coals revealed that Cl is present entirely as ions bonded to the coal matter and as inorganic halides (Gibb *et al.*, 1993; Wright *et al.*, 1997). Potassium notably is typically bound to the clay mineral (illite), and only trace amounts of water-soluble K are present in UK coals (Wright and Krause, 1997b). Sodium exists in two modes; mainly as an ionic form bound to the coal

matter in UK coals, but it can also be associated with the clay minerals (Gibb and Angus, 1983).

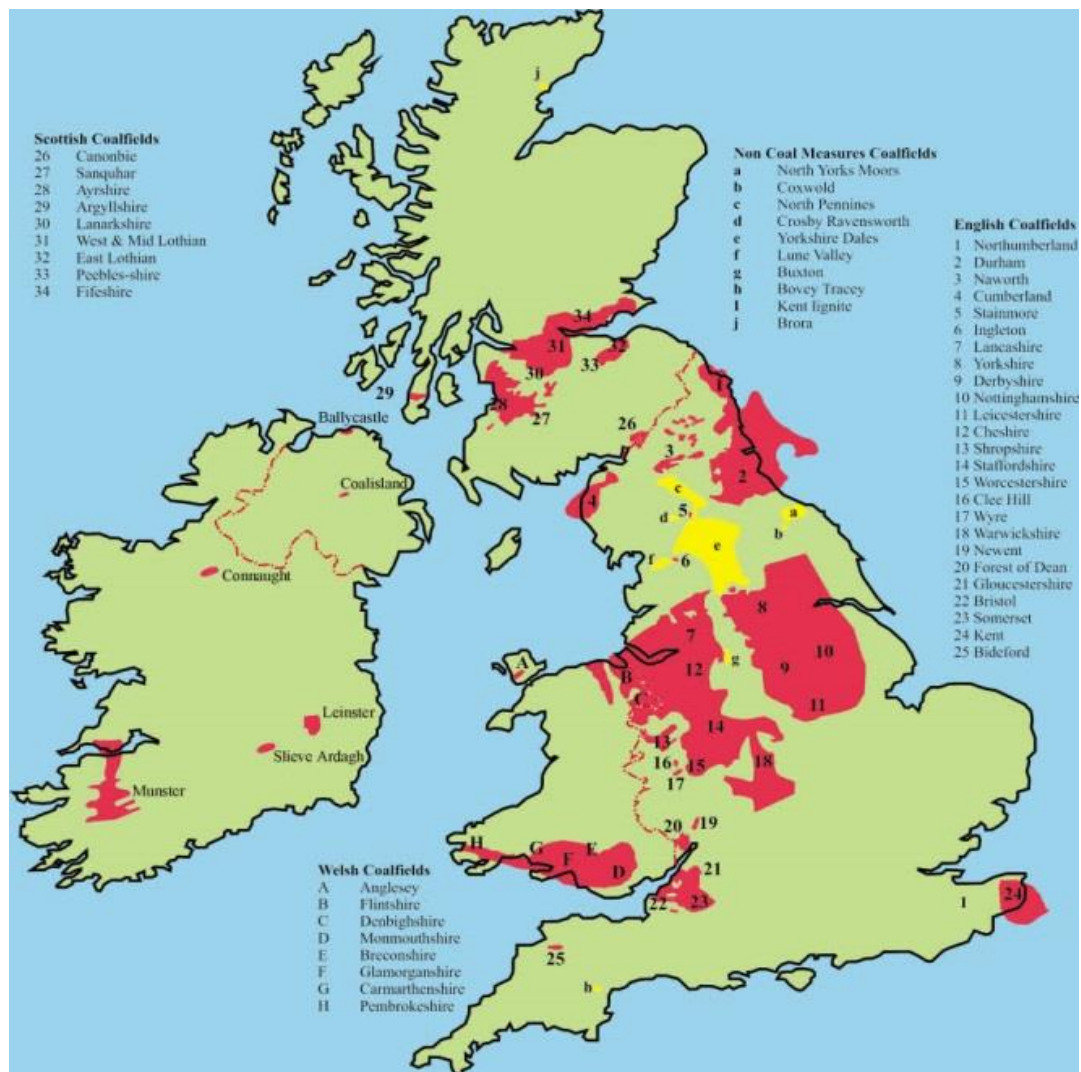


Figure 2-7: Major coalfields of the British Isles (English, Scottish, Welsh and Northern Ireland coalfields) (Northern Mine Research Society, 2016)

Table 2-4: Chemical analysis of coals from different mines (UK) (Wigley and Williamson, 1993; Energieonderzoek Centrum Nederland (ECN) Phyllis2, 2012)

Coal	Daw Mill	Hem Heath
Proximate analysis (wt %, dry basis); Calorific value		
Moisture	3.20	1.70
Ash	12.80	5.10
Volatiles	28.50	34.60
Fixed carbon	58.70	60.30
GCV (BTU/lb)	11677	13869
Ultimate analysis (wt %, dry basis); Chemical Analysis		
Carbon	69.30	79.20
Hydrogen	4.30	4.70
Nitrogen	1.20	1.80
Sulphur	1.48	0.90
Oxygen	10.66	7.60
Chlorine	0.24	0.70
Ash Composition (wt. %)		
SiO ₂	53.20	34.10
Al ₂ O ₃	21.0	24.90
TiO ₂	1.10	0.70
Fe ₂ O ₃	10.70	21.10
CaO	5.00	8.10
MgO	1.90	1.90
Na ₂ O	1.20	2.10
K ₂ O	2.50	1.00
P ₂ O ₅	0.20	1.20
SO ₃	2.90	4.90

2.4.1.2 United States

In the United States, the eleven states with the largest recoverable coal reserves are Montana, Wyoming, Illinois, West Virginia, Kentucky, Pennsylvania, Ohio, Colorado, Texas, New Mexico and North Dakota (Miller, 2011) (Figure 2-8). The eleven US coal types considered as a standard in coal characterisation include Upper Freeport, Wyodak, Illinois #6, Pittsburgh, Pocahontas #3, Utah Blind Canyon, Upper Kanawha, Beulah-Zap, Lower Wilcox, Dietz and Buck Mountain (Smith and Smoot, 1990). These eleven coals represent many of the major coal seams in the US. They originate from many different geographical areas and are representative of the different coal provinces in the US (Smith and Smoot, 1990).

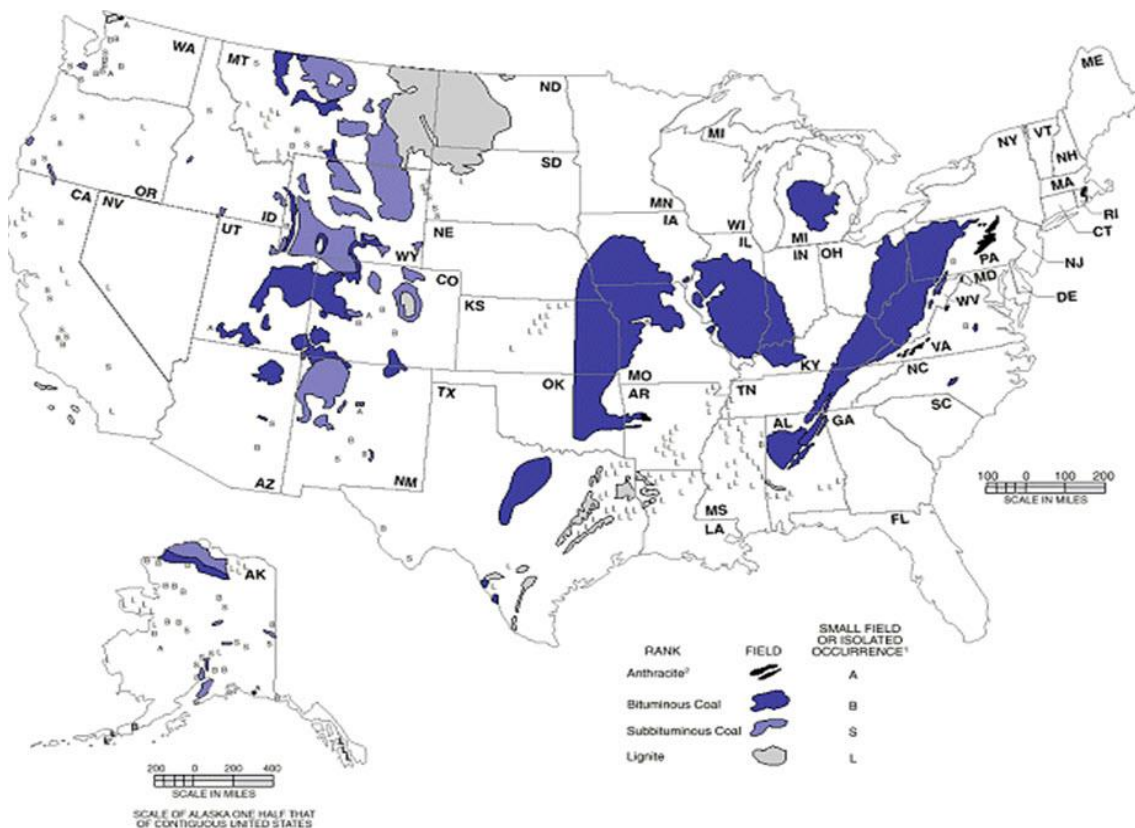


Figure 2-8: Major coalfields of the United States (Energy Information Administration, 1999)

US coals can be classified according to geographical location, rank and inorganic content, i.e. *Eastern* or *Western* coals (Lutz *et al.*, 2015). Western coals are primarily low-sulphur, sub-bituminous or lignite. All of the brown sub-bituminous coal reserves

are located in the west, mainly in Montana and Wyoming. Lignites are mostly found west of the Mississippi River (including Montana, Texas and North Dakota) (Miller, 2011). Eastern coals are generally bituminous and are located east of the Mississippi River (Illinois, West Virginia, Kentucky, Pennsylvania and Ohio) (Miller, 2011).

About 53% of US coal is bituminous. Minerals such as illite account for most of the K in bituminous coals, whilst montmorillonite $\{(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2.n\text{H}_2\text{O}\}$ and halite (NaCl) are the dominant Na-bearing minerals in bituminous and other lower rank coal (Huggins *et al.*, 2009). However, in lignites, the alkali metals are believed to occur as salts of humic or carboxylic acids (Huggins *et al.*, 2009). US coals generally have low Cl content; a notable exception is coal mined from Illinois basin (Bryers, 1978). However they have a range of S content from medium, i.e. 0.8-2.2 wt % for bituminous coal, and 0.5-1.3 wt % for lignite; to high, i.e. > 2.2 wt % for bituminous and > 1.3 wt % for lignite. (Miller, 2011).

Sulphur levels are generally lower in US coals than UK coals, but specific coal results are largely dependant on the geographic location which was impacted by the prevalent resident bacterial activity and deposition characteristics during the coal peatification stage. For instance, sulphate concentration is low in freshwater but is high in seawater (Smith and Smoot, 1990). Western coals (e.g. Montana sub-bituminous) generally have low S content as they were deposited in freshwater swamps during coalification. Eastern coals, on the other hand (e.g. Pittsburgh 8, Table 2-5), are typically high in S due to deposition into inland seawater swamps during the coalification process (Smith and Smoot, 1990).

Table 2-5 displays the composition of selected US coals.

Table 2-5: Chemical Analysis of Various Coals (US) (*Smith and Smoot, 1990; **Laumb, 2008)

Coal	Pittsburgh No. 8 (Eastern)*	Eastern Kentucky*	Wyoming (Western)**	Western Bituminous**	Lignite**
Proximate analysis (wt %, dry basis); Calorific value					
Moisture	1.52	1.11	25.30	6.30	30.50
Ash	7.73	7.59	4.90	7.30	7.00
Volatiles	39.49	38.15	34.20	42.10	33.00
Fixed carbon	52.78	54.26	35.60	48.30	29.00
GCV (BTU/lb, ar)	14032	13642	9020	11962	7715
Ultimate analysis (wt %, dry basis); Chemical Analysis					
Carbon	78.24	77.21	51.5	71.20	44.50
Hydrogen	5.21	5.34	6.60	5.40	6.50
Nitrogen	1.41	1.60	0.70	1.40	0.60
Sulphur	2.84	0.84	0.40	0.60	1.10
Oxygen	4.84	7.55	35.70	14.20	40.40
Chlorine	0.11	-	-	-	-
Ash Composition (wt %)					
SiO ₂	42.83	51.75	28.30	38.60	26.70
Al ₂ O ₃	22.11	34.49	16.30	19.70	9.50
TiO ₂	0.98	1.53	1.30	0.90	0.60
Fe ₂ O ₃	20.06	5.20	5.70	12.70	8.30
CaO	5.73	1.97	22.50	12.40	19.00
MgO	1.12	0.63	6.90	3.60	8.80
Na ₂ O	1.06	0.34	1.50	1.70	4.60
K ₂ O	1.21	1.42	0.30	1.20	0.50
P ₂ O ₅	0.47	1.76	1.30	0.50	0.50
SO ₃	4.93	0.35	16.0	8.80	21.70

2.4.1.3 Russia

Russia is the leading exporter of coal to the UK (Yaxley, 2007). Russia has extensive coal reserves, primarily of sub-bituminous and lignite rank, which account for approximately 63%, and the balance (37%) as hard coals (bituminous, anthracite) (Podbaronova, 2010). It is widely dispersed in major basins including the Moscow Basin in the far west and the eastern end of the Donetsk Basin in the south (World Energy Council, 2018). The coals exhibit a wide range in rank depending on the region from which it is mined (Podbaronova, 2010). The S content is generally low (0.3 wt %-0.8 wt %) (Laumb, 2008; Miller, 2011) and the ash content varies from 9 - 43% (Miller, 2011). Table 2-6 shows the proximate and ultimate analysis of typical Russian coal culled from ECN Phyllis database (Energieonderzoek Centrum Nederland (ECN) Phyllis2, 2012).

2.4.1.4 Indonesia

Indonesia is one of the top coal producers in the world and is currently the leading exporter of sub-bituminous coal (BP PLC, 2018). The majority of the country's coal reserves are in the south, Sumatra, with the balance in Kalimantan, West Java, and Sulawesi (Green Trade Australia, 2018). Despite the global unpopularity of coal as a fuel for power generation due to climate change concerns, the quest to increase affordable electricity has boosted coal production not just in Indonesia but other developing countries as well (The Financial Times Limited, 2018). The country's coal consists mainly of lignite, approximately 59%; 27% is sub-bituminous coal, and the balance (about 14%) consists of high ranking coals such as bituminous and anthracite (BP PLC, 2018). Coals from this region are noted for its low-rank, low ash and low-sulphur content similar to Russian coal (Laumb, 2008) (Table 2-6).

Table 2-6: Chemical Analysis of Selected World Traded Coals: Russia, Indonesia

(Energieonderzoek Centrum Nederland (ECN) Phyllis2, 2012)

Coal	Russian Coal*	Kaltin Prima Coal Indonesia*
Proximate analysis (% wt, dry basis), Calorific value		
Moisture	4.50	1.14
Ash	14.10	5.15
Volatiles	32.00	44.10
Fixed carbon	53.10	50.75
GCV (BTU/lb)	11952	12270
Ultimate analysis (% wt, dry basis)		
Carbon	68.00	74.13
Hydrogen	4.00	5.21
Nitrogen	0.87	1.72
Sulphur	0.35	0.73
Chlorine	0.01	0.01
Oxygen	11.60	13.29
Major Elements (% wt)		
Si	3.48	1.03
Al	1.66	0.67
Ti	0.062	0.025
Fe	0.608	0.26
Ca	0.275	0.067
Mg	0.128	0.054
Na	0.041	0.049
K	0.239	0.091
P	0.039	0.021

2.5 Mineral Matter Transformation during Coal and Biomass Combustion

The variation in element composition, volatile matter and ash content of the different ranks of coal, including coals of the same rank but from different seams, have created complexity in their behaviour during combustion leading to different fireside corrosion issues. The chemical variation of the fuel (dependent on the coal source) contributes to the different corrosion behaviour experienced by heat exchangers in coal-fired boilers. The manner in which the species are combined in the fuel dictates their activity in the gas phase, with organically bound elements easily released to the flue gas during combustion thus accelerating the corrosion process. On the other hand, fuel elements bound to the mineral matter such as in anthracite coals will be less prone to release corrosive species (e.g. Na, K, Ca, Cl, S) that can react with other fuel species, thus less fouling damage can be expected under those circumstances. The variation in coal properties from the different regions (as well as biomass) will be highlighted in the following sub-section to assess their impact post-combustion.

Coal combustion transforms coal-minerals, originally in the form of shale, silicates and other compounds of Na, K, Ca, Mg and Ti, and vapour phase species to ash components (Wilfred *et al.*, 1980). The volatile components are vaporised and form part of the flue gas. The non-volatile, coarse ash components move down to the bottom of the furnace and are collected as bottom slag (Pisa and Lazaroïu, 2012). Smaller particles (i.e. fly ash and inorganic compounds entrained in the vapour phase) are transported with the flue gas upstream from the furnace to the superheater and reheater tubes (Figure 2-9).

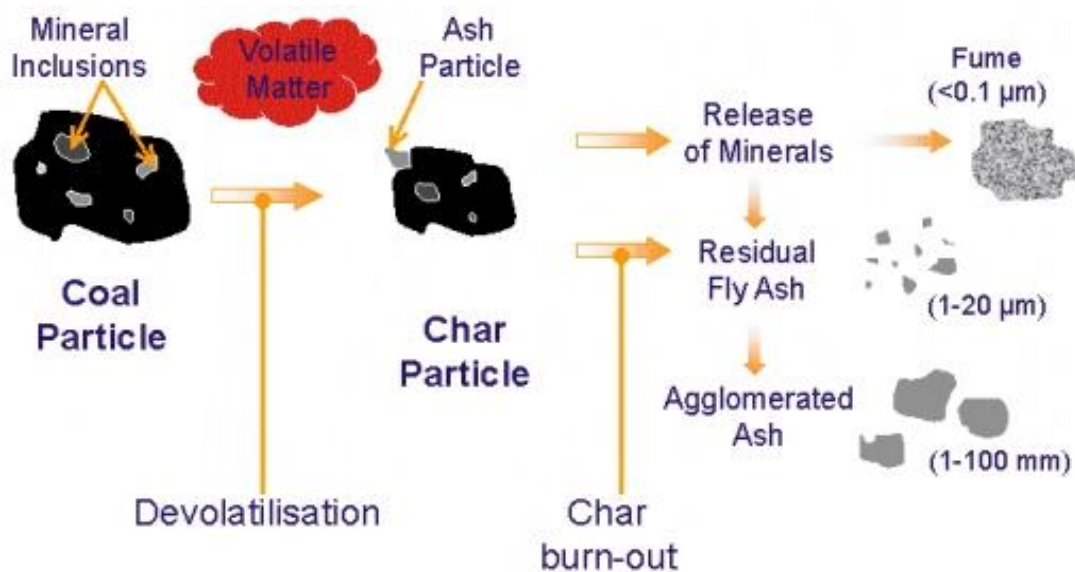


Figure 2-9: Schematic diagram showing the transformation of mineral matter during coal combustion (CoalTech Pty Ltd, 2007)

2.5.1 Impact of Coal Chemistry in Combustion (UK vs the US)

The chemical and physical properties of coal determine its commercial value (Bains and Robinson, 2016), with high-grade coals defined as having less of inorganic impurities. For instance, Cl is considered detrimental in coal and biomass combustion because of its effect on corrosion in power plant boilers (Bains and Robinson, 2016). High S coals are equally challenging because of their corrosive potential in coal-fired boilers and atmospheric pollution when released as SO_x (i.e. $\text{SO}_2 + \text{SO}_3$) (Bains and Robinson, 2016). Hence as a result of SO_x emission legislation in the US, coal utilisation is mainly restricted to high-grade coals (low S content) and the US imports mostly low-S coal from South America (Colombia, Venezuela) (Laumb, 2008). US boiler manufacturers recommended burning coal (for power generation) with Cl levels below 0.3 wt % following experiences from the UK where increased corrosion rate was linked to burning high Cl content coals (James *et al.*, 1997; Wright and Krause, 1997b). Although UK coals have been generally characterised as having high S and Cl content, most UK coals show highly diverse chemistry dependent on the geographical locations, typically with high ash content (up to 20%), broad spread in Cl, S levels (Figure 2-10) and varying levels of alkali content. In the US, Cl is present in substantial amounts in the Appalachian and Illinois basin (in the range 0.1-0.4 wt %) (Chou *et al.*, 1999; Rod Hatt,

2015); however, further studies showed that the fireside corrosion experience in the US is very different from the UK (Wright and Krause, 1997b). More importantly, the chemical variations in US coal compared to UK coal (Table 2-7) will lead to different corrosion behaviour. Notably, UK coals typically have higher ash content compared to US coals (Wright and Krause, 1997b), hence the fireside corrosion experience will be different.

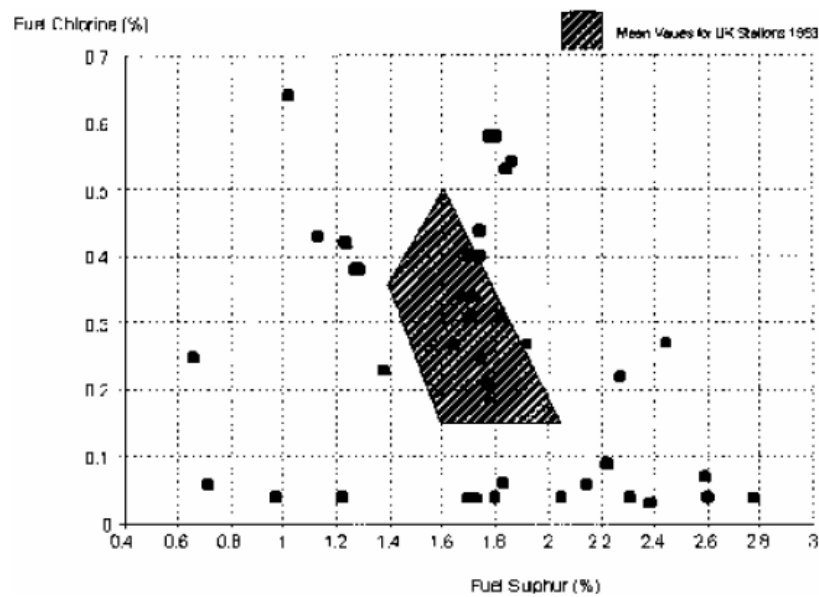


Figure 2-10: Broad spread in sulphur and chlorine levels in UK coals delivered to two UK power stations over the period 1992-1994. The striped region shows the mean value for UK stations (Wright and Krause, 1997b)

Table 2-7: Total Cl, S, and ash content from three selected coals (British coal, high-Cl Illinois (US) coal and low-Cl Illinois coal (US)) (Chou *et al.*, 1999)

Wt % Dry Coal Basis	High-Cl British Coal	High-Cl Illinois Coal	Low-Cl Illinois Coal
Total Cl	0.46	0.44	0.14
Total S	1.32	1.22	4.48
Total ash	23.56	7.90	9.38

2.5.2 Impact of Biomass Chemistry in Combustion

Biomass is generally characterised as having low S content compared to coal, but some species (especially the herbaceous group) have higher Cl and total alkali content. The alkali and alkaline earth metals in biomass fuels are very volatile and thus easily released at combustion temperatures (Hurley *et al.*, 1993; Jenkins *et al.*, 1998). Also, Cl facilitates the mobility of many compounds, especially K, which is present in the form of water-soluble inorganic salts which can easily volatilise during combustion; thus the tendency for fouling of tube materials may increase in biomass combustion (E.ON UK, 2004; Shao *et al.*, 2012).

In summary, the variation of chemical properties in the fuels (coal and biomass) from different regions gives rise to different fireside corrosion experiences as a function of the different levels of impurities carried by the flue gas. The implication is that, during combustion, these species are released into the flue gas and interact with the boiler components and almost always result in erosion, deposition or/and corrosion of superheater/reheaters (Wright and Krause, 1997b), thus creating significant maintenance issues in industrial steam boilers.

2.6 Factors that Affect Deposition Rate and Composition

2.6.1 Deposit Composition

The combustion of pulverised coal yields deposits (as condensed vapour or particles) which consist of a porous matrix containing (Simms, 2011a):

- Si-Al-O compounds derived from alumina-silicate minerals.
- Ca/Mg carbonates, sulphates, chlorides.
- Na/K sulphates, chlorides.
- Iron sulphates, chlorides, oxides, sulphides.

For biomass-fired plants, the deposit composition is slightly different from coal as the chemical constituents are different. For instance, alkali chlorides are the most likely bonded deposit in biomass-fired combustion compared to alkali sulphates in coal combustion. With co-firing, the deposit interactions are even more complicated.

2.6.2 The Effect of Temperature

The temperature-dependent relationship of coal-ash corrosion for austenitic stainless steels is defined by a bell-shaped curve (Figure 2-11), featuring damage peaks in fireside corrosion (Weele and Blough, 1990; Simms, 2011a). The fireside corrosion rate increases in the metal temperature range of about 600 °C-700 °C, in which the molten deposits are stable, up to approximately 670 °C-700 °C, where maximum damage rates are observed (Simms *et al.*, 2007). The temperatures for the maximum corrosion rate, as shown by the bell curve (Figure 2-11), shifts and varies in width as a function of alloy composition, SO₂/SO₃ levels, and alkali levels. Beyond the peak temperature, the molten deposits become unstable and decompose into solid sulphates. The main reason for the instability of the molten deposits is the unavailability of SO₃ to stabilise some sulphate phases as the SO₃/SO₂ balance favours SO₃ at lower temperatures (Simms *et al.*, 2007). This research focuses on the lower temperature region where the corrosive alkali-iron-trisulphate compound is thermodynamically stable.

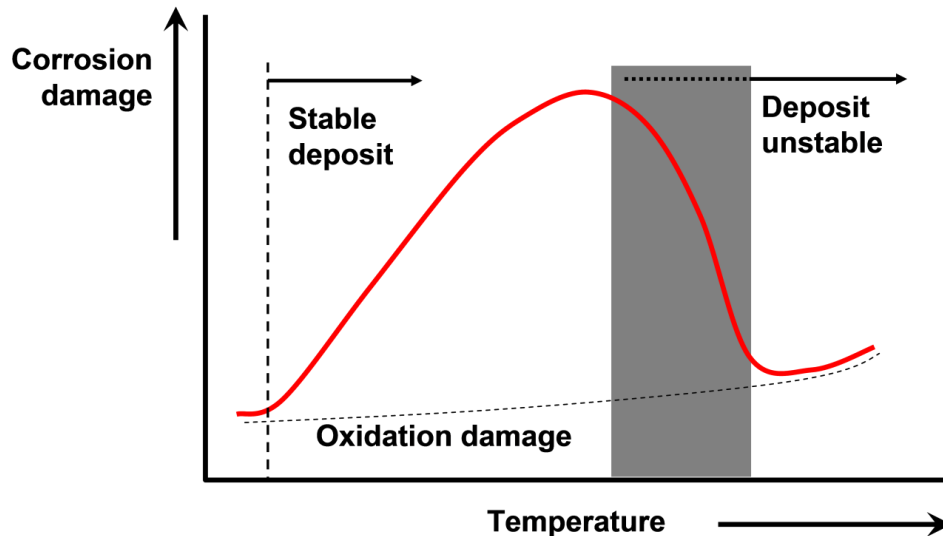


Figure 2-11: Corrosion dependence on temperature (Simms *et al.*, 2007)

Michelsen *et al.* (1998) simulated and compared deposit compositions at metal temperatures of 450 °C and 550 °C in a straw-fired boiler. SEM analysis revealed a thick layer of condensed alkali chloride on the 550 °C probe (20-30 µm) and a less dense material on the 460 °C probe; with the outer surface consisting mainly of fly ash

particles. On the 550 °C probes, the inner layers consisted of almost pure KCl. However, with the lower temperature probe, the metal temperature (460 °C) was not high enough to form eutectic melts between FeO, KCl, and other corrosion products. The result in this analysis underscores the relationship of the deposits' composition as a function of the metal temperature and temperature gradient. Biomass generally has low S content. In this study, S as SO₂ present in the gas (for woody biomass) was about 50 ppm - not enough to result in the sulphating of the K in the deposit (James *et al.*, 1997; Uniper Technologies, 2016b) hence damage rates for the austenitic tubes were relatively low (discussed in chapter 4). Likewise, from the literature cited (Michelsen *et al.*, 1998), at temperatures at or below 450 °C, the corrosion rate was negligible but became more prominent at steam temperatures above 550 °C.

2.6.3 The Effect of SO₃

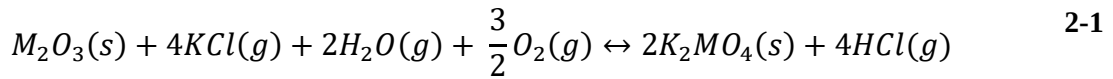
Sulphur plays a crucial role in the fireside corrosion mechanism; hence the S levels in coal and biomass are vital. During coal combustion, pyrite (FeS₂) burns to form SO₂ and FeO which can be further oxidised to SO₃ in the flue gas as it cools. Laboratory experiments have revealed that higher SO₃ partial pressures can be generated by catalytic oxidation of SO₂ beneath the tube deposits hence ensuring the stability of complex sulphates up to 700°C (Wright and Shingledecker, 2015). Fireside corrosion studies reveal that the rate of dissolution of the protective scale increases when the local partial pressures of SO₃ in flue gas increases from 1000 ppm to 5000 ppm (James *et al.*, 1997). However, if the metal temperature is raised above the decomposition temperature for iron sulphate (Figure 2-11), the molten sulphate layer ceases to exist, and the corrosion rate drops (Weele, 1991).

2.6.4 The Effect of Chlorine on Corrosion

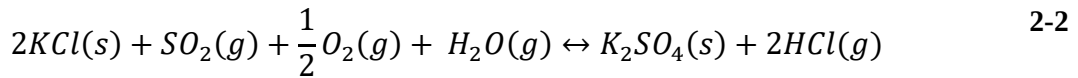
Although it is generally accepted that high Cl fuels may speed up the fireside corrosion process, it has been difficult to predict the degree to which the Cl content contributes to fireside corrosion, and previous investigations have shown that very little or no Cl is ever present in the deposit in coal combustion (Wright and Krause, 1997b; Riley, 2007). When present in a deposit, Cl occurs as an alkali chloride (Robinson *et al.*, 2002).

Viswanathan (1989) suggested that Cl acts as a catalyst for the molten trisulphate attack, rather than participating directly.

By contrast, in biomass combustion, different mechanisms are observed particularly when burning low S biomass fuels (Cl attack), as the fireside corrosion is mainly attributed to alkali chloride deposits (Shao *et al.*, 2012; Okoro *et al.*, 2017). Deposition of the alkali chloride occurs via a condensation mechanism, which is driven by the temperature difference between the gas and the boiler tubes (superheaters/reheaters) (Seraffon *et al.*, 2016). The KCl in the deposit can react with the oxide of the alloy elements (equation 2-1) (Okoro *et al.*, 2017) or with the gaseous species in the gas stream (equation 2-2) (Okoro *et al.*, 2017).



Where M = oxide of the alloying element

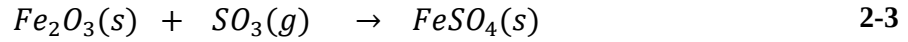
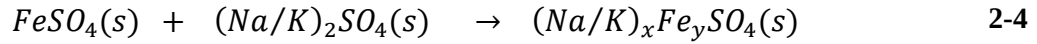


Fireside corrosion is increased in biomass boilers by the formation of metal chlorides by the Cl-bearing species produced from the above reactions (i.e. HCl). Fe or Cr are selectively removed from the steel alloy (equation 2-1) (Michelsen *et al.*, 1998; Okoro *et al.*, 2017) thus exposing the bare tubes to further corrosion.

2.6.5 The Effect of Alkali Metals on Corrosion

The water-soluble alkali metal compounds in coal represent the amount of volatile alkali metal released during combustion and can react with other species in the gas and thus contribute to deposit formation (James *et al.*, 1997). The bonded deposits on tube surfaces, in most cases, are held in place by the alkali sulphates formed in the furnace (Laumb, 2008). Biomass contains more water-soluble K but lower amounts of S and Na when compared to coal. Potassium in UK coal is mostly bound to the clay minerals with less potential to volatilise during combustion. However, if the furnace temperature is high enough, K might be released into the combustion gas (Hurley *et al.*, 1993). On a broader note, if the alkali content is high, this could lead to the deposition of alkali sulphate ((Na/K)₂SO₄) which could form a low melting point compound with another species,

e.g. Fe_2O_3 , the oxide scale on the tube surface or from the ash which melts at 560 °C (Weele, 1991).



2.6.6 The Effect of Alloy Materials

Field investigations employing different tube materials have reported varying degrees of fireside corrosion damage suggesting that the degree of metal loss is also dependent on the tube alloy (Uniper Technologies, 2016b). The low alloy ferritic steels usually suffer severe damage compared to austenitic and nickel-based alloys. High Cr (austenitic) steels, up to 25 wt % Cr, form an adherent protective chromia scale (Cr_2O_3) which increases the corrosion resistance of the steel. However, above 900 °C, there is an increased tendency for Cr_2O_3 to react with O_2 and H_2O and volatilise as $Cr_2O_2(OH)_2$ (Sharp, 2010). Aluminium oxide (Al_2O_3) and silicon dioxide (SiO_2) are more stable oxides as they exhibit the slowest transport rates for metal and oxygen ions and do not react to a higher oxidation state (Lai, 2007b). Refractory metals such as Mo have been known to be detrimental at high temperatures. Thus low levels of Mo are usually recommended (Patel *et al.*, 2013). There has been increasing interest and advancement towards the utilisation of high-temperature corrosion resistant nickel-based alloy (e.g. Inconel 740) to meet the stringent material requirements for AUSC steam boilers (Sharp, 2010; Patel *et al.*, 2013; Aung and Liu, 2014).

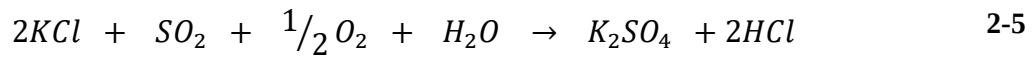
2.6.7 The Effect of Co-firing Coal and Biomass

Co-firing biomass in existing (coal) boilers is an alternative to burning fossil fuels due to its potential for reducing net carbon dioxide emissions and thus encourages the large-scale utilisation of biomass. However, a large amount of water-soluble compounds in some classes of biomass (mainly grassy energy crops) leads to highly mobile and active inorganic material (namely K, Na, Ca and Cl compounds) which can form vapour phase alkali chloride compounds that are likely to foul boiler tube surfaces (Shao *et al.*, 2012). This phenomenon promotes the formation of deposit layers and accelerates the corrosion process. Some biomass fuels are also known to contain large amounts of

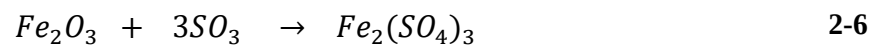
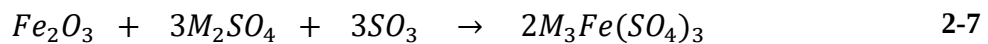
silica, particularly the herbaceous class of biomass such as rice straw, miscanthus etc. The silicates can melt at 800-900 °C during combustion and form deposit on heat exchanger surfaces (Shao *et al.*, 2012).

2.7 Fireside Corrosion Mechanism

The reactions of SO₂ and chlorides produce sulphates by homogeneous gas phase reaction according to equation 2-5 below (Wright and Shingledecker, 2015):-



As heat is being transferred from the gas to the working fluid in the heat exchangers, the flue gases are cooled and, subsequently, alkali metal sulphates (Na₂SO₄, K₂SO₄) form in the furnace and condenses on the tube surface (Simms *et al.*, 2007; Lant *et al.*, 2010; Wright and Shingledecker, 2015). The alkali compounds can be deposited via direct condensation on the tube surface, or impaction of fly ash particles carrying the condensed alkali, or by thermophoresis of smaller particles (Wright and Krause, 1997b). The presence of a sticky layer is due to the condensing salts which facilitate the deposition of ash particles, some of which may stick to the surface or rebound and adhere to another position on the tube. These deposits will eventually grow to the extent that they insulate the tube surface from the gas stream thereby impeding heat transfer to the tubes (Hurley *et al.*, 1993). Above 580 °C, and in the presence of SO₃, the mixed deposits become molten at the tube surface, react with another constituent of the deposit and form a layer of highly corrosive alkali iron trisulphate mixture (2Na/K₃Fe(SO₄)₃) beneath the ash deposit. The molten alkali iron sulphate dissolves the protective oxide scale thereby causing accelerated oxidation and sulphidation (equations 2-6 and 2-7) (Wright and Krause, 1997b).



Where 'M' represents the alkali metal (Wright and Kung, 2018).

These deposits, as depicted in Figure 2-12, occur as wastage flats on the tube surface, or as an array of deep pitting (Lant *et al.*, 2010). Wastage flats for leading tubes (i.e. heat

exchangers facing the gas flow) are located at the 2 o'clock and 10 o'clock positions (Figure 2-12) (Wright and Shingledecker, 2015). Wastage flats on non-leading tubes tend to appear on the 3 o'clock and 9 o'clock positions as these are somewhat shielded from the main gas flow (James *et al.*, 1997). The deposit composition found on the tubes depends on the type of fuel burnt, the alloy material and combustion conditions (Simms, 2011a). For example, deposits from coal-fired boilers are mainly molten complex alkali iron sulphate compounds. For biomass boilers, deposits are usually alkali chlorides (Wright and Krause, 1997b).

As an example, on austenitic steels, the scale on the corroded tube consists mainly of magnetite (Fe_3O_4) with intermittent layers of iron sulphides and Cr-rich sulphides (James *et al.*, 1997). The outer 'melt' is an infusion of haematite (Fe_2O_3) and ash debris (Wright *et al.*, 1995; Wright *et al.*, 1997).

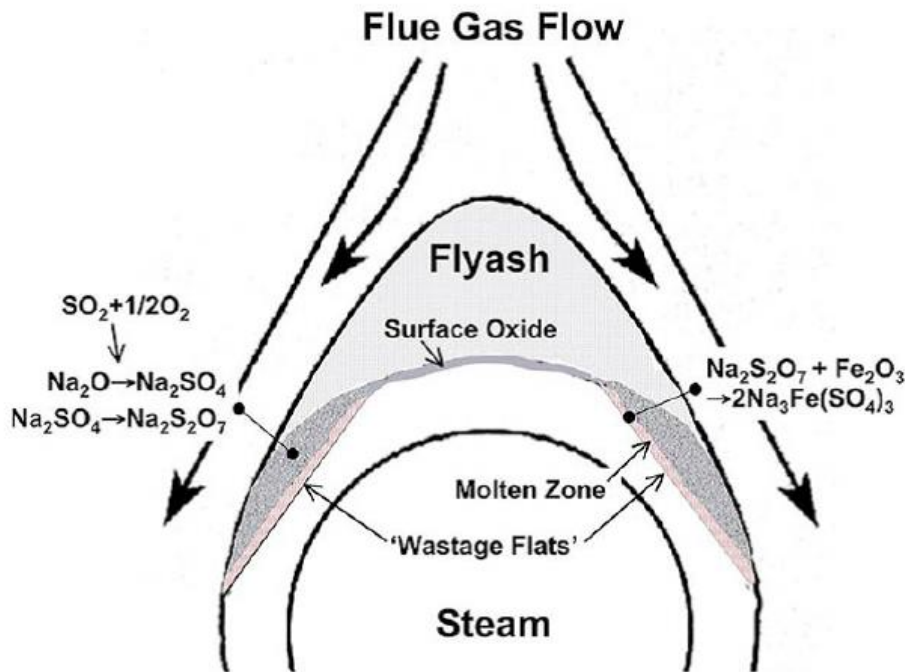


Figure 2-12: Schematic illustration of the deposit formed on the upstream side of the superheater tube (Wright and Kung, 2018)

2.8 Review of Previous Fireside Corrosion Models

Several collaborative research projects involving plant test runs, laboratory-scale experiments, and deposit characterisation have been undertaken to improve understanding of fireside corrosion behaviour and to predict the degree of fireside corrosion (Blough and Seitz, 1990; James *et al.*, 1997; Robinson *et al.*, 2002; Lant *et al.*, 2010). A conventional method of analysing deposit samples from high-temperature corrosion is the installation of air-cooled probes situated in the vicinity of the superheaters/reheaters to simulate the heat exchanger tubes and then investigate the resultant deposit. Thermocouples are installed into the exterior of a deposition probe to monitor the surface temperature of the probe.

Harb *et al.* (1993) developed a speciation model to estimate the equilibrium phases of coal ash systems to predict the slagging behaviour of coal ash. This was achieved by the use of computer calculations (using Gibbs free energy minimisation) to determine the amount and chemical composition of the liquid phase in silica-based systems, i.e. a variety of oxide systems containing Si, Al, Ca, Na, Mg and Fe. The expression given for the chemical potential of the liquid system is shown in equation 2-8 (Harb *et al.*, 1993).

$$\mu_j = \mu_j^\circ + RT \ln \left(n_j / n_T \right) \quad 2-8$$

Where;

μ_j = chemical potential of species j

n_j = moles of species j

n_T = total number of species

μ_j° = standard state chemical potential of species j

R = gas constant

T = Temperature in K

n_j / n_T = mole fraction of species j in the melt.

The goal was to provide more insight on ash deposition behaviour and to distinguish between coal ashes which produce deposit and those which do not. The authors (Harb *et al.*, 1993) however cited amongst other limitations the inherent complexity of the model and the lack of experimental data for all systems of interest.

Huang *et al.* (1996) modelled the flow characteristics and deposition process to predict the build-up of ash deposit on superheaters. The deposition model is the cumulative effect of four main methods of deposition (equation 2-9), i.e. inertial impaction (I_i), thermophoresis (T_i), condensation (C_i) and heterogeneous reaction (R_i) (Huang *et al.*, 1996).

$$\frac{d_{mi}}{d\tau} = I_i(t, \tau) + T_i(t, \tau) + C_i(t, \tau) + R_i(t, \tau) \quad 2-9$$

Where;

m_i = mass of component, i , in the deposit.

t = residence time relative to the time of injection of the particles.

τ = elapsed time corresponding to an arbitrary time of day independent of the particle residence time.

The model developed by Huang *et al* (1996) focused on the deposition processes of ash particles, however, only thermophoresis and inertial impaction were considered, and hence the C_i and R_i terms were omitted from equation 2-9 (Huang *et al.*, 1996). One of the conclusions drawn from the predicted results was that the denser iron-rich particles were more inclined to deposit than the less dense silica-rich particles.

Other attempts have been made to derive correlations among the species present in coal and their role in fireside corrosion. One of such highlighted in Wright and Shingledecker's (2015) and Viswanathan (1989) reports is the Borio's Index (I_c), developed for Eastern US bituminous coals. Here the corrosive potential of the alkali metals (Na and K) were offset with the moderating effects of Ca and Mg. The index value was derived from a nomograph defining factors using the convention of all metals expressed at their highest oxides including acid-soluble K_2O , acid-soluble Na_2O , CaO and MgO and Fe_2O_3 (Fe_2O_3 was used as a measure of the sulphur content of coal)

(Borio *et al.*, 1968). The coal corrosivity index derived was of the range 0-22, with an increasing value denoting increased risk of corrosion following coal combustion. However, employing this index to represent the corrosive nature of other coals was less successful. Another limitation of this approach was that the combustion environment was not considered in the derivation of the index; just the corrosive components found in the coal with no reference to their transformation during combustion.

An alternative corrosivity potential ranking cited by Wright and Shingledecker (2005) was the Raask index. The water-soluble content of Na and K were derived from calorimetric bomb measurements of coal and provided a simplistic ranking of coal corrosivity; i.e. < 0.5 wt % (Na + K) denotes low corrosion potential, and > 1.0 wt % denote high corrosion potential.

The Central Electricity Research Laboratory (CERL, UK) developed a corrosion model tagged the PE-8 model following probe investigations on the performance of austenitic alloys in UK coal-fired plants (Clapp, 1991; Wright and Shingledecker, 2015). This equation correlated the fireside corrosion rate with the coal Cl content of the form:

$$\text{Corrosion rate} = AB(T_g/G)^m \left[\frac{(T_m - C)}{M} \right]^n (\%Cl - D) \quad 2-10$$

Where;

A = tube position factor (leading or non-leading)

B = material factor for austenitic steels

T_g = average flue gas temperature (range: 870 – 1200 °C)

T_m = tube metal temperature (range: 605 – 680 °C)

% Cl = average fuel chlorine composition (wt %)

Corrosion rate = fireside corrosion rate in nm/hr.

C, G, M, D, m and n are constants that need to be determined for each specific location in a given boiler (Wright and Shingledecker, 2015). The material factor, B, differentiated the relative corrosion behaviour of different austenitic steels.

Corrosion rate values for alloys with higher Cr and Ni content (e.g. 25Cr, 20Ni steels, 310) were less than those with lower Cr content such as the 15-19% Cr steels (e.g. TP316, 321, 347, Esshete 1250). The Cl content alone represented the fuel's corrosive potential as the premise was that the increase in corrosion rate of boiler tubing is proportionate to the increase in Cl content of the coal. This used the basic misunderstanding of assuming that for UK coals, the Cl content served as an indicator for the Na/K available to volatilise and participate in deposit formation (Wright and Krause, 1997b). However, subsequent US studies that specifically burnt Illinois basin coals with Cl levels over 0.3 wt % (Table 2-7) showed little or no (worsening) effect on fireside corrosion compared to UK (fireside corrosion) studies (Wright and Krause, 1997b).

A different variant of the PE-8 model, i.e. the CERL Modified PE-8 equation, used different assumptions. The modified PE-8 version (equation 2-11) was obtained via a least squared regression of the PE-8 dataset (Lant *et al.*, 2010):

$$\text{Corrosion rate} = \exp[(r/T_m) + s(\%Cr_{\text{alloy}}) + t(T_g - T_m) + u + v(\%Cl_{\text{fuel}})] \quad 2-11$$

A fireside corrosion model using laboratory data was also developed (equation 2-12), and the inputs to the model included S, alkali metals (Na + K), HCl_(gas), and SO_x (Lant *et al.*, 2010; Wright and Shingledecker, 2015):

$$\begin{aligned} \text{Corrosion rate} & \quad 2-12 \\ = \exp[(a/T_m) + b + c(HCl) + d(SO_x) + e(Na + K)_{\text{dep}}\% + f(\%S_{\text{dep}}) + g(\%Cl)] \end{aligned}$$

Where;

a, b, c, d, e, f and g are constants; and the suffix dep indicates the measured values from the deposit.

Although the correlation in equation 2-12 accounted for significant parameters attributed to fireside corrosion in coal-fired boilers, the duration of the experiment was for 1000 hrs, and only six alloys were studied.

Wright and Shingledecker (2015) formulated a mass balance-based approach to account for the relative differences in corrosion potential as a function of the composition of coal burned. The authors conceded that there was no publicly available algorithm that

provided a widely applicable means linking the differences in the fireside corrosion behaviour of SH/RH tubes to the composition of the fuel, hence an alternative method that was based on the fate of the coal species during combustion was proposed. A parameter termed the *Relative Corrosion Potential* (RCP) was generated by calculating the maximum amount of species (Na, K, Ca, Mg, S, Cl) available in the superheater/reheater tube region to form the corrosive alkali iron trisulphate relative to that for a typical Eastern (US) bituminous coal (arbitrarily assigned a value of 10). The chart in Figure 2-13, culled from Wright and Shingledecker's report (2015), shows the values of RCP determined for over 50 coals (from CEGB data) plotted against the reactants, namely Na_2O , K_2O , MgO , CaO , S_2 and Cl as obtained from standard coal analysis.

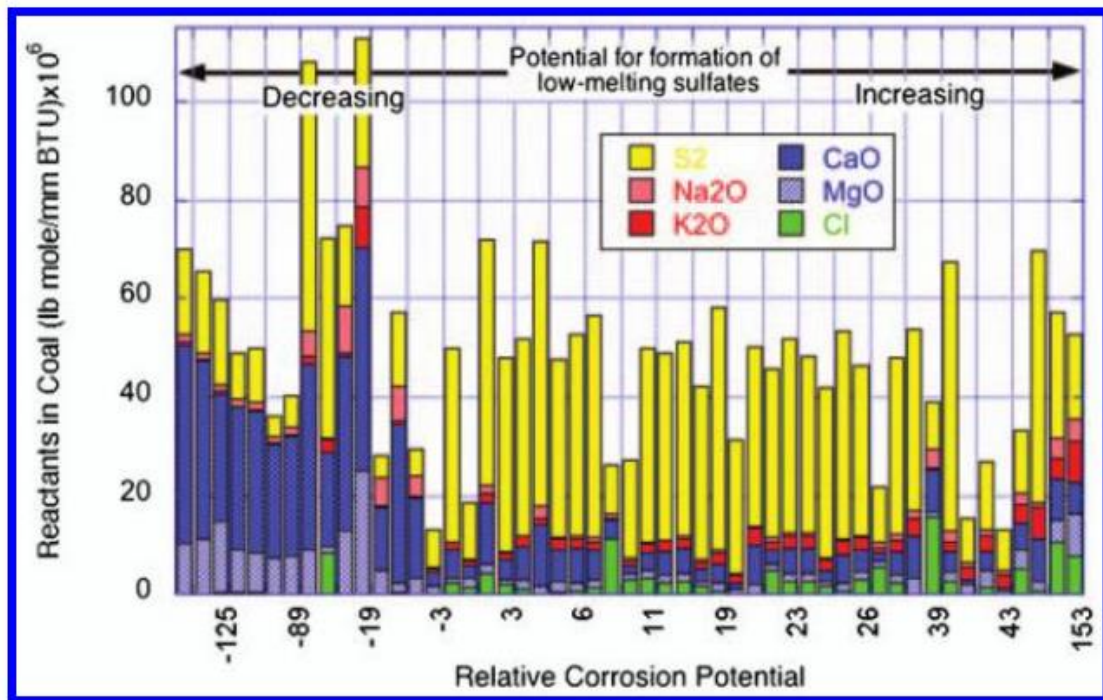


Figure 2-13: Comparison of reactive species for a range of coals with calculated RCP values (Wright and Shingledecker, 2015)

Negative and decreasing values of RCP indicated insufficient alkali metals and Cl (or increased contents of $\{\text{CaO} + \text{MgO}\}$) to form the complex alkali sulphates as depicted on the chart. The authors did not find a link of the RCP value with S content as it appears it was sufficient to react with available $(\text{Na}_2\text{O} + \text{K}_2\text{O})$. Ultimately it was shown that fireside corrosion was commensurate with an increasing RCP value for both the

leading and non-leading position of the SH/RH tubes. However the authors highlighted the limitations under different combustion conditions where different RCP values were encountered; for instance, higher corrosion rates were measured for low NO_x firing boilers (Wright and Shingledecker, 2015).

Michelsen *et al.* (1998) performed deposition and corrosion measurements on a 10MW wheat straw-fired boiler located at Rudkobing, Denmark. Fireside corrosion damage was observed on tube surfaces with metal temperatures above 520 °C, and the deposits were enriched in K and Cl. Selective corrosion was found to occur where Cl from KCl attacked the Cr and Fe in the steel thus producing volatile Fe and Cr chlorides. The ensuing deduction was that the metal chlorides had diffused out and formed metal oxides at positions with higher oxygen partial pressures. This had impeded the formation of a protective barrier that would have formed on the tube surface.

Kumari *et al.* (2017) used an artificial neural network model for predicting the fireside corrosion rate of superheater tubes in a coal-fired boiler using operational data from an Indian thermal power plant. The input parameters were: percentage air intake, coal ash and S content, flue gas temperature, SO_x concentrations in flue gas and oxides of Na and K. The S content of coal in the dataset ranged from 0.3 - 1.0 wt %. The authors acknowledged that there was comparatively less S content present in Indian coal compared to British coal. However, there was sufficient S to form fusible sulphates with Na and K in the flue gas. A portion of the result showed that the corrosion rates were observed to increase from 0.1 – 1.0 mm/year with increasing S content in the coal ranging from 0.3 – 1.0 wt % (Figure 2-14) and SO_x from the flue gas ranging from 230 – 245 mg/m³ (Figure 2-15) (Kumari *et al.*, 2017).

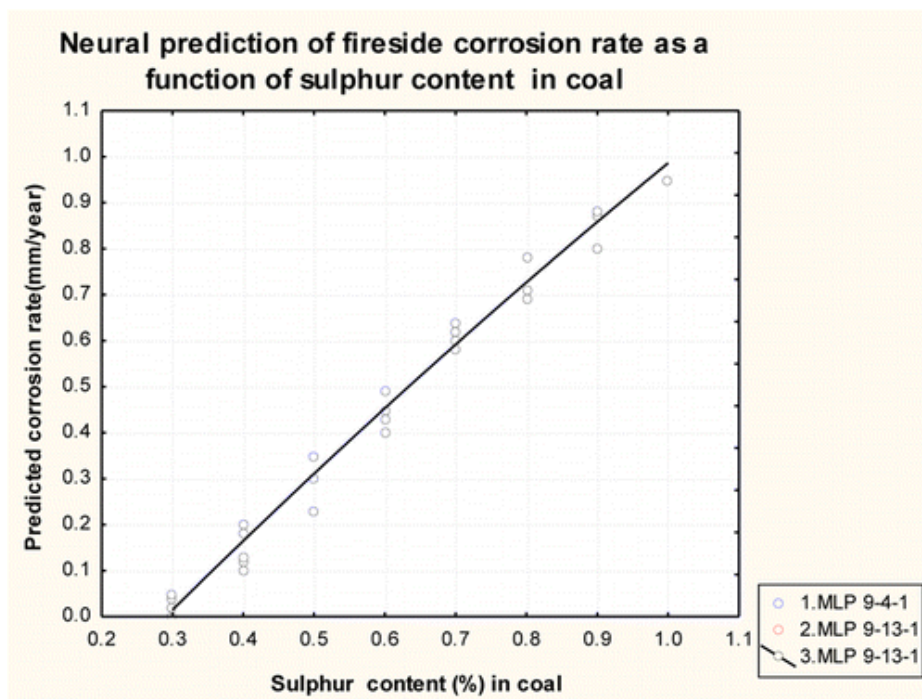


Figure 2-14: Neural prediction of fireside corrosion rate as a function of sulphur content in a typical thermal Indian coal (Kumari *et al.*, 2017)

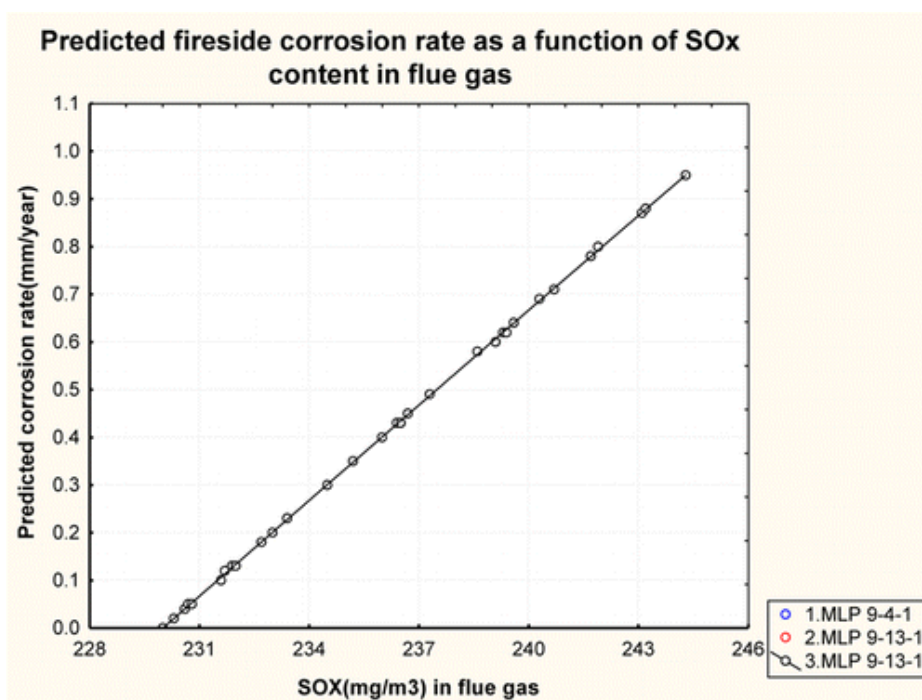


Figure 2-15: Neural prediction of fireside corrosion rate as a function of SOx content in the flue gas (Kumari *et al.*, 2017)

2.8.1 Research Gap in Fireside Corrosion Model Development

Fireside corrosion investigations have been carried out and the mechanism has been attributed to the formation of low melting complex sulphates for coal combustion, and alkali chlorides for biomass combustion. However, the effect of burning different fuels has not been fully explained. With respect to coal-firing, the initial consensus from UK investigators following probe studies conducted in the '60s was that metal loss was highest in stations firing fuels with high Cl content (Wright and Krause, 1997b); even though the deposits were sulphates (coal-firing), Cl was being used as an indicator of the alkali metals (Na/K). Thus, the Cl content has been the only fuel-related term in the proposed coal-fired corrosion models. However, subsequent tests for different coal types have produced mixed results underscoring the error in assuming that the Cl content is equivalent to the (Na+K) content. Indigenous UK coals tend to have S content ranging from 0.5 – 4 wt %, enough to be in excess (Wright and Krause, 1997b), hence UK based studies did not correlate fireside metal wastage rates to S content (Lant *et al.*, 2010). Results from studies sponsored by the U.S Department of Energy (Purgert *et al.*, 2008) however showed that U.S. Mid-western and Eastern coals containing high S content are very corrosive.

Fireside corrosion models have been proposed but, as recent studies (Wright and Shingledecker, 2015) have suggested, new boiler operating modes employing higher steam temperature and pressure and staged combustion process tend to produce increased corrosion rates. The fireside corrosion prediction models proposed have either left out or not considered other input parameters that could influence the corrosion rate. For example, the boiler operating conditions (metal and gas temperatures) excluded from the Borio's and Raask indices (Wright and Shingledecker, 2015), and the possibly wrong assumption of including only Cl as the marker for the fuel's corrosivity in the PE-8 model (Wright and Krause, 1997b). This research aims to contribute to filling the knowledge gap by incorporating relevant attributes with the current understanding of fireside corrosion and thus develop a series of models (using plant data) to predict the behaviour of fireside corrosion on the superheaters and reheaters.

2.9 Statistical Technique Employed to Analyse Fireside Corrosion Data and Build Fireside Corrosion Prediction Models

To tackle the complexity of a highly correlated (plant) corrosion dataset and achieve the objective of building fireside prediction models from it, statistical techniques were employed to analyse plant data gathered from probe (fireside) investigations (chapter 3). The approach taken in this research is to avoid a situation known as ‘multicollinearity,’ which occurs when the predictor variables are highly correlated. The techniques applied in this work are introduced in the following subsections, and step-by-step procedures of this technique are detailed in subsequent chapters.

2.9.1 Principal Component Analysis - Overview

Principal Component Analysis (PCA) is a statistical technique that linearly transforms an original set of variables into a smaller set of uncorrelated variables (called principal components, PCs) that represent most of the information in the original dataset (Dunteman, 1989). The goal is to reduce the dimensionality of a set of variables while retaining its maximum variability, thus revealing the underlying structure of the data. PCA is typically employed as a tool in exploratory data analysis and works by rotating a cloud of (data) points (red dots, Figure 2-16) in such a way that maximum variability is visible (blue axes, Figure 2-16).

Karl Pearson invented PCA in 1901, and it was developed by Hotelling in 1933 (Dunteman, 1989). It was primarily applied in the social sciences, psychology and specialities such as image compression (Afifi, May and Clark, 2012), face recognition, visual tracking, etc. (Naik, 2018), in an attempt to discover the underlying structure of the data studied. PCA is now gaining popularity in many fields of sciences and engineering (Seggiani and Pannocchia, 2003; Camperos *et al.*, 2015; Tambe *et al.*, 2018).

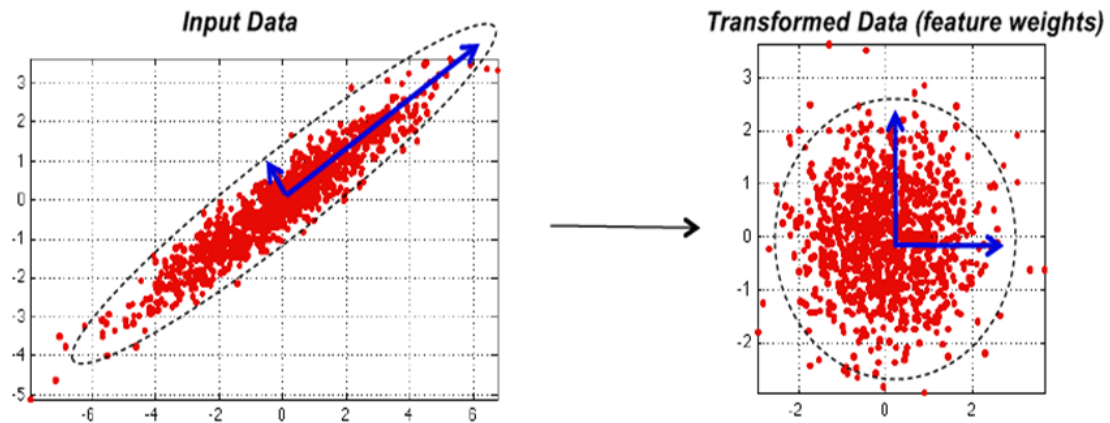


Figure 2-16: Transformation of input data using PCA; the blue arrows show the derived principal components. The horizontal axis on the graph at the right is PC 1, and the vertical axis is PC 2 (University of Illinois, 2000)

PCA usually serves as an intermediate step to a much larger investigation by, in the first instance, reducing the dimensionality of the problem and providing a more straightforward interpretation of the dataset. To obtain a prediction model, principal component regression (PCR) must be done, and in this respect, PCA *orthogonalizes* the regression problem and thus counteracts the effects of multicollinearity in regression modelling.

2.9.2 Partial Least Squares - Overview

Partial Least Squares (PLS) is a multivariate dimension reduction technique that has been widely used in chemometrics (Ng, 2013). It is particularly useful for large datasets with more predictor (independent) variables than observations. As with PCA, PLS is a valuable technique that handles multicollinearity issues where ordinary least squares regression techniques become less reliable as it results in unstable regression coefficients. In PLS, the predictor variables, X , and output or response variable(s), Y , are decomposed by orthogonal rotation into a set of new variables so that the original datasets can be described as a combination of scores, loadings and residuals (Yamashita *et al.*, 2017).

2.9.3 The difference between PCA and PLS

PCA and PLS differ in the methods used in extracting the latent variables. PCA produces a weight matrix reflecting the covariance structure between the predictor

variables. The objective is to maximise variability in the input data space by using a new set of coordinate systems (i.e. the PCs) that is lesser in dimension than the number of original independent variables (Jolliffe, 2002). PLS, on the other hand, produces a weight matrix indicating the covariance structure between the predictor and response (output) variables (Statistica Documentation, 2012). The variance in the input data is maximised in such a way that it explains the variance in the output data or dependent variable(s), Y . This is the principal advantage of PLS over PCA, as there is no guarantee that the latent variables (PCs) which explain the X (input) variables optimally in PCA are good predictors of the Y (output) variable(s); thus PLS is more oriented towards prediction (Collins, 2010).

2.9.4 Concluding Remarks on the use of Statistical Techniques for Fireside Corrosion Modelling

A host of other data modelling and exploratory techniques can be found in the literature. Each method is unique to the nature of the dataset, the expected outcome (clustering, classification, prediction etc.) and limiting conditions for which they are employed. Examples of other statistical techniques used in various research include:

- Neural network modelling
- Correlation statistics
- ANOVA
- Factor analysis (a variation of the PCA technique)
- Regression and classification models such as Quantitative Structure Activity Relationship and Quantitative Structure Property Relationship (QSAR/QSPR).

For this research, plant data consisting of highly correlated data with very close similarity in the range of variables has been exclusively used to derive prediction models using a different modelling approach; i.e. Principal Component Analysis (PCA) and Partial Least Squares (PLS).

3 METHODOLOGY

As outlined in chapter 2, numerous reports exist in the literature on fireside corrosion and its effects, but more work needs to be done to build predictive models. Such models need to take into account the alloy composition, the varying chemical composition of coal and biomass, changing operating conditions, and the difference in boiler design and layout. Thus, the objectives of this research include collating fireside corrosion data from various field investigations and using statistical methods to develop fireside corrosion predictive models over a specific temperature/operation range. This chapter details the fireside corrosion datasets compiled and the statistical techniques applied to build the models. In particular, a summary of the datasets is presented here (section 3.1); and a step-by-step procedure of the statistical techniques employed to build the fireside corrosion models is presented in section 3.2. Finally, section 3.3 introduces the structure of the fireside corrosion models.

3.1 Data Collection and Gathering

Fireside corrosion data extracted from plant investigations (i.e. excluding laboratory testing) assessing materials' performances in coal and biomass-fired boilers were collated. Where the data was incomplete, additional information was obtained to complete all input parameters such that datasets were easily comparable. Additional information included the chemical composition of the alloys (not just the Cr content) and the chemical composition of the fuel in cases where only the ashed fuel analysis was available. Moreover, for the statistical technique employed to build predictive models, gaps in the dataset are not permissible and may prevent the analysis from progressing. The resulting dataset covers a range of austenitic and ferritic tube materials, coatings/claddings, and different fuel types. Input parameters in these datasets include metal temperature, gas temperature, alloy composition and fuel composition. The following subsections outline the data subsets used for model building. The data subsets outlined (and the modelling results discussed in chapter 4) will be in the order illustrated in Figure 3-1.

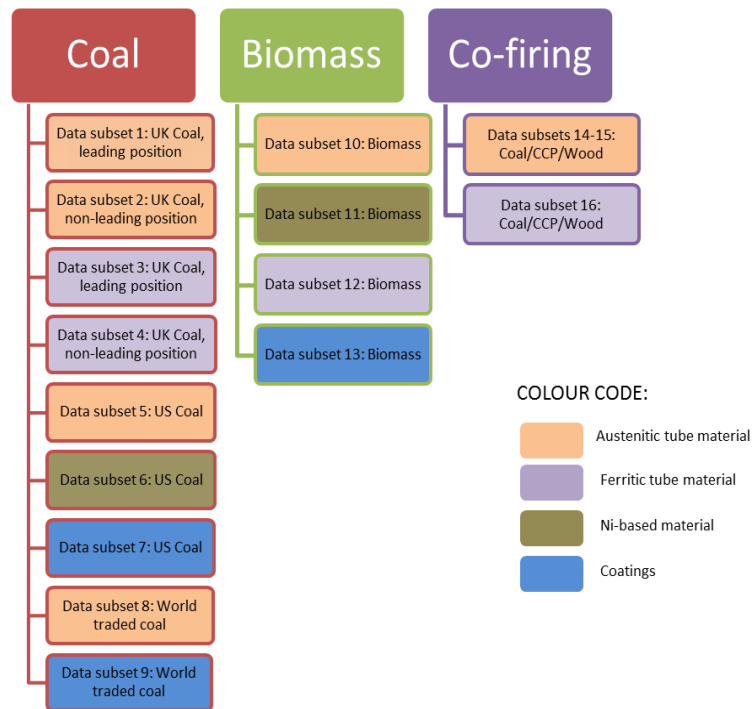


Figure 3-1: Block chart of data subsets analysed classified according to the fuel type

3.1.1 CEGB PE-8 UK Dataset: Field Investigations on UK Utility Boilers Burning UK Coal

Plant tests were conducted by the CEGB from the early 1960s until the early 1980s. These were used to produce a robust corrosion dataset and, ultimately, the modified PE-8 fireside corrosion model discussed in chapter 2 (section 2.8). In the current work, the original PE-8 dataset (James *et al.*, 1997) has been expanded to include the full composition of the alloys used and the compositions of fuels. The fuels were sourced from two regions in the UK: The Midlands and North Eastern regions.

The PE-8 dataset has been divided into four subsets, categorised according to the alloy types, and the position of the SH/RH in the plant:

- Austenitic leading tubes (data subset 1)
- Austenitic non-leading tubes (data subset 2)
- Ferritic leading tubes (data subset 3)
- Ferritic non-leading tubes (data subset 4)

The fireside corrosion rates reported in the PE-8 dataset were the maximum metal loss rates. These rates, for austenitic and ferritic steels, were gathered from plant exposures carried out in twenty power stations. The dataset documented the corrosion rates along

with the Cl content (Cl was used as an indicator for soluble alkali metals), gas temperature, and metal temperature.

Also, a part of the PE-8 dataset were the analyses from forty-seven selected UK coal samples (Table 3-1) that make up major deliveries to the different power stations (UK) chosen by CEGB for the fireside corrosion investigation. However, in the original report, links were not made between the coal and the UK power stations where fireside corrosion was measured. Hence where this information was lacking, assumptions were made by matching the colliery closest to the power station. This is based on the fact that in the period of the CEGB study, most UK coal-fired stations were more likely to obtain fuel from nearby coal mines.

The coal fuel compositions presented were mainly ashed fuel analyses, expressed in terms of the highest oxide (James *et al.*, 1997; Wright and Krause, 1997b). Missing trace elemental compositions i.e.: Na, K, Ca, Mg, Al, Fe, Si, S, Mn, Ba, or P, for specific coals were deduced by converting the oxides presented in the ashed fuel analyses (Table 3-1) to their elemental forms and scaling up to give the actual ash content in the coal (wt % dry). The rationale for doing this follows from the fact that coal ash is a mixture of silicates, oxides and sulphates, but they are usually reported as oxides from the ashing procedure. The oxides do not represent their actual forms (Stringer, 1995; Riley, 2007; Patra *et al.*, 2012). The main fuel elements presented in this data subset and used for model building in this work are a reasonable indication of the amounts of volatile species released into the flame upon combustion and potentially present in the combustion gas. The water-soluble fuel components (Na, K, Mg and Ca, with Al and Fe in minimal quantities) are assumed to be the volatile species released during combustion (Gibb and Angus, 1983), whilst the insoluble mineral species remain tied to the clay matter and are assumed to not participate in the combustion reaction (Gibb and Angus, 1983; James *et al.*, 1997).

The final revision of the fuel data used for model development in this thesis, specifically Na, K, Mg, Ca, Al and Fe in the coal-fired environment for austenitic and ferritic tubes in the leading and non-leading position, reflects the percentage of metal released during combustion (details in Appendix A, Table A-1). Table 3-1 shows the ash composition for the UK coals and the ashed fuel analyses presented in their highest oxide form. In

Table 3-1, sodium oxide (Na_2O) was not included in the ashed analysis as it was not reported in the original (CEGB) report; however, figures for the water-soluble Na component were specified and are included in Table A-1 (Appendix A).

Table 3-1 shows the ashed analysis for various UK coals; Table 3-2 and Table 3-3 show the alloy types and corresponding compositions used as input parameters for the fireside corrosion model building.

Table 3-1: Ashed fuel analyses (excluding Na_2O) and ash and sulphur contents of Midlands and North Eastern region coals (UK) (Wright and Krause, 1997b)

Coal	% in dry coal		Ashed fuel analyses (%)						
	S (%)	Ash	SiO_2	Al_2O_3	MgO	K_2O	Fe_2O_3	TiO_2	CaO
Ackton Hall	2.15	22.20	48.50	26.90	1.10	3.50	11.80	0.90	1.30
Askern	1.40	29.20	52.20	28.00	1.20	4.30	7.60	0.90	1.10
Babbington	2.20	21.20	49.80	25.20	1.30	3.20	11.20	1.00	1.80
Bentinck	1.83	11.90	50.20	26.60	1.50	3.30	10.00	1.00	2.40
Bentley	1.72	18.20	50.30	26.20	1.20	3.70	10.00	0.90	1.90
Bilsthorpe	2.01	19.80	49.80	26.20	2.60	3.40	10.30	1.00	2.00
Cotgrave	1.01	20.20	52.60	29.50	1.50	2.90	5.50	1.40	2.90
Creswell	1.54	22.40	56.90	23.10	1.20	3.10	8.10	1.00	2.30
Daw Mill	1.65	12.60	42.90	24.90	1.70	2.00	7.70	1.00	6.90
Florence	1.61	22.60	47.80	27.80	1.40	2.00	9.30	1.00	4.00
Frickley	1.99	17.00	50.90	26.20	1.30	3.30	11.30	1.00	1.50
Gascoigne Wood Drift	1.32	20.40	55.40	24.90	1.60	4.00	7.20	0.90	2.50
Glasshoughton	1.85	18.40	48.40	27.10	1.30	3.80	10.00	0.80	2.00
Granville	0.82	14.70	48.50	27.10	2.00	2.10	4.40	1.00	5.90
Goldthorpe	1.90	22.20	51.00	26.50	1.10	3.30	11.40	0.90	1.10
Hatfield Main	1.24	21.20	56.20	24.40	1.50	3.70	5.80	0.90	2.00
Hem Heath	1.94	17.80	47.20	26.40	1.20	2.60	12.20	0.90	3.40
Hickleton	1.69	14.80	5.35	24.30	1.20	3.00	11.10	1.00	1.40
Horse Hay	1.19	11.40	48.90	34.30	0.60	11.40	7.50	1.30	1.80

Coal	% in dry coal		Ashed fuel analyses (%)						
Hucknall	2.02	22.80	52.20	26.10	1.60	3.40	11.00	1.10	2.50
Kellingley	2.00	21.10	49.50	28.40	1.30	4.00	10.60	0.90	1.10
Kiveton	1.76	15.70	48.80	23.30	1.30	2.50	15.70	0.90	2.60
Lea Hall	1.48	15.40	48.80	20.80	1.30	2.60	9.20	1.00	5.20
Littleton	1.88	16.70	43.60	22.80	1.30	2.20	12.00	0.90	5.80
Lofthouse	2.62	23.10	49.50	27.00	1.30	3.90	12.00	0.90	1.20
Markham Main	1.42	20.20	53.70	24.00	1.30	3.30	8.60	1.00	2.20
Markham – Staveley	2.25	18.90	49.60	26.90	1.20	3.40	11.60	1.00	1.50
Moorgreen	2.24	18.40	50.10	26.60	1.40	3.40	12.40	1.00	2.00
Peckfield	1.91	13.30	47.60	30.00	1.30	3.80	11.90	1.10	1.20
Prince of Wales	2.24	26.30	52.50	24.80	1.40	3.40	12.30	0.90	1.00
Pye Hill	2.13	15.90	47.90	27.30	1.50	3.40	12.60	1.00	2.40
Rossington	1.39	17.10	49.60	26.20	1.40	3.50	9.20	1.00	2.60
Rothwell	1.77	17.20	54.80	26.30	1.00	2.90	8.50	0.90	1.40
Royston Drift	1.60	22.60	46.80	24.50	1.20	2.70	13.90	0.90	2.20
Seymour	1.79	9.40	41.10	24.90	1.60	2.50	15.80	0.90	3.70
Sharlston	1.94	23.10	49.30	27.00	1.40	3.80	10.70	0.90	1.50
Sherwood	1.66	17.50	50.40	26.90	1.30	3.60	9.30	1.00	2.30
Shirebrook	1.86	24.70	51.90	25.10	1.30	3.60	9.00	0.90	1.80
Shireoaks	1.18	19.80	57.40	22.40	1.30	2.50	7.60	0.90	2.40
Silverdale	3.34	18.40	43.90	24.40	1.00	1.80	20.20	0.90	3.50
South Kirkby	1.47	23.40	55.40	26.00	1.30	3.60	8.10	1.00	1.00
Thoresby	1.50	19.70	49.10	25.10	1.40	3.10	7.70	0.90	4.10
Treeton	1.93	22.70	50.70	26.50	1.60	4.00	10.40	0.90	1.90
Whitwell	1.35	27.50	60.80	22.10	1.20	2.40	8.00	0.90	1.90
Yorkshire Main	1.37	17.10	53.50	25.30	1.20	3.50	8.60	1.00	1.60

Table 3-2: Nominal alloy compositions (for austenitic tubes) for data subsets 1 and 2

Alloy	Alloy composition (max wt %)											
	C	Mn	P	S	Si	Cr	Ni	Mo	Nb	Ti	V	Fe
316	0.08	2.0	0.05	0.03	0.75	18	14	2.30	-	-	-	Bal
310	0.25	2.0	0.05	0.03	1.5	26	22	-	-	-	-	Bal
E1250	0.1	6.3	0.04	0.02	0.5	15	9.5	1.0	1.0	-	0.3	Bal
321	0.08	2.0	0.05	0.03	0.75	19	12	-	-	0.7	0.00	Bal
347	0.10	2.0	0.05	0.03	1.0	19	13	-	1.0	-	-	Bal

Table 3-3: Nominal alloy compositions (for ferritic tubes) for data subsets 3 and 4

Alloy	Alloy composition (max wt %)									
	C	Mn	P	S	Si	Cr	Ni	Cu	Mo	Fe
2.25Cr 1Mo	0.1	0.43	0.01	0.009	0.23	2.46	0.043	0.07	0.94	Bal
1Cr 0.5Mo	0.17	0.65	0.04	0.04	0.8	1.5	-	-	0.6	Bal

3.1.2 US Coal Data: Field Investigations on US Utility Boilers Burning US Coal

The US dataset was obtained from three different power plant-based US fireside corrosion investigations. The first pertains to field studies involving air-cooled retractable fireside corrosion probes installed in various utility boilers (Blough *et al.*, 1998; Blough *et al.*, 2000). The second was gathered from the results of a materials' testing program conducted at Reliant Energy's Niles plant in Niles, Ohio (USA) (McDonald, 2001). The third was from air-cooled probe investigations installed in three utility boilers in Ohio, Indiana, and Colorado in ultra-supercritical steam conditions with metal temperatures ranging from 505-818 °C (Purgert *et al.*, 2015). After assembly, the US coal-based dataset has been divided into three new subcategories representing fireside corrosion exposures involving austenitic materials (data subset 5), nickel-based materials (data subset 6), and coatings (data subset 7). The compositions of the alloys tested and the inorganic compositions of the coal used were added to the dataset. The coal fuel types ranged from low S coal from the Eagle Butte Mine near Gillette, Wyoming (Smith and Smoot, 1990; Blough *et al.*, 2000), to 3 - 3.5 wt% S Ohio

coal (Smith and Smoot, 1990; McDonald, 2001) and a combination of Eastern and Western US coals (Purgert *et al.*, 2015).

The compiled data subsets 5-7 covering the US coal fuels (obtained from fuel ashed analyses expressed as highest oxides) are listed in Table 3-4. Missing coal data were obtained from a coal databank prepared by the US Geological Survey (USGS) known as *USGS Coalqual* (Palmer; *et al.*, 2015), and from the general literature (Smith and Smoot, 1990; The British Coal Utilisation Research Association, 2002). The Coalqual databank cited contains an extensive record of coal data from different regions in the US sorted according to state, county, region, coalfield, formation, bed, mine and estimated rank. For instance, there were three main coal types in the data gathered from Purgert *et al.* (2015); i.e. Eastern coal (mid-sulphur bituminous Pittsburgh #8), Midwestern high S bituminous coal (Illinois #5) and Western coal (usually Powder river basin from Eagle Butte mine). However, their compositions (including ash composition) were absent from the original report, and hence the elemental breakdowns were obtained from different sources (Smith and Smoot, 1990; Palmer; *et al.*, 2015). Cl data for the Midwestern and Western coals was also absent in the Coalqual database (Cl is not recorded in this databank). Hence a rough Cl estimate was deduced from measured flue gas composition obtained from a laboratory fireside corrosion test contained in the same report where the plant data was extracted.

The alloys and coatings used in the various investigations forming data subsets 5-7 are listed in Table 3-5, Table 3-6, and Table 3-7.

Table 3-4: Ashed fuel analyses (expressed as highest oxides), Cl and S for US coal from data subsets 5-7

Coal	Source	Ashed fuel analyses (wt %)											
		Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO / Mn ₃ O ₄	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	Cl (wt %)	S (wt %)
Constain	(Blough <i>et al.</i> , 2000)	-	0.04	1.6	0.03	0.02	-	0.03	-	-	-	0.28	1.73
Island Creek	(Blough <i>et al.</i> , 2000)	-	0.12	1.5	0.11	0.04	-	0.02	-	-	-	1.49	3.08
Warrior	(Blough <i>et al.</i> , 2000)	-	0.35	2.7	0.13	0.08	-	0.008	-	-	-	0.05	3.12
Pyro	(Blough <i>et al.</i> , 2000)	-	0.21	1.9	0.14	0.06	-	0.03	-	-	-	0.32	3.35
Warren	(Blough <i>et al.</i> , 2000)	-	0.43	2.2	0.16	0.07	-	0.03	-	-	-	0.1	3.19
Dotiri	(Blough <i>et al.</i> , 2000)	-	0.43	1.7	0.12	0.05	-	0.03	-	-	-	0.21	3.38
Pattiki	(Blough <i>et al.</i> , 2000)	-	0.26	1.7	0.09	0.04	-	0.06	-	-	-	0.19	3.34
Lodestar	(Blough <i>et al.</i> , 2000)	-	0.06	1.9	0.04	0.03	-	0.04	-	-	-	0.29	3.2
Wyodak	(Smith and Smoot, 1990)	17.3	21.8	6.8	0.33	5.11	0.04	2.2	1.3	32.9	1.3	-	0.54
Ohio	(Smith and Smoot, 1990)	24.7	6.4	13	1.7	1.5	0.1	0.5	1	43.4	1.1	-	0.28

Coal	Source	Ashed fuel analyses (wt %)											
		Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO / Mn ₃ O ₄	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	Cl (wt %)	S (wt %)
Upper Kanawha	(Smith and Smoot, 1990)	35.8	0.8	3.2	3	1.6	0.03	2.03	-	51.2	-	0.1	0.71
Composite	(Blough <i>et al.</i> , 2000)	-	0.22	2.1	0.11	0.06	-	0.009	-	-	-	0.2	3.21
Pittsburgh 8 (Eastern Coal)	(Smith and Smoot, 1990)	24.6	1.13	17.2	2.65	0.62	-	0.74	0	51	1.1	-	2.3
Illinois 5 (Sample W189302)	(Palmer; <i>et al.</i> , 2015)	16	3.4	6.9	2.3	1.16	0.03	0.72	-	56	0.84	0.02*	2.8
Powder River Basin (Sample D165436)	(Palmer; <i>et al.</i> , 2015)	17	21	3.9	0.81	2.05	0.15	1.1	-	30	-	0.001*	0.76

* (Purgert *et al.*, 2015)

Table 3-5: Nominal alloy composition of austenitic tubes for data subset 5 (Blough, Seitz and Girshik, 1998; Blough *et al.*, 2000; Purgert *et al.*, 2015)

Alloy	Alloy composition (max wt %)																			
	C	Mn	P	S	Si	Cr	Ni	Mo	Nb	Ti	Cu	V	Al	N	Ce	W	B	Ta	Co	Fe
17-14 CuMo	0.08	0.88	0.02	0.01	0.72	16.37	14.08	1.95	-	-	3.34	-	-	-	-	-	-	-	-	Bal
304	0.08	2.00	0.05	0.03	0.75	20.00	12.00	-	-	-	-	-	-	0.10	-	-	-	-	-	Bal
347H	0.08	1.48	0.03	0.01	0.49	18.4	12.6	-	0.78	-	-	-	-	-	-	-	-	-	-	Bal
800HT	0.10	1.50	0.05	0.02	1.00	23	35	-	-	0.60	0.75	-	0.60	-	-	-	-	-	-	Bal
RA85H	0.24	0.50	0.02	-	3.90	18.5	15.26	0.06	-	-	0.39	-	0.70	0.10	-	-	-	-	-	Bal
347	0.10	2.00	0.05	0.03	1.00	19	13	-	1.00	-	-	-	-	-	-	-	-	-	-	Bal
NF 709	0.20	1.50	0.03	0.01	0.70	21.5	24.30	2.00	0.07	0.05	-	-	-	0.02	-	2.45	0.01	-	-	Bal
RA253MA	0.10	0.80	0.04	0.03	2.00	22	12	-	-	-	-	-	-	0.20	0.08	-	-	-	-	Bal
310 mod.	0.07	1.67	0.01	-	0.63	24.7	21.2	-	-	0.01	-	-	-	-	-	-	-	-	-	Bal
HR3C	0.06	1.26	0.01	-	0.39	24.6	20.1	-	0.47	-	-	-	-	0.25	-	-	-	-	-	Bal
Save 25	0.10	0.48	-	-	0.13	22	18	-	0.44	-	3.51	-	-	0.22	-	-	-	-	-	Bal
800 mod	0.10	1.93	-	0.01	0.00	20.87	31.08	2.01	0.19	0.29	-	0.47	0.02	0.01	-	-	-	-	-	Bal
347HFG	0.10	2.00	0.04	0.03	0.75	18	11	-	1.00	-	-	-	-	-	-	-	-	-	-	Bal
310 Ta	0.10	2.00	0.05	0.03	1.00	25	20	-	-	-	-	-	-	-	-	-	-	1.50	-	Bal
310 HCBN	0.10	2.00	0.03	0.03	0.75	26	23	-	0.60	-	-	-	-	0.35	-	-	-	-	-	Bal
HR 120	0.05	0.70	-	-	0.60	25	37	2.50	0.70	-	-	-	0.10	0.20	-	2.50	-	-	3.00	Bal

Alloy	Alloy composition (max wt %)																			
	C	Mn	P	S	Si	Cr	Ni	Mo	Nb	Ti	Cu	V	Al	N	Ce	W	B	Ta	Co	Fe
304H	0.10	2.00	0.05	0.03	0.75	20	10.5	-	-	-	-	-	-	0.10	-	-	-	-	-	Bal
309S	0.08	2.00	0.05	0.03	0.75	24	15	-	-	-	-	-	-	-	-	-	-	-	-	Bal
S304H	0.10	0.50	-	-	0.30	18	9.5	-	0.40	-	3.00	-	0.02	0.10	-	-	0.01	-	-	Bal

Table 3-6: Nominal alloy compositions of nickel-based metals for data subset 6 (Blough *et al.*, 2000; Purgert *et al.*, 2015)

Alloys	Alloy composition (max wt %)														
	C	Mn	P	Si	Cr	Ni	Mo	Nb	Ti	Cu	Al	W	B	Co	Fe
690	0.05	0.17	0.01	0.26	31.65	Bal	0.05	-	-	-	-	-	-	-	9.09
671	0.05	-	-	0.00	48.00	Bal	-	-	0.35	-	-	-	-	-	-
Tempaloy CR30A	0.06	0.20	-	0.27	30.50	Bal	2.11	-	0.18	-	0.14	-	-	-	15.54
CR30A	-	-	-	0.00	30.00	Bal	2.00	-	0.25	-	0.25	-	-	-	-
Inconel 740	0.03	0.30	-	0.50	25.00	Bal	0.50	2.00	1.80	-	0.90	-	-	20.00	0.70
HR6W	0.08	1.20	-	0.40	23.00	Bal	-	0.08	0.08	-	0.00	6.00	-	-	29.16
230	0.10	0.70	-	0.50	22.00	Bal	2.00	-	-	-	0.35	14.00	0.01	5.00	3.00
740	0.04	1.00	-	1.00	24.50	Bal	2.00	1.50	1.50	0.50	1.10	-	-	18.50	3.00
617	0.10	1.00	-	1.00	22.00	Bal	9.00	0.00	0.60	0.04	1.20	-	-	12.50	3.00

Table 3-7: Nominal coating compositions for data subset 7 (Blough, Seitz and Girshik, 1998; Blough *et al.*, 2000; Purgert *et al.*, 2015)

Alloy	Coatings composition (max wt %)																
	C	Mn	P	S	Si	Cr	Ni	Mo	Nb	Ti	Cu	V	Al	N	Ce	Ta	B
Chromised T91	0.01	0.40	0.01	-	0.39	9.5	0.00	1.05	0.08	-	-	0.25	0.02	0.04	-	-	-
FW-4C	0.05	2.20	0.00	-	2.40	20	18	0.00	-	-	-	-	2.00	0.00	-	-	-
253 MA	0.09	0.32	0.01	-	1.73	21	11	0.03	-	-	-	-	0.00	0.18	0.08	-	-
310Nb (HR3C)	0.06	1.28	0.01	-	0.42	24.95	20.45	0.00	-	-	-	-	0.00	0.23	-	-	-
Fe3Al - 5Cr	0.00	0.00	0.00	-	0.00	5.6	0.00	0.00	-	-	-	-	15.9	0.00	-	-	-
Fe3Al - 2Cr	0.00	0.00	0.00	-	0.00	2.19	0.00	0.00	-	-	-	-	15.93	0.00	-	-	0.01
Fe3Al	0.10	0.00	0.00	-	0.00	5.00	0.00	0.00	-	-	-	-	28	0.00	-	-	-
52 WO	0.04	1.00	0.02	0.02	0.50	29	59.43	0.50	0.10	1.00	0.30	-	1.10	0.00	-	0.10	-
72 WO	0.01	0.10	0.00	0.01	0.10	44	55	0.00	0.00	0.60	0.20	-	0.00	0.00	-	-	-
671 clad	0.06	0.10	0.00	-	0.11	48.5	50.56	0.05	0.05	0.46	0.05	-	0.05	0.01	-	-	-

3.1.3 UK Data on Austenitic Materials: Field Investigation on UK Utility Boilers Burning Eastern European Coal

This dataset contains fireside corrosion data compiled from plant exposures carried out in a UK coal power station where air-cooled probes were installed in the convective section of the combustion boiler to evaluate the performance of tube materials. The test materials were predominantly austenitic tube materials cut into 35 interlocking ring sections arranged along the probe length. The total exposure period was approximately 7,500 hours. The fuel burnt consisted of two distinct coal types: medium-high bituminous coal of low S content imported from Eastern Europe and sub-bituminous coal of low S content imported from Indonesia. However, only the compiled mean values of the ash composition, S content and Cl content were provided. Thus it was not possible to associate the coal to the fireside corrosion rates that were measured and, as a result, the fuel composition was not included in the PCA/PLS analyses of fireside corrosion data as there was no variation in the fuel data. Only austenitic tube materials were employed in this study; hence the corrosion data was compiled as a single subset tagged data subset 8, with input parameters comprising metal temperature, gas temperature and the alloy composition (Table 3-8 and Table 3-9).

Table 3-8: The average ashed fuel analyses (expressed as highest oxides) values for data subset 8 (Doosan Babcock, 2011)

Ashed fuel analyses (wt %)										
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O	K ₂ O	SO ₃	S*	Cl*
49.4	19.4	5.9	4.2	1.9	0.8	0.9	1.8	1.0	0.28	0.01

* Average (as received)

Table 3-9: Nominal alloy compositions of austenitic tubes for data subset 8 (Doosan Babcock, 2011)

Alloy	Alloy composition (max wt %)																	
	C	Si	P	S	V	Cr	Mn	Fe	Ni	Nb	Mo	Ti	N	W	Cu	B	Al	Co
E1250	0.11	0.41	-	-	0.22	16.09	6.00	Bal	12.19	0.87	1.19	-	-	-	-	-	-	-
347HFG	0.09	0.34	0.023	0.001	-	18.1	1.48	Bal	11.33	0.9	-	-	-	-	-	-	-	-
Tempaloy AA1	0.09	0.32	0.036	0.001	-	17.85	1.43	Bal	10.14	0.21	-	0.17	-	-	2.81	-	-	-
Super304H	0.09	0.20	0.034	0.001	-	18.37	0.81	Bal	8.83	0.49	-	-	0.11	-	2.79	0.004	0.008	-
Sanicro25	0.06	0.20	0.025	0.015	-	22.5	0.50	Bal	25.1	0.47	-	-	0.23	3.60	3.00	-	0.05	1.5
HR3C	0.06	0.38	0.013	0.001	-	24.49	1.16	Bal	20.03	0.47	-	-	0.25	-	-	-	-	-

3.1.4 UK Data on Coating Materials: Field Investigation on UK Utility Boiler Burning UK and World -Traded Coals

This dataset (data subset 9) contains fireside corrosion data gathered from plant exposures carried out in a UK power station involving coated tubes deployed to assess fireside corrosion resistance in a pulverised coal-fired combustion environment. The primary objective of this investigation was to assess the protective ability and corrosion resistance of coatings compared to higher alloy uncoated austenitic steels. The trial tubes were exposed for approximately 24,880 hour's operation. Different coating materials were applied using *High-Velocity Oxy-Fuel* (HVOF) and arc wire spray.

The fuel burnt to generate this corrosion data was a mixture of coal type sourced from the indigenous UK mined pits and world-traded coals (from North and Central America, Russia). However, with respect to the fuel composition, the data subset had similar issues to data subset 8; i.e. no variation in the fuel data, hence the input parameters were limited to the plant's operating data (metal and gas temperatures), and the coating compositions.

The fuel analysis (mean values) are shown in Table 3-10. The coating materials are listed in Table 3-11.

Table 3-10: Fuel analyses covering the UK and World Traded Coals for data subset 9

Fuel Analysis (As Received)	Mean Values
Moisture (%)	13.1
Volatiles (%)	29.9
Fixed Carbon (%)	44.7
Ash (wt %)	12.4
Calorific Value (kJ/kg)	24,884
Sulphur (wt %)	1.38
Chlorine (wt %)	0.11

Table 3-11: Coating analyses determined via X-ray elemental analysis for data subset 9

(Uniper Technologies, 2016c)

Alloy	Coating composition (wt %)													
	Al	C	Cr	Fe	Mo	Nb + Ta	Ni	Si	W	Y	O	Mn	Co	Cu
50Cr50Ni	0.2	-	44.2	3.8	-	-	46.8	2.4	0.3	-	2.2	-	-	-
FeCrAl	5.3	-	21.6	69.8	-	-	0.2	1.4	-	-	1.8	-	-	-
NiCrAlY	9.1	-	21.0	3.8	-	-	62.5	0.6	-	1.4	1.3	-	-	-
NiCrMoWFe (C276)	0.3	-	14.5	6.6	16.9	-	55.1	0.5	4.5	-	2.2	-	-	-
Cr3C2-NiCr Matrix	0.5	12.5	48.2	3.2	-	-	31.2	0.6	-	-	3.8	-	-	-
NiCrMo (Nb + Ta) (IN625)	0.3	-	19.1	3.0	9.3	3.2	60.7	0.5	-	-	3.9	-	-	-
ARCIN625	0.0	0.1	23.0	7.0	10.0	3.2	55.0	0.8	-	-	-	1.0	0.1	0.5

3.1.5 Biomass Dataset: Field Investigations on UK Utility Boilers Burning Biomass

The fireside corrosion dataset linked to biomass combustion was compiled from unpublished reports on probe investigations carried out in four biomass plants in the UK. The first plant assessed the fireside corrosion of superheaters and reheaters following the exposure of three superheater probes positioned in a 500MW coal-fired boiler that had been retrofitted as a 370MW pulverised wood pellet-fired boiler (Uniper Technologies, 2016b). The second plant studied boiler tube fireside corrosion following probe exposures in a boiler burning waste wood with final steam conditions of 81 bar and 490°C. Probes included specimens fabricated from typical boiler tubing alloys and also included some trial fireside corrosion-resistant coatings applied by laser cladding. The third plant investigated forestry waste wood combustion and its impact on SH/RH fireside corrosion rates. The boiler operated with final steam conditions of 530°C and 136 bar. Metal wastage rates were recorded for coatings/claddings as well as unprotected tubing. The fourth plant investigated the fireside corrosion performance of superheaters/reheaters via probe investigations for a pulverised boiler converted to a 300MWe boiler firing 100% wood pellets.

The existing report dataset was expanded to include the chemical composition of the alloys and, on the fuel side; the elemental compositions, which were deduced from the ashed fuel analysis. This dataset is classed into sub-categories depending on the alloy and coating material type. Thus, the biomass combustion dataset used in this study was split into four sub-categories:

- Austenitic alloys (data subset 10)
- Nickel-based alloys (data subset 11)
- Ferritic alloys (data subset 12)
- Coating materials (data subset 13)

For this dataset, all tubes are assumed to be in the leading position. The inorganic fuel elements were deduced from the ashed analysis (presented as highest oxides, Table 3-12) following the same procedure stated in section 0. Table 3-12 to Table 3-16 summarise the data in the biomass dataset.

Table 3-12: Ashed fuel analysis (expressed as highest oxides) for biomass (woody) fuels from data subsets 10-13 (E.ON Technologies, 2015b; Uniper Technologies, 2016a)

Ashed fuel analysis (wt %)				
	Data subset 10	Data subset 11	Data subset 12	Data subset 13
Al ₂ O ₃	3.86	7.21	11.66	8.26
BaO	0.20	0.5	0.63	0.6
CaCO ₃	46.86	31.59	24.43	24.45
Fe ₂ O ₃	2.21	4.18	5.98	5.1
K ₂ O	12.26	2.68	5.5	5.36
MgO	5.72	3.13	3.97	3.95
Mn ₃ O ₄	1.61	0.31	0.75	0.74
Na ₂ O	1.08	2.84	4.62	3.41
P ₂ O ₅	2.45	0.74	2.01	1.74
SiO ₂	23.52	41.31	39.36	40.82
TiO ₂	0.23	5.5	7.14	5.56

Table 3-13: Nominal alloy compositions (for austenitic tubes) for data subset 10 (E.ON Technologies, 2015b; Uniper Technologies, 2016a)

Alloy	Alloy composition (max wt %)																	
	C	Mn	P	S	Si	Cr	Ni	Mo	Nb	Ti	V	N	Cu	W	B	Al	Co	Fe
E1250 (SA)	-	6.04	-	-	-	15.82	10.31	1.1	0.99	-	0.32	-	-	-	-	-	-	Bal
TP321 (SA)	0.08	1.81	0.05	0.03	0.75	18.23	10.48	0.22	-	0.51	0.11	0.1	-	-	-	-	-	Bal
HR3C (SA)	-	1.05	-	-	-	25.17	19.82	0.11	0.48	-	-	-	-	-	-	-	-	Bal
Eshette 1250	0.15	6.62	0.04	0.03	1.56	15.32	9.34	-	0.48	-	0.3	-	-	-	0.006	-	-	Bal
DMV310N	0.07	1.46	0.03	0.03	0.71	24.99	20.36	0.34	0.57	-	0.17	0.25	-	-	-	-	-	Bal
XA704	0.03	1.85	0.03	0.001	0.28	18.32	10.22	-	0.38	-	-	0.19	-	1.77	-	-	-	Bal
Super304H	0.08	0.81	0.04	0.001	0.18	18.40	8.80	-	0.000	-	-	0.12	3.0	-	0.004	-	-	Bal
TP347HFG	0.1	1.54	0.03	0.001	0.37	18.40	11.50	-	0.88	-	-	-	-	-	-	-	-	Bal
NF709	0.02	1.04	0.03	0.002	0.45	22.12	25.16	1.4	0.3	0.01	-	0.17	-	-	0.004	-	-	Bal
Sanicro25	0.06	0.5	0.03	0.02	0.2	22.50	25.10	-	0.47	-	-	0.23	3.0	3.6	-	0.05	1.5	Bal
HR3C	0.06	1.2	0.02	0.001	0.4	24.86	19.76	-	0.45	-	-	0.25	-	-	-	-	-	Bal
347HFG	0.09	1.48	0.02	0.001	0.34	18.10	11.33	-	0.9	-	-	-	-	-	-	-	-	Bal

Table 3-14: Nominal alloy compositions (for nickel-base tubes) for data subset 11 (E.ON Technologies, 2015b; Uniper Technologies, 2016a)

Alloy	Alloy composition (max wt %)													
	C	Mn	P	S	Si	Cr	Mo	Nb	Ti	B	Al	Co	Fe	Ni
Super625	-	0.27	0.001	0.16	0.40	22	8.76	0.53	0.24	-	0.17	-	16	Bal
HR6W	0.08	1.15	0.008	0.001	0.20	23	-	0.19	0.11	0.002	-	-	22	Bal
HR11N	0.03	0.66	0.03	0.03	0.35	30	1.5	-	-	-	-	-	28	Bal
DMV617	0.07	0.30	0.01	0.008	0.30	22	9	-	0.40	0.01	1.0	12	1.5	Bal
IN740H	0.03	0.30	-	-	0.50	25	0.5	2	1.8	-	0.90	20	0.7	Bal

Table 3-15: Nominal alloy compositions (for ferritic tubes) for data subset 12 (E.ON Technologies, 2015b; Uniper Technologies, 2016a)

Alloy	Alloy composition (max wt %)										
	C (%)	Mn (%)	P (%)	S (%)	Si (%)	Cr (%)	Ni (%)	Mo (%)	V (%)	Cu (%)	Fe (%)
T22	0.1	0.46	0.03	0.03	0.5	2.32	-	1.03	0.04	-	Bal
16Mo3	-	0.48	-	-	-	0.22	0.24	0.29	-	0.18	Bal
X20CrMoV121	-	0.74	-	-	0.32	0.19	-	0.38	-	-	Bal
15Mo3	-	0.44	-	-	0.48	0.1	-	0.79	-	-	Bal

Table 3-16: Nominal coatings' compositions for data subset 13 (E.ON Technologies, 2015b; Uniper Technologies, 2016a)

Coating	Measured composition (wt %)													
	C	Al	Si	P	S	V	Cr	Mn	Fe	Ni	Nb	Mo	W	O
FeCrAl Powder	0.01	5.85	0.75	<0.01	<0.005	0.00	22.3	0.69	70.4	0.00	0.00	0.00	0.00	0.02
IN625 Powder	0.01	0.02	0.44	0.00	<0.003	0.00	21.0	0.36	0.52	67.8	0.00	9.27	0.09	0.52
50Cr50Ni Powder	<0.1	0.00	2.11	0.00	0.00	0.00	46.9	0.00	1.12	49.7	0.00	0.00	0.00	0.03
C276 Powder	0.12	<0.01	0.65	0.00	0.004	0.00	15.3	0.00	2.93	bal	0.00	15.70	4.34	0.02
FeCrAl Cladding	0.00	4.3	1.00	0.00	0.00	0.00	21.3	0.9	68.8	2.90	0.00	0.00	0.00	0.00
IN625 Cladding	0.00	0.00	0.80	0.00	0.00	0.00	20.2	0.9	68.8	2.90	0.00	0.00	0.00	0.00
50Cr50Ni Cladding	0.00	0.00	1.90	0.00	0.00	0.00	35.6	0.00	20.3	38.3	0.00	0.00	0.00	0.00
C276 Cladding	0.00	0.7	0.00	0.00	0.00	0.5	14.5	1.2	9.8	50	0.00	16.3	4.2	0.00
NiCrAlY Cladding	0.00	7.2	0.40	0.00	0.00	0.00	20.9	0.00	16.8	52.4	0.00	0.00	0.00	0.00
HVOF FeCrAl	0.00	7.7	0.50	0.00	0.00	0.00	23.7	0.00	64.3	0.70	0.00	0.00	0.00	3.3
HVOF IN625	0.00	0.00	0.50	0.00	0.00	0.00	15.2	0.00	1.8	62.5	3.7	9.7	0.00	6.5
HVOF 50Cr50Ni	0.00	0.3	2.30	0.00	0.00	0.00	44.1	0.00	4.6	45.9	0.00	0.00	0.00	2.7
HVOF NiCrAlY	0.00	8.5	0.50	0.00	0.00	0.00	21.9	0.00	2.8	63.2	0.00	0.00	0.00	3.0

3.1.6 Co-firing Data: Field Investigations on UK Utility Boilers Co-firing Coal and Biomass

This dataset was gathered from investigations carried out on tube specimens on air-cooled fireside corrosion probes exposed to simulated superheater and reheater environments in a 1MW_{th} pulverised coal-fired combustion plant. Biomass fuels (wood pellets and, straw-based cereal co-product (CCP)) were co-fired with Daw Mill coal (on a 20% or 10% thermal basis). The blend was calculated by first converting the composition from thermal to weight basis and then computing from the oxides of the corresponding ash analyses (Table 3-17; details in Appendix A.2, Table A-3 and Table A-4). The UK co-firing dataset is subdivided into three categories: data subset 14 covers austenitic tube materials, data subset 15 is an extract of data subset 14 analysing the behaviour of just one alloy, TP316, and, data subset 16 is the one ferritic tube material. The alloy compositions are shown in Table 3-18.

Table 3-17: Ashed fuel analyses (expressed as highest oxides) of Daw Mill coal, wood and CCP for data subsets 14-16 (Powergen, 2004)

Ash Analysis (wt %)	Daw Mill Coal	Wood	Cereal co-product (CCP)
SiO ₂	49.18	43.56	1.62
Al ₂ O ₃	26.78	3.81	0.27
Fe ₂ O ₃	9.11	9.61	0.49
CaO	7.79	26.43	2.89
MgO	2.11	4.79	12.43
K ₂ O	2.07	3.84	35.82
Na ₂ O	0.97	2.42	1.26
TiO ₂	1.09	2.58	0.02
BaO	0.26	0.49	0.05
Mn ₃ O ₄	0.25	1.13	0.27
P ₂ O ₅	0.35	0.83	41.88

Table 3-18: Nominal alloy compositions for tube materials (austenitic and ferritic) for data subsets 14, 15 and 16 (Powergen, 2004)

Alloy	Alloy composition (wt %)						
	C	Si	Cr	Ni	Nb	N	Mo
TP316	0.04	0.75	18.00	14.00	0.00	0.00	3.00
HR3C	0.10	1.50	27.00	23.00	0.60	0.35	0.00
T22	0.15	0.50	0.60	2.60	-	-	1.13

3.1.7 Data Gathering and Collection Concluding Remarks

A total of 16 data subsets have been developed. The parameters included in the data subsets are the inputs for the fireside corrosion rate model and include metal temperatures, gas temperatures, alloy compositions, tube positions (leading or non-leading) and fuel compositions. A summary table showing the range of metal temperatures, gas temperatures and alloys is provided as Table 3-19.

Table 3-19: Metal and gas temperatures and alloys analysed within the 16 data subsets

DATASET	METAL TEMP (°C)	GAS TEMP (°C)	ALLOYS/COATING MATERIALS														
Data subset 1	605 - 680	870-1150	316	310	E1250	321	347										
Data subset 2	605 - 690	870-1130	316	310	E1250	321	347										
Data subset 3	500 - 640	800-1210	2.25Cr 1Mo	1Cr 0.5Mo													
Data subset 4	520 - 670	840-1300	2.25Cr 1Mo	1Cr 0.5Mo													
Data subset 5	505 - 806	871-1149	800 mod	310 HCbN	310 Ta	309S	347HFG	HR3C	NF709	S304H	304	HR 120	800HT	17-14 CuMo	Save 25	310 mod	RA85H
Data subset 6	493 - 818	871-1149	690	671	Tempaloy CR30A	Inconel 740	HR6W	230	740	617							
Data subset 7	562 - 825	-	FW-4C	253 MA	Chromise d T91	310Nb (HR3C)	Fe3Al - 5Cr	Fe3Al - 2Cr	Fe3Al	52 Wo	72 WO	671 clad	622WO/230	50/50LC/230	33WO/230		
Data subset 8	470 - 805	800-1000	E1250	347HFG	Tempaloy AA1	Super30 4H	Sanicro2 5										
Data subset 9	485 - 560	-	50Cr50Ni	FeCrAl	NiCrAlY	NiCrMo WFe	Cr3C2-NiCr	NiCrMo	ARCIN62 5								
Data subset 10	489 - 740	781-1000	HR3C	E1250	Super304 H	TP321	347HFG	HR3C	NF709	304H	DMV310 N	XA704	Sanicro 25				
Data subset 11	534 - 736	781-1000	Super625	HR6W	HR11N	DMV61 7	IN740H										

DATASET	METAL TEMP (°C)	GAS TEMP (°C)	ALLOYS/COATING MATERIALS														
Data subset 12	420 - 611	520-900	T22	16Mo3	X20CrMo V121	15Mo3											
Data subset 13	420 - 635	520-900	FeCrAl	IN625	Cr3C2-NiCr Matrix	C276	NiCrAlY	NiCrMo (Nb+Ta)	50Cr50Ni								
Data subset 14	598 - 693	-	HR3C	TP316													
Data subset 15	478 - 693	-	T22														
Data subset 16	598 - 693	-	TP316														

3.2 Multivariate Statistical Analysis

The datasets used as inputs for the fireside corrosion model are a combination of corrosion rate measurements, fuels, alloys and plant operating conditions. To build these models, two statistical techniques, *Principal Component Analysis* and *Partial Least Squares*, have been employed to reduce the dimensionality of the datasets and improve parameter (regression) estimates. The software platform employed for both techniques is STATISTICA developed by StatSoft. The steps adopted for model development are detailed in sections 3.2.2 and 3.2.3.

3.2.1 Descriptive Statistics and Data Visualisation

Descriptive statistics such as the mean and standard deviation are useful tools to analyse the spread of the data.

Graphical descriptors such as box and whisker plots were used to identify different properties of the dataset. The plot consists of three components: a middle line, the box and the whiskers. The middle line (denoted Q2) indicates the central tendency (the mean or the median). The box indicates variability around the central tendency; e.g. the 25th percentile denoted as Q1, the 75th percentile denoted as Q3 (Statistica Documentation, 2012; Shardt, 2015). The whiskers located at the top and bottom of the box indicates either the range of the data points or the interquartile range (i.e. Q3-Q1) (Shardt, 2015). Data points outside the whisker limits are outliers which serve as pointers to unexpected or unusual observations (Shardt, 2015).

A scatterplot matrix is a data visualisation tool useful to identify patterns in the data structure as well as bivariate associations between the predictor variables in each of the data subsets.

3.2.2 Principal Component Analysis

In this study, Principal Component Analysis (PCA) was used to improve the precision of the regression parameter estimates associated with the independent variables. The principal components (PCs) derived, as envisaged by its proponents (Hotelling, 1957; Jeffers, 1967; Jolliffe, 1982; Jolliffe, 2002) were to replace the original independent variables thus *orthogonalizing* the regression problem and counteracting the effects of

multicollinearity in regression modelling. However, in the context of this research, PCA has been used indirectly to improve the precision of the regression parameter estimates but not to replace the regressors (i.e. the independent variables, X) in the predictive model. The outputs from the analysis have been used to select subsets of predictor variables for the regression model. Predictive models are obtained by doing regression analysis.

3.2.2.1 Computation of Principal Components

PCA maximises the correlation between the original variables to extract and form new variables (i.e. PCs) that are mutually orthogonal, or uncorrelated (Abdul-Wahab *et al.*, 2005). The orthogonal sets of vectors are obtained by diagonalizing a correlation (or covariance) matrix (Duntelman, 1989; Jolliffe, 2002). This is equivalent to finding the eigenvalues and eigenvectors of a diagonal matrix. The new coordinate axis represents the eigenvectors, and the diagonal entries of the matrix are the eigenvalues. The new features derived are linear combinations of the original variables hence simplifying the structure of the data.

The transformation can be represented as equation 3-1 (Liu *et al.*, 2003):

$$C_i = U_{i1}X_1 + U_{i2}X_2 + \dots + U_{ip}X_p \quad 3-1$$

Where;

C_i = principal components 1, 2, 3... i.

U_{ip} = coefficients of the linear combinations, i.e. the eigenvectors.

X_p = input variables.

It can be seen from equation 3-1 that the PCs are functions of U_{ip} (the eigenvectors). The PCs are ordered so that the first PC explains the largest variation in the data, and each subsequent PC accounts for a proportion of variability that was not accounted for by the previous PCs (Abdul-Wahab *et al.*, 2005).

The newly derived PCs must satisfy the following requirements (Afifi, May and Clark, 2012):

- The derived factors (PCs) have zero correlation.

- The variance of the first PC must be as large as possible; i.e. $\text{VarPC1} \geq \text{VarPC2} \geq \text{VarPCp}$.
- The sum of squares of the coefficients (eigenvectors) for all of the PCs is equal to one.

The procedure for using PCA for model building is outlined below (Fekedulegn *et al.*, 2002; Jolliffe, 2002; Liu *et al.*, 2003; Statistica Documentation, 2012):

- The correlation matrix ($R(X_iX_j)$) is produced (see section 3.2.2.1.1).
- The eigenvalues and eigenvectors are computed from the correlation matrix. The eigenvectors correspond to the PCs and the eigenvalues to the variance explained by the PCs.
- Dimension reduction achieved by the selection of PCs for regression using a pre-defined criterion.
- Important (predictor) variables are apparent from the loadings plot which also shows the correlation between the variables.
- Varimax rotation is done to obtain a clear set of loading (highly correlated variables) patterns. The predictor (independent) variables to be used for model building are then selected based on a pre-defined criterion (high loading value, usually > 0.5).
- Stepwise Regression is done to select PCs which have a strong correlation with the dependent variable.
- Finally, Principal Component Regression (PCR) is done to develop the fireside corrosion model.

The sequence of steps in PCA is summarised in Figure 3-2. The steps shown in the blue section of the chart were computed using STATISTICA, and the steps shown in the brown section of the chart were manually computed/completed using a spreadsheet (MS Excel).

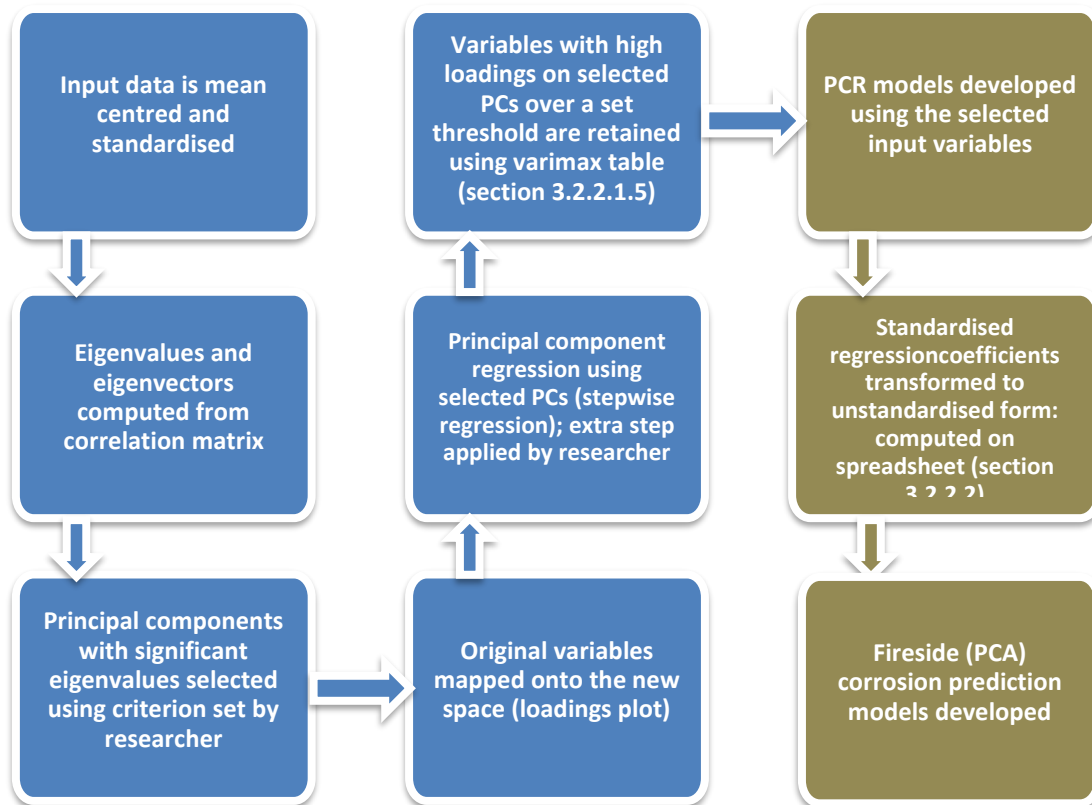


Figure 3-2: Summary of steps in principal component analysis (steps represented in blue are via the PCA module in STATISTICA and brown portion represents computation in MS Excel)

3.2.2.1.1 Correlation matrix

The PCs are computed from the correlation of the input data matrix. The correlation matrix shows the interrelationships among the X (independent) variables and between the Y (dependent) variable and each of the X variables (Smith, 2002; Statistica Documentation, 2012; Cox, 2013). The correlation coefficient, R , in particular, reveals the strength and direction of any linear association between X_i and X_j (Cox, 2013). Thus, this step also serves as a preliminary test for multicollinearity.

The transformation of X (input data) to a correlation matrix, $R(X_i, X_j)$ is given in equations 3-2 and 3-3.

$$COV(X_i X_j) = \frac{\sum_{i,j=1}^n (X_i - \bar{X}_i)(X_j - \bar{X}_j)}{(n - 1)} \quad 3-2$$

$$R(X_i, X_j) = \frac{COV(X_i, X_j)}{S_{x_i} S_{x_j}} \quad 3-3$$

Where;

$R(X_i, X_j)$ = the correlation of the variables X_i and X_j

$\bar{X}_i$ and $\bar{X}_j$ = the respective means of the variables X_i and X_j .

$COV(X_i, X_j)$ = the covariance of the variables X_i and X_j

S_{x_i} and S_{x_j} = the standard deviations of the variables X_i and X_j .

Hence for 3-dimensional data consisting of X_i , X_j , and X_k variables, the correlation matrix will be in the form of equation 3-4:

$$R_x = \begin{bmatrix} R(X_i, X_i) & R(X_i, X_j) & R(X_i, X_k) \\ R(X_j, X_i) & R(X_j, X_j) & R(X_j, X_k) \\ R(X_k, X_i) & R(X_k, X_j) & R(X_k, X_k) \end{bmatrix} \quad 3-4$$

Where the diagonal of the variances = 1.

Initial screening of the correlation matrix (i.e. before the analysis) is particularly helpful in determining the relationship between the predictor variables and between the dependent variable and each of the predictor variables (Statistica Documentation, 2012). It also serves as a preliminary guess as to which variables might be selected for model building using PCA.

3.2.2.1.2 Computation of eigenvalues / eigenvectors

The eigenvectors are the weight vectors which reveal the input variables that result in the most spread in the data, and the directions in the data. The eigenvalues indicate how much information or variation in the dataset the various PCs explain (Dunteman, 1989).

PCA proceeds by finding the optimal weight vector (the eigenvector) and the associated variance of the first PC (PC 1, i.e. the PC with the most variance; usually the highest eigenvalue). The second PC (PC 2) is obtained by finding a second weight vector such

that the variance of PC 2 is maximized, subject to the constraints that it is uncorrelated with the first PC (Statistica Documentation, 2012).

The eigenvalues and eigenvectors of the standardized correlation matrix are calculated from equation 3-5 (Sousa *et al.*, 2007; Statistica Documentation, 2012):

$$|R_x - \lambda I|.U = 0 \quad 3-5$$

Where;

R_x = the correlation matrix of the standardized variables X

λ = the eigenvalue

I = the identity matrix of the correlation matrix, R_x with diagonals = 1 (and zeros everywhere else)

U = the eigenvector of the correlation matrix R_x (i.e. a non-zero vector) associated with its corresponding eigenvalue.

3.2.2.1.3 Selection of principal components

Table 3-20 illustrates a set of eigenvalues. It also shows how much variation each PC explains. The criteria for the selection of PCs in the regression are based on several ‘rules of thumb’ proposed by various authors:

- Examining the magnitude of the eigenvalues of the correlation matrix and excluding those components with eigenvalues less than 1.0 (Kaiser’s criterion; (Jolliffe, 2002));
- From a Student’s test (t-test) of the significance of the components (Mason and Gunst, 1985; Foucart, 2000);
- Selecting only PCs that explains a certain percentage of the total variance (Jolliffe, 2002).
- Eliminate k PCs using the cumulative eigenvalue rule product rule (i.e. Kaiser’s selection rule that keeps the first PCs whose eigenvalues are greater than 1.0), and then further screen the remaining PCs using a significance level of 15% (Fekedulegn *et al.*, 2002)

The decision to exclude or retain principal components is highly subjective, and it has been proven in the literature that adopting Kaiser’s criteria alone (the most popular selection basis) can lead to the exclusion of PCs which could be useful for predictions (Jolliffe, 1982; Jolliffe, 2002). It is also possible that the smallest PC (i.e. PCs with small eigenvalues) could very well be the component carrying information that could be relevant to the final model (Shalizi, 2009), bearing in mind that PCA only analyses a single matrix with no direct connection to the Y (dependent variable) matrix. In light of these discretionary aspects, PCs with eigenvalues greater than 0.5 were selected for model building in this work (shaded region in Table 3-20).

Table 3-20: Eigenvalues of the correlation matrix (PCA) for data subset 1 – shaded cells are the eigenvalues greater than 0.5 (selection criteria)

PC number	Eigenvalues of the correlation matrix			
	Eigenvalue	% Total eigenvalue	Cumulative eigenvalue	Cumulative %
1	6.84	31.08	6.84	31.08
2	4.84	21.98	11.67	53.07
3	3.04	13.81	14.71	66.88
4	1.93	8.77	16.64	75.65
5	1.46	6.64	18.10	82.29
6	1.14	5.18	19.24	87.47
7	1.01	4.57	20.25	92.04
8	0.66	3.01	20.91	95.05
9	0.41	1.86	21.32	96.91
10	0.26	1.17	21.58	98.08
11	0.19	0.85	21.76	98.93
12	0.12	0.56	21.89	99.48
13	0.07	0.31	21.95	99.79
14	0.03	0.12	21.98	99.92
15	0.01	0.07	22	99.98
16	0.00	0.02	22	100

3.2.2.1.4 Loadings plot

The loadings plot in PCA describes the weight of importance of each independent input variable to the various PCs (Jolliffe, 2002; Statistica Documentation, 2012). The loading factors give insight into the data structure and rank the original input variables on how highly they load or correlate with each PC. Hence for a given PC, the

coefficients or loading values on each input variable can be compared, and important variables can be identified.

To obtain the loadings plot (also referred to as ‘factor loading’ in STATISTICA), the eigenvector, U , is transformed into a correlation between the variables and the PC, r . This is computed as shown in equation 3-6 (Statistica Documentation, 2012):

$$r_{\alpha k} = U_{\alpha k}(\lambda)^{1/2} \quad 3-6$$

Where;

$r_{\alpha k}$ = the correlation between the α_{th} PC (displayed as ‘factor’ in STATISTICA) and the k_{th} variable

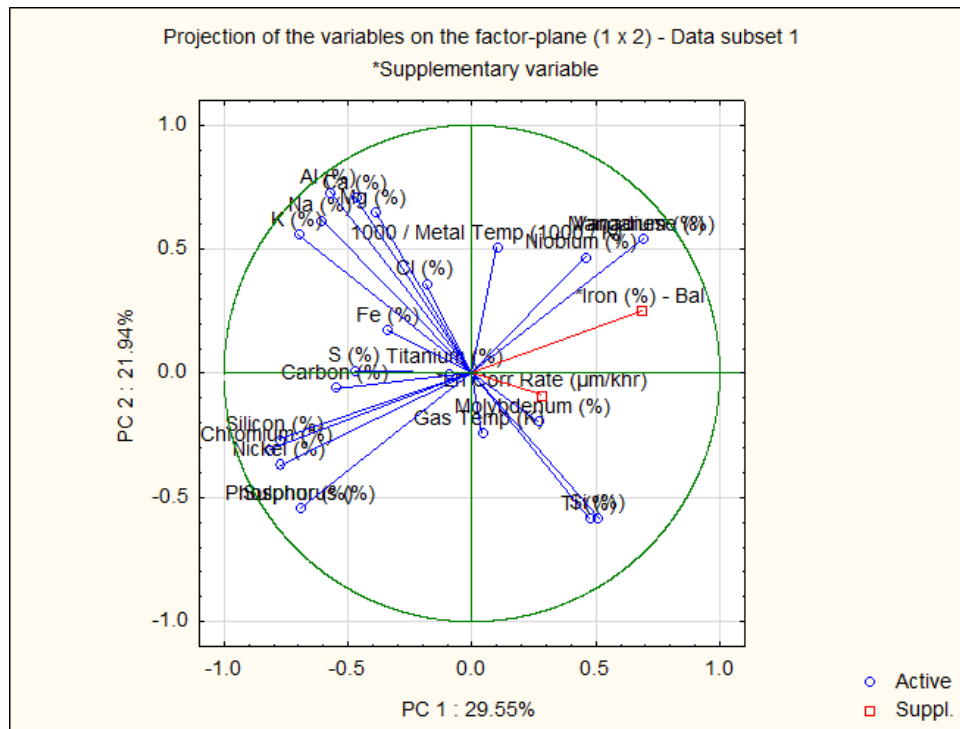
λ = the eigenvalue of the α_{th} PC.

Table 3-21 is an example of the loadings table that provides the coordinates used to produce the loadings plots in Figure 3-3.

Table 3-21: Factor-variable correlations (loadings) that describe the weight of importance of each independent input variable to the PCs. The alloy elements are written in full, and the fuel elements are shown in symbols. Marked loadings (in red) are > 0.5

Variable	Factor-variable correlations (Factor loadings)							
	*Supplementary variables							
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
1000/Metal Temp (1000 / K)	0.10	0.51	0.33	0.30	-0.49	-0.38	0.20	-0.17
Gas Temp (K)	0.04	-0.24	-0.59	-0.33	0.33	0.18	-0.43	-0.18
Carbon (wt %)	-0.55	-0.06	-0.74	-0.14	-0.20	-0.05	0.19	0.21
Manganese (wt %)	0.69	0.54	-0.43	-0.06	0.05	-0.01	0.11	0.17
Phosphorus (wt %)	-0.69	-0.54	0.43	0.06	-0.05	0.01	-0.11	-0.17
Sulphur (wt %)	-0.69	-0.54	0.43	0.06	-0.05	0.01	-0.11	-0.17
Silicon (wt %)	-0.78	-0.27	-0.47	-0.05	-0.28	-0.06	0.08	-0.06
Chromium (wt %)	-0.81	-0.31	-0.42	0.00	-0.20	-0.03	0.07	0.15
Nickel (wt %)	-0.77	-0.37	-0.35	-0.27	-0.09	-0.02	0.20	0.13
Molybdenum (wt %)	0.26	-0.19	0.53	-0.59	0.42	0.05	0.23	-0.02
Niobium (wt %)	0.46	0.47	-0.39	0.13	-0.29	-0.11	-0.09	-0.50
Titanium (wt %)	-0.09	0.00	0.24	0.74	-0.02	0.10	-0.34	0.49
Vanadium (wt %)	0.69	0.54	-0.43	-0.06	0.05	-0.01	0.11	0.17
Na (wt %)	-0.61	0.62	0.15	-0.23	0.07	-0.28	-0.20	0.01
K (wt %)	-0.70	0.56	-0.13	0.00	0.24	-0.24	-0.09	-0.07
Mg (wt %)	-0.39	0.65	0.02	-0.13	-0.24	0.53	-0.11	-0.05
Ca (wt %)	-0.47	0.71	0.17	-0.07	-0.21	0.37	0.00	-0.09
Al (wt %)	-0.57	0.73	-0.01	0.02	0.03	0.26	-0.15	-0.03
Fe (wt %)	-0.34	0.17	-0.40	0.37	0.59	-0.15	-0.27	-0.11
Si (wt %)	0.51	-0.58	-0.30	0.07	-0.25	-0.03	-0.28	-0.12
Cl (wt %)	-0.19	0.36	0.23	-0.48	-0.13	-0.55	-0.38	0.19

Variable	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
S (wt %)	-0.47	0.01	-0.21	0.48	0.42	-0.12	0.38	-0.19
Ti (wt %)	0.47	-0.58	-0.24	-0.01	-0.25	-0.02	-0.26	-0.04
*Iron (wt %)- Bal	0.69	0.25	0.53	0.27	0.11	0.03	-0.23	-0.20
*Ln Corr Rate ($\mu\text{m}/\text{hr}$)	0.28	-0.09	0.27	-0.43	0.27	-0.21	-0.52	0.20



* Supplementary variables in red; Active variables in blue;

Figure 3-3: An example of a loadings plot of PC 1 vs PC 2 constructed using independent input values of PC 1 and PC 2 from the loadings table in Table 3-21. The loadings plot shows the correlation between the variables and the PCs and the correlation (positive or negative) between the variables.

3.2.2.1.5 Varimax normalized rotation

Varimax rotation is a strategy utilised to make the loading patterns clearer, that is, PCs that are marked by high loadings for some independent input variables and low loadings for others (Statistica Documentation, 2012). This is achieved by rotating the existing PCA loadings plots to identify the most important variables in a principal component (Jolliffe, 2002; Sousa *et al.*, 2007; Dean, 2009; Statistica Documentation, 2012). The values for the varimax normalized loadings are obtained by dividing the factor loadings (e.g. loadings from Table 3-21) by the square roots of the respective *communalities*, *C*

(Statistica Documentation, 2012). The communalities, C , are defined as the proportions of variance that each variable has in common with other variables and is derived from equation 3-7 (Statistica Documentation, 2012).

$$C_{\alpha k} = \lambda_{\alpha}(U_{\alpha k})^2 \quad 3-7$$

The rotation ensures that each independent input variable is maximally correlated with only one PC and has a near-zero association with the other PCs (Joliffe, 1982; Abdul-Wahab *et al.*, 2005). This is important as it clearly shows which variables are important in the interpretation of the PC (e.g. variables that load nearly 1) (Bryant and Yarnold, 1995). This new set of ‘rotated loadings’ represents the contribution of each variable in a specific PC (Sousa *et al.*, 2007). Only independent variables with high loadings (> 0.5) on the rotated PCs were retained as predictor variables for later use in the regression model. An example of a varimax rotated loadings table (compared to the original (aka ‘raw’ loadings in Table 3-21) is shown in Table 3-22. There is a clear pattern of loadings on all PCs (at least one highly correlated independent input variable for all 8 PCs) unlike in Table 3-21 where the loadings > 0.5 are clustered around the first 6 PCs.

Table 3-22: Example of varimax rotated loadings plot showing the correlations between the independent input variables and the PCs. The alloy elements are written in full, and the fuel elements are shown in symbols

Variable	Factor Loadings (Varimax normalised) (Marked loadings are > 0.5)							
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
1000/Metal Temp (1000 / K)	-0.12	0.17	-0.18	0.37	-0.02	0.19	-0.81	-0.03
Gas Temp (K)	-0.10	-0.14	0.16	0.15	0.07	0.02	0.87	0.16
Carbon (wt %)	-0.11	0.09	0.97	0.01	0.11	0.02	0.13	0.03
Manganese (wt %)	-0.98	-0.01	-0.15	0.08	-0.04	-0.01	0.01	0.03
Phosphorus (wt %)	0.98	0.01	0.15	-0.08	0.04	0.01	-0.01	-0.03
Sulphur (wt %)	0.98	0.01	0.15	-0.08	0.04	0.01	-0.01	-0.03
Silicon (wt %)	0.37	0.10	0.89	0.17	0.12	0.02	0.08	0.06
Chromium (wt %)	0.38	0.09	0.90	-0.03	0.13	0.01	0.09	-0.10
Nickel (wt %)	0.39	0.06	0.86	-0.21	0.07	0.04	0.14	0.16
Molybdenum (wt %)	0.12	-0.12	-0.48	-0.60	-0.18	0.06	0.09	0.54
Niobium (wt %)	-0.55	0.04	-0.14	0.77	0.03	-0.03	-0.08	0.18
Titanium (wt %)	0.14	0.03	-0.14	-0.06	0.10	-0.06	-0.14	-0.95
Vanadium (wt %)	-0.98	-0.01	-0.15	0.08	-0.04	-0.01	0.01	0.03

Variable	Factor Loadings (Varimax normalised) (Marked loadings are > 0.5)							
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
Na (wt %)	0.11	0.64	0.11	-0.02	0.26	0.66	-0.10	0.05
K (wt %)	0.06	0.60	0.27	0.04	0.57	0.44	-0.01	0.02
Mg (wt %)	-0.05	0.93	0.10	0.14	-0.20	-0.03	0.05	-0.05
Ca (wt %)	0.03	0.95	0.04	0.10	-0.06	0.05	-0.15	-0.01
Al (wt %)	-0.02	0.92	0.11	0.08	0.21	0.16	0.03	-0.13
Fe (wt %)	-0.04	0.11	0.10	0.13	0.81	0.10	0.36	-0.23
Si (wt %)	-0.04	-0.70	0.00	0.38	-0.32	-0.17	0.28	-0.08
Cl (wt %)	0.00	0.17	-0.01	-0.04	-0.16	0.94	-0.08	0.05
S (wt %)	0.16	0.08	0.25	-0.05	0.82	-0.27	-0.15	0.00
Ti (wt %)	-0.02	-0.66	0.02	0.28	-0.38	-0.13	0.28	-0.07

3.2.2.1.6 Stepwise regression/selection of predictor variables

Stepwise regression was done to determine the correlation of the dependent variable (i.e. Y , which is the fireside corrosion rate) with the selected PCs. According to Dunteman (1989), if the PCs are to be used as predictors of a dependent variable; their correlations with the dependent variable must be considered as well. This is because the dependent variable (Y) is not part of the analysis (in PCA). Therefore in doing a stepwise regression, the number of predictors (PCs) is reduced to find the most parsimonious possible model that still guarantees a good prediction performance (Cox, 2013). In STATISTICA, the ‘best subset stepwise’ regression method was used to retain PCs that correlate strongly with the dependent variable (Y). The independent input variables ultimately selected for the regression model (extracted from the rotated loadings table, section 0) correspond to the retained PCs determined from stepwise regression. The selection is based on their contribution to the variation in the response variable judged from the adjusted R^2 value and p-value. The adjusted R^2 shows the percentage of variation in the dependent variable explained by the independent (predictor) variables, i.e. how well the model fits the data but adjusts for the number of terms (predictor variables) in a model (Cox, 2013). The p-value statistic represents a decreasing index of the reliability of a result (Shardt, 2015).

3.2.2.1.7 Principal Component Regression (PCR)

Principal component regression is a method for modelling correlation (Bair *et al.*, 2006) and, as intended by the original authors of this technique, the standard PCR method is to regress the outcome, Y , on the selected PCs (following eigenvalue criteria). However, it

has been well documented that if the goal is prediction (Jolliffe, 1982; Jolliffe, 2002; Bair *et al.*, 2006; Afifi *et al.*, 2012), then this approach may not work as expected. Many authors from various fields of science have employed PCR but have fine-tuned its use to suit their purpose (Fekedulegn *et al.*, 2002; Liu *et al.*, 2003; Abdul-Wahab *et al.*, 2005), while others merely used PCA for classification of data or pattern recognition (Lengyel *et al.*, 2004). However, the goal of this research is to develop a model that reflects the original variables. Hence, adopting the approach of Liu *et al.* (2003); Abdul-Wahab *et al.*, (2005); Tan *et al.*, (2016) and Fekedulegn *et al.* (2002), PCA was used in this context as a variable selection tool to identify the most appropriate explanatory variable subset for the regression model.

From the original multiple linear regression contexts, the least squares solution is given by equation 3-8:

$$Y = XB + \varepsilon \quad 3-8$$

Where;

Y = dependent variable

X = input data

ε = standard error

B = regression coefficient given by equation 3-9:

$$B = (X^T X)^{-1} X^T Y \quad 3-9$$

The problem is $X^T X$ is singular, and this, as is the case with the datasets analysed in this research, could be due to the number of variables exceeding the number of observations giving rise to multicollinearities (Wehrens and Mevik, 2007), and/or duplicated observations in a data subset. PCR circumvents this by decomposing X into orthogonal scores, Z , and weight vectors, U , i.e. (equation 3-10):

$$Z = XU \quad 3-10$$

Hence the dependent variable, Y , is not regressed on X but the scores, Z .

In the first instance, the dependent variable (fireside corrosion rate) was regressed on the selected PCs (i.e. matrix of PC scores, Z), but this was done as stepwise regression (section 3.2.2.1.6). Then the independent variables (with loadings > 0.5) were selected from the varimax table for the selected PCs to build the PCA corrosion model in the form of equation 3-11:

$$Y = \sum B_j Z_j \quad 3-11$$

Where Z from equation 3-10 is substituted in equation 3-11 (B is the regression coefficient obtained from the stepwise module). The goal is to obtain a good fit of the data at relatively low model complexity.

3.2.2.2 General Linear Model

The general regression model takes the form (Fekedulegn *et al.*, 2002; Liu *et al.*, 2003):

$$y = \beta_o + \beta_1 x_{1i} + \beta_2 x_{2i} + \dots + \beta_k x_{ki} + \varepsilon_i \quad 3-12$$

Where;

β_k = principal component estimators of the regression coefficient

ε_i = standard error

X_{ki} = predictor variables

Y = dependent variable

Fekedulegn *et al.* (2002) proposed a method to transform the standardised regression coefficients (β_k) to the unstandardized form:

$$\beta'_k = \frac{\beta_k}{s_{xk}} \quad 3-13$$

Where;

$j = 1, 2 \dots k$

$\bar{s}_{xk}$ = the standard deviation of the original variable x_k .

β_k = principal component estimators of the regression coefficient in standardised form

β'_k = principal component estimators of the regression coefficient of the variables in unstandardised form and in the form of equation 3-12.

The intercept in the unstandardized form is given by, β_0 :

$$\beta_0 = \beta_{0,pc} - \frac{\beta_{1,pc}\overline{x_1}}{\overline{s_{x1}}} - \frac{\beta_{2,pc}\overline{x_2}}{\overline{s_{x2}}} - \dots - \frac{\beta_{k,pc}\overline{x_k}}{\overline{s_{xk}}} \quad \mathbf{3-14}$$

Where;

β_0 = intercept in unstandardized form

$\beta_{0,pc}$ = principal component estimators of the regression coefficient in standardised form

$\overline{x_k}$ = mean of the original variables X_k .

$\overline{s_{xk}}$ = standard deviation of the original variables X_k .

3.2.3 Partial Least Squares

According to Dijkstra (2010), Partial Least Squares (PLS) is a regression-based approach devised to analyse high dimensional data and reduce multicollinearity in regression models. The technique works by finding linear functions of the independent variables, X_i , that has maximum covariance with the dependent variable (Y_i) (Maitra and Yan, 2008). The original data, X , is transformed into a set of t-scores, t (equations 3-15 and 3-16). Similarly, Y , is used to define another set of components known as the u-scores, u ; equation 3-17. The transformation is finalized to maximise covariance between t and u (Maitra and Yan, 2008; Ng, 2013). PLS is implemented as a regression model in STATISTICA.

$$t = XW \quad \mathbf{3-15}$$

$$X = tP^T + E_x \quad \mathbf{3-16}$$

$$Y = uQ^T + E_y \quad \mathbf{3-17}$$

Where;

t = the latent variable (i.e. the X scores) which is a linear combination of the input variables X with the weight vector, W .

P = a matrix of regression coefficients (loadings) for t

Q = a matrix of regression coefficients (loadings) for u

$E_{x,y}$ = an error (noise) term.

The PLS prediction model is equivalent to equation 3-18:

$$Y = XB + E \quad 3-18$$

Where;

$$B = WQ$$

W = the weight vector

Q = matrix of regression coefficients as in equation 3-17.

An important distinction between PCA and PLS is that PCA only maximises variation in the predictor variable (X_i) domain. PLS, on the other hand, determines the maximum variance in the predictor variable space (X_i) that explains the variance in the dependent variable space (Y). Hence with PLS, there is a guarantee that the changes in fireside corrosion rates (Y) are associated with the variance extracted from the input data (X_i).

3.2.3.1 Computation of Partial Least Squares

The first part of the analysis was implemented using the non-linear iterative partial least squares algorithm (NIPALS) in STATISTICA. The scores and weights were extracted, and additional steps were computed/completed on a spreadsheet (MS Excel). The steps are summarised in Figure 3-4.

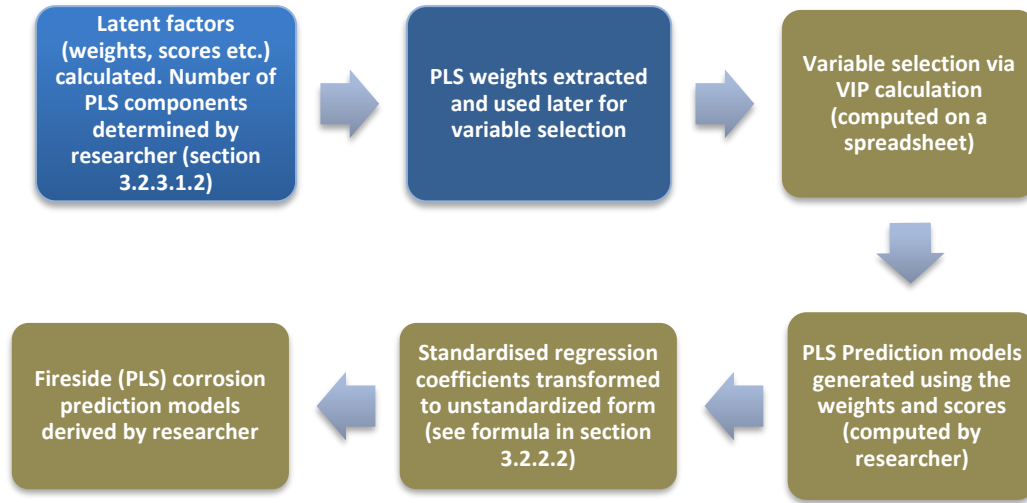


Figure 3-4: Summary of steps of partial least squares (blue section implemented using PLS application in STATISTICA and brown portion computed in MS Excel)

3.2.3.1.1 Calculation of Latent (PLS) Components

STATISTICA uses the NIPALS algorithm for finding the latent variables and the loadings (equations 3-16 to 3-17). First, the input variables are standardised to have a mean of zero and a standard deviation of one. The first PLS component comprising the X scores (t) and Y scores (u) is obtained by computing a set of weights W by determining the maximum covariance between Y and the transpose of X as shown in equation 3-19, which is equivalent to equation 3-20 (Abdi, 2003).

$$Cov(X_i, Y_j) = \frac{\sum_{i=1}^n (X_i - \bar{X}_i)(Y_j - \bar{Y}_j)}{(n - 1)} \quad 3-19$$

Where;

X_i = independent variable, i

$\bar{X}_i$ = mean of independent variable, i

Y_j = dependent variable in case j (or row j)

$\bar{Y}_j$ = mean of independent variable in case j (or row j)

n = number of cases (or rows of observations)

$$W_i = X^T Y \quad 3-20$$

Where;

X = the standardised form of X ,

Y = standardised form of Y

X^T = the transpose of X

W_i = the weight vector for the X columns

The weight vector, W_i , is then scaled into a vector with length equal to one, i.e. W^* (equation 3-21).

$$W_a^* = \frac{W_i}{\|W_i\|} = \frac{W_i}{\sqrt{W_i^T \cdot W_i}} \quad 3-21$$

W_a^* represents the weight vector for PLS component 1. Hence the first component score, t is obtained using the relationship in equation 3-15. Subsequent scores are obtained by deflating the original values of X and Y until X becomes a null matrix (Abdi, 2003; Garson, 2014): i.e. equations 3-22 and 3-23:

$$X = X - t \cdot P^T \quad 3-22$$

$$Y = Y - u \cdot Q^T \quad 3-23$$

The steps are repeated to obtain new values of t and u (P and Q defined in equations 3-16 and 3-17).

These latent variables are oriented in a direction that best explains X and Y , and has the most significant possible relationship between X and Y (Dunn, 2016). As is the case for PCA, subsequent PLS components derived are orthogonal to the first component in the X space (Dunn, 2016).

3.2.3.1.2 Selection of PLS Components

The optimum number of PLS components to use for model building can be ascertained through several means. The easiest way to do this is to observe a graphical summary of the R-squared (R^2) and an increase in R^2 values for the PLS components extracted in the analysis (Figure 3-5). This graph is obtained from a *summary* sheet in STATISTICA (e.g. Table 3-23), which shows: 1) the averaged R^2 values and increase in average R^2 values for the independent (X) variables, and 2) the averaged R^2 values and increase in average R^2 values for the dependent (Y) variable (Statistica Documentation, 2012). These R^2 values are computed relative to the sums of squared deviations from the origin for the centred X and/or Y variable and show the level of model complexity depending on the number of PLS components. The summary table also shows the percentage of variation of the dependent variable explained by the predictor (independent) variable. Thus Table 3-23 shows that approximately 23% of the predictor variable (X data) in PLS component 1 is used to explain 48% variation in the dependent variable (Y); 15% variation in predictor variable (X data) in PLS component 2 is used to explain 30% variation in Y... and so on.

Table 3-23: The average R^2 values and increase in average R^2 values for the predictor (X) and dependent (Y) variables

	Summary of PLS Responses: Ln Corr Rate ($\mu\text{m}/\text{hr}$)			
	Increase R^2 of Y	Average R^2 of Y	Increase R^2 of X	Average R^2 of X
Comp 1	0.48	0.48	0.23	0.23
Comp 2	0.30	0.78	0.15	0.39
Comp 3	0.06	0.84	0.12	0.51
Comp 4	0.01	0.86	0.14	0.65
Comp 5	0.01	0.87	0.12	0.77
Comp 6	0.01	0.88	0.06	0.83
Comp 7	0.01	0.89	0.05	0.87
Comp 8	0.01	0.89	0.04	0.91
Comp 9	0.01	0.90	0.02	0.93
Comp 10	0.00	0.90	0.03	0.96
Comp 11	0.00	0.90	0.02	0.98
Comp 12	0.01	0.91	0.00	0.98
Comp 13	0.00	0.91	0.01	0.99
Comp 14	0.00	0.91	0.01	1.00
Comp 15	0.00	0.91	0.00	1.00
Comp 16	0.00	0.91	0.00	1.00

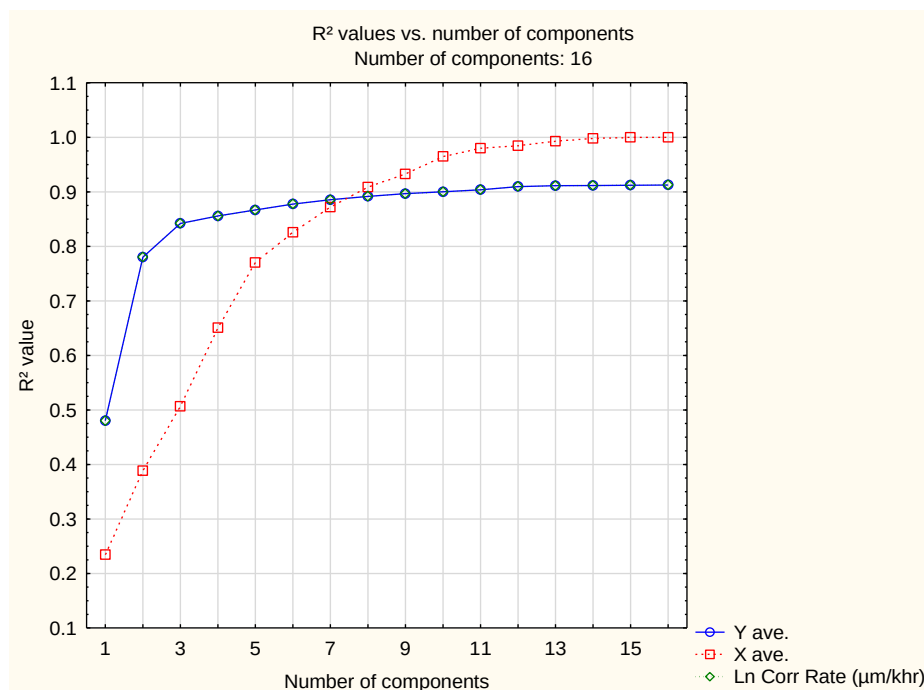


Figure 3-5: Average R^2 values of the predictor (red) and dependent variable (blue) versus the number of PLS components

The idea behind the selection of the appropriate number of PLS components is to match the number of components on the chart (i.e. horizontal axis, Figure 3-5) to the point on the vertical axis where the average R^2 values for the response variable (Y) flattens out as shown in Figure 3-5. The point at which the curve thins or flattens indicates the number of PLS components recommended for model building. However, this is too simplistic and in so many ways can be erroneous because it could lead to the selection of more PLS components than is necessary for model building. On one hand, the average R^2 Y value (blue curve) appears to level off at the 6th or 7th PLS component, but on close inspection, it flattens out at the 13th PLS component which is a lot to use for model building.

A more reliable indication of the number of PLS components to retain in the final model can be determined using cross-validation via the *hold-out* method. According to Statistica Documentation (2012), cross-validation refers to the process of assessing the predictive accuracy of a model in a test sample relative to its predictive accuracy in the learning sample from which the model was developed. The hold-out method is the simplest form of cross-validation in STATISTICA, and the procedure follows from the

definition, i.e. the dataset is divided in half, with half ‘held-out.’ The first half of the data becomes the learning sample from which the first PLS model is developed, while the model’s predictive accuracy is tested by using a new set of observations (i.e. the other half of the data or the test sample) (Statistica Documentation, 2012). Then a validation procedure known as PRESS statistic (predicted residual error sum of squares) is used to ascertain the optimum PLS components (Statistica Documentation, 2012). The PRESS statistic is computed as the sums of squares of the prediction residuals for the new observations. The optimum number of PLS components used for model building is determined by choosing components up to the smallest PRESS value in STATISTICA hence producing Table 3-24 which suggests retaining 9 out of 16 PLS components (hence PLS components 10-16 omitted from the table). Note that these R^2 values are computed relative to the sums of squared deviations from the origin (0, 0) for the centred predictor and dependent (response) variable.

Table 3-24: The average R^2 values and increase in average R^2 values for the predictor (X) and dependent (Y) variables obtained via cross-validation. A total of 9 out of 16 PLS components in red text are suggested following the PRESS statistic in the last column (the procedure stops at the smallest PRESS value hence components 10-16 were not indicated)

	Summary of PLS Responses: Ln Corr Rate ($\mu\text{m}/\text{hr}$)				
	Increase R^2 of Y	Average R^2 of Y	Increase R^2 of X	Average R^2 of X	Average PRESS
Comp 1	0.63	0.63	0.20	0.20	1.00
Comp 2	0.11	0.74	0.29	0.49	1.01
Comp 3	0.08	0.82	0.19	0.68	0.60
Comp 4	0.08	0.89	0.07	0.75	0.53
Comp 5	0.01	0.91	0.10	0.85	0.59
Comp 6	0.01	0.92	0.05	0.90	0.59
Comp 7	0.01	0.93	0.05	0.95	0.63
Comp 8	0.01	0.94	0.02	0.97	0.58
Comp 9	0.01	0.94	0.01	0.98	0.51

Although the cross-validation criterion is useful, especially for large datasets, the selection of training (or learning) and test data tends to be random due to the structure

the data subsets employed for this research; e.g. the lack of variability in the learning data or small data subsets (e.g. data subsets 9, 11, 12, 14-16).

A second method used as a selection criterion which also serves as a check on the initial PLS components retained for model building is via a test of significance judged by the p reliability index (Statistica Documentation, 2012). The p index (or p-value) is a test of significance that indicates decreasing reliability of the result. The higher the p-value estimated for a sample data, the less reliable the output of the result (Statistica Documentation, 2012). Thus, the p index uses the scores to determine the optimum number of PLS components to retain. The outcome of the p index test of significance sometimes matches the initial selection. Ultimately, the number of PLS components selected for model building in this work were determined by the p index (univariate) test of significance.

3.2.3.1.3 Variable Selection for Model Building

Predictor variables selected for model building using PLS were determined using a technique known as *Variable Importance in Projection* (VIP) (Akarachantachote *et al.*, 2014). VIP scores are calculated as the sum of squares of the PLS weights, W (equation 3-21), which takes into account the amount of explained variance from the dependent variable (fireside corrosion rate) in each extracted PLS component (Mehmood *et al.*, 2012; Farres *et al.*, 2015). The VIP measure is defined as (Farres *et al.*, 2015):

$$VIP_j = \sqrt{J \cdot \left(\frac{\sum_{f=1}^F W^2 \cdot SSY_f}{SSY_{total}} \right)} \quad 3-24$$

Where;

J = the total number of predictor (X) variables

W^2 = the weight vector which signifies the importance of the j^{th} variable in each extracted f^{th} (PLS) component

SSY_f = the sum of squares of explained variance for each f^{th} component (i.e. values from column 1 in Table 3-23)

SSY_{total} = the total sum of explained variance of the f^{th} component (i.e. the last row of column 2 in Table 3-23 (Farres *et al.*, 2015).

The selection is made by assessing the calculated VIP scores for each predictor variable (X) and those that score higher than a pre-defined cut-off mark, v ($VIP_j > v$) are retained for model building. Thus only those input parameters that provide an increase in the predictive ability of the PLS model are retained. The generally accepted threshold is $VIP = 1$ because the average of the squared values of the calculated VIP scores equals one (Farres *et al.*, 2015). However, assuming this threshold may invariably lead to the elimination of crucial real-world variables that may be useful in model building (Akarachantachote *et al.*, 2014). Although this is also not a statistically justified threshold, 0.8 has been chosen for this research following the lower end of a range of threshold values proposed by Mehmood *et al.* (2012) to correct for this.

3.3 Fireside Corrosion Model Structure

The general model for a reaction rate is derived from the Arrhenius equation (equation 3-25) for fireside corrosion. This equation is representative of the lower temperature region of the ‘bell-shaped curve’ behaviour of high-temperature alloys with respect to fireside corrosion damage (section 2.6.2) (Simms, 2011a). The higher temperature region of the bell-shaped curve, where the fireside corrosion rate starts to drop, will be more relevant in corrosion studies with higher metal temperatures, such as in ultra-supercritical boiler conditions where the Arrhenius rate equation may not apply.

$$\ln K = \ln \left(A \exp^{-\frac{E_a}{RT}} \right) = \ln A - \frac{E_a}{RT} \quad 3-25$$

Where;

K = the reaction rate ($\mu\text{m}/\text{hr}$)

A = the reaction constant ($\mu\text{m}/\text{hr}$)

E_a = the activation energy (kJ/mol)

R = the universal gas constant ($\text{J}/\text{mol K}$)

T = the metal temperature (K)

The goal is to obtain a regression model expressed as:

$$\ln y = \ln(\beta_o) + \underbrace{\beta_1 x_{1i}}_{\substack{1000 / \text{Metal temp} \\ (1000 / K)}} + \underbrace{\beta_2 x_{2i} + \beta_3 x_{3i} \dots}_{\text{Alloy elements (wt \%)}} + \underbrace{\beta_k x_{ki}}_{\text{Fuel elements (wt \%)}} + \varepsilon_i \quad 3-26$$

Where;

$\ln y$ ($\mu\text{m}/\text{hr}$) = the natural logarithm of corrosion rate, equivalent to $\ln K$ in equation 3-25

β_k = the estimated coefficients for each variable

ε_i = the standard error, and x_{ki} = the nominated predicted variables.

3.4 Fireside Corrosion Model Development Flow Chart/Summary

Figure 3-6 is a regression flowchart adapted from Shardt (2015) that is modified to summarise the model building process in this research.

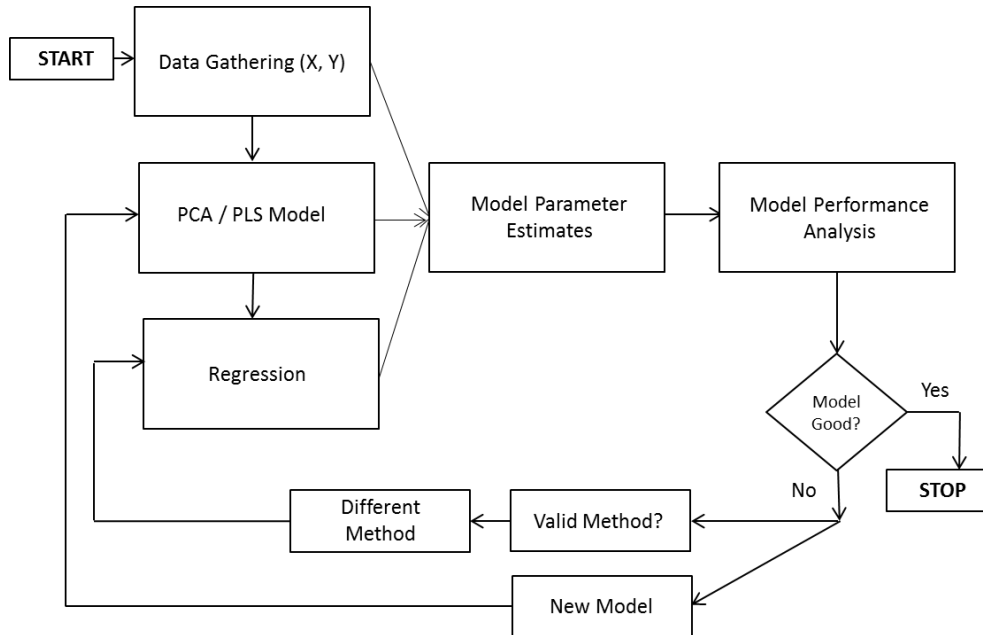


Figure 3-6: Flow chart adapted from Shardt (2015) summarising the PCA/PLS fireside corrosion model building

To expand on the corrosion building process illustrated in Figure 3-6; the final stage in the data collection and gathering phase involves grouping the fireside corrosion dataset into different subcategories based on the type of alloying material (ferritic, austenitic or coatings) and location of the tubes within the tube bank, resulting in 16 data subsets. The 16 data subsets are analysed using PCA and PLS with the goal of extracting important input variables used for fireside corrosion model building. An initial model is derived using the framework model in the form of equation 3-26, and the model performance is judged using the coefficient of determination (R^2). Other framework models are tested using the same data subsets to improve the fireside corrosion model (Chapter 4, section 4.2.1). The final step is model validation. A regression model relies on a variety of assumptions to provide a reasonable approximation to the association between the response (Y) and predictor variables (X_i) (Pardoe, 2012). These assumptions are tied to the distribution of errors in the derived model and must be verified for the model to be valid (Shardt, 2015). Performance statistics are done to assess the model performance (Chapter 6) and to test the validity of the model; e.g. via graphical residual testing to ensure that the following model assumptions have not been violated (Pardoe, 2012; Shardt, 2015); i.e.

- The errors have a mean of zero
- The errors are independent
- The errors have constant variance, referred to as homoscedasticity.
- The errors are normally distributed.

A small set of residuals is an indication that the model provides a good fit. However, the residuals must also satisfy the assumptions listed above for it to be wholly validated, otherwise, as indicated in the flowchart (Figure 3-6), a different method should be applied, and/or a new model derived. This can be achieved by including interaction terms, and/or including more predictor variables or power terms where necessary (Pardoe, 2012; Cox, 2013; Shardt, 2015).

4 RESULTS AND DISCUSSION: MODEL DEVELOPMENT

A total of thirty-two corrosion models were developed: sixteen models were derived using PCA, and sixteen derived using PLS. This chapter addresses first the limitations of the fireside corrosion datasets and the resulting impact on the input parameters selected for model building (section 4.1). The next section details the fireside corrosion model development, with an introduction to the different framework models (section 4.2), and then presents the results for the PCA/PLS derived fireside corrosion models including the variables selected for model building and the corresponding standardised regression coefficients estimated (sections 4-3 to 4-6).

4.1 Corrosion Dataset

The statistical techniques (PCA and PLS) employed in this research are sensitive to the structure of the dataset being analysed, particularly PCA (Oh and Kwak, 2018). The input parameters must have sufficient variation for the analysis to perform optimally; otherwise, it stalls, and/or the regression performance will be poor. The size of the dataset is also a factor as both techniques were designed to tackle large datasets, with Comrey and Lee (1992) citing a scale of 500-1000 entries ideally needed for PCA. However, deriving a single, unified corrosion model in this instance is not viable. This is due to the variations in fireside corrosion behaviour experienced by tube materials in different exposure conditions and for different fuel types. Hence the dataset was split and grouped according to the fuel, and then sub-divided according to the alloy materials (i.e. austenitic, ferritic, nickel-based etc.) with each subset analysed separately. The modelling results and ensuing discussion will be in the order illustrated in Figure 3-1 (chapter 3).

4.1.1 Limitations in Dataset Construction

The dataset used in this work was collated from plant data, which is likely to have a lower spread in input data and/or repeating measurements (as compared to laboratory data where the input parameters are easily controlled) which could result in multicollinearities. Although this underscores the benefit of employing a robust technique such as PCA and PLS to deal with multicollinearities, in some instances, however, the quality of the dataset can affect the output and subsequent inferences that can be made.

One of the main limitations in constructing the corrosion dataset was in obtaining complete and accurate fuel data. For the PE-8 plant data for instance, and as explained in section 0, the Cl content was the only fuel parameter presented in the original corrosion dataset. Hence, as part of the data collection and gathering phase, additional data comprising the complete fuel compositions (Na, K, Mg, Ca, etc.) for the coal types investigated were located and included; and in some cases, some assumptions had to be made for missing coal data. As an example, the PE-8 dataset (data subsets 1-4) was generated at a time when it was common practise to utilise local coals. Hence missing coal data was obtained by matching the location of the power station to the closest coal mine (via other literature and a google search). This was equally required for the US coal dataset, as this also provided insufficient data on some of the coal types in the original literature. The available information in some cases was limited to the region from which the coal was sourced or the coal's rank. For example, the coal was indicated as from Powder River Basin (PRB) from Eagle Butte mine, or the coal type identified simply as say, Western sub-bituminous etc.; hence more data had to be sourced externally. Notably, the USGS *Coalqual* database (Palmer *et al.*, 2015), introduced in section 3.1.2, was utilised to provide a portion of the chemical components of US coal used in this study. The *Coalqual* database keeps a record of various coal types and this database can be filtered and sorted via the province, region, coalfield, bed, mine or power plant and estimated rank (an example is presented in Figure 4-1). However, these specific fields of data are not commonly included in the literature; furthermore, to call up information on a particular coal type, there needs to be at most three search criteria indicated in the literature to narrow down the search result (see Figure 4-1). Hence it is important to note that these assumptions in identifying specific coals made may not



COALQUAL Database

Sample Detail for D165436

Sample Description		Proximate & Ultimate		Oxide		Trace Element	
Sample ID	D165436	Sample ID	D165436	Sample ID	D165436	Sample ID	D165436
State	Wyoming	Moisture	25.82	Remnant Moisture	5.36	GS Ash Dry	11.6
County	CAMPBELL	Moisture Q		Remnant Moisture Q	L	GS Ash Dry Q	
Latitude	44.1242	Volatile Matter	32.44	GS Ash	11	Si	16300
Longitude	-105.7058	Volatile Matter Q		GS Ash Q		Si Q	d
Province	NORTHERN GREAT PLAINS	Fixed Carbon	33.25	SiO ₂	30	Al	10500
Region	POWDER RIVER	Fixed Carbon Q		SiO ₂ Q		Al Q	d
Field	POWDER RIVER	Standard Ash	8.48	Al ₂ O ₃	17	Ca	17400
District		Standard Ash Q		Al ₂ O ₃ Q		Ca Q	d
Formation	FORT UNION	Proximate Validation	Incomplete Data	CaO	21	Mg	1440
Group		Hydrogen		CaO Q		Mg Q	d
Bed	NO DATA ENTERED	Hydrogen Q	B	MgO	2.05	Na	904
Member		Carbon		MgO Q		Na Q	d
Coal Zone		Carbon Q	B	MnO	0.15	K	783
Depth (in)	5400	Nitrogen		MnO Q		K Q	d
Thickness (in)	96	Nitrogen Q	B	Na ₂ O	1.05	Fe	3170
System	Tertiary	Oxygen		Na ₂ O Q		Fe Q	d
Series/Epoch	Paleocene	Oxygen Q	B	K ₂ O	0.81	Ti	
Literature		Sulfur	0.76	K ₂ O Q		Ti Q	B
Comments		Sulfur Q		Fe ₂ O ₃	3.9	TS	9.3
Map	PLEASANTDALE (7.5')	Ultimate Validation	Incomplete Data	Fe ₂ O ₃ Q		TS Q	d
Collector	MTBMG-MATSON R E	Btu	8324	TiO ₂		Ag	
Mine/Power Plant	NO DATA ENTERED	Btu Q		TiO ₂ Q	B	Ag Q	B
Drill Core No	HOLE NO US-7326	Sulfate Sulfur	0.01	P ₂ O ₅		As	3.17
Point Id	531	Sulfate Sulfur Q	L	P ₂ O ₅ Q	B	As Q	
Submit Date	11/06/1973	Pyritic Sulfur	0.75	SO ₃	22	Au	
Sample Description	SUBBITUMINOUS COAL	Pyritic Sulfur Q		SO ₃ Q		Au Q	B
Estimated Rank	SUBBITUMINOUS	Organic Sulfur	0.01	LOI		B	81.4
Apparent Rank	Subbituminous C	Organic Sulfur Q				B Q	
Analytical Labs	USBM and USGS	Ash Deformation				Ba	232
Sample Type	Drill Core	Ash Deformation Q	B			Ba Q	
Analysis Type	As Received	Ash Softening				Be	0.349
Values Represent	Single sample	Ash Softening Q	B			Be Q	
Township	48N	Ash Fluid				Bi	
Range	74W	Ash Fluid Q	B			Bi Q	B
Section	24	Free Swelling				Br	
Quarters		Free Swelling Q	B			Br Q	B
Tract	BCDA	HGI				Cd	0.116
Location Detail		HGI Q	B			Cd Q	
Strat		EQ Moisture				Ce	
		EQ Moisture Q	B			Ce Q	B
		Btu Moist MMF	8896			Cl	
		Btu Moist MMF Q				Cl Q	B
		VM Dry MMF	47.03			Co	5.81
		VM Dry MMF Q				Co Q	
		Fixed C Dry MMF	57.59			Cr	8.14
		Fixed C Dry MMF Q				Cr Q	
		Moisture Ash Free Btu	12670			Cs	
		MAF Btu Q				Cs Q	B
		Total Carbon				Cu	13.7
		Total Carbon Q	B			Cu Q	
		Carbonate C				Dy	
		Carbonate C Q	B			Dy Q	B
		Organic C				Er	
		Organic C Q	B			Er Q	B
		Air Dry Loss				Eu	
		Air Dry Loss Q	B			Eu Q	B
		Residual Moisture	6.36			F	21.1
		Residual Moisture Q				F Q	
						Ga	2.32

<https://ncrdspublic.er.usgs.gov/coalqual/DataDetail.aspx?ID=832&SampleID=D165436>

1/3

Figure 4-1: A screenshot of detailed result from Coalqual database for US coal. The sample description (LHS) can be used to filter the search field (Palmer; et al., 2015)

completely reflect the plant conditions from which the fireside corrosion measurements were derived.

One other crucial concern was the presentation of the fuel data as average compositions in the original literature, as was the case with data subsets 8 and 9 (Table 3-8 and Table 3-10); i.e. there was only one fuel composition in the corrosion data. PCA/PLS analysis cannot proceed when the input parameters in the design matrix have no variance, i.e. all values are constant. As a result, the fuel variables were omitted from data subsets 8 and 9 to effectively analyse and build the fireside corrosion model. For the same reason on the alloy side, if only one alloy material is considered (e.g. data subsets 15 and 16; see Table 3-19), the analysis can only proceed with the other input variables (i.e. the boiler operating conditions and fuel elements) because of a lack of variation of the input data for the alloy. This lack of variation in input data is more likely to be a problem in small datasets as was the case in data subset 14 (co-firing data; see Table 3-19). For instance, the exclusion of Mn (alloy) from the analysis (i.e. for data subset 14) does not imply the absence of Mn from the alloy, but it was left out because the weight composition for Mn for the two alloys, TP316 and HR3C, from the source (corrosion) data was the same, i.e. the weight percentage of Mn = 2.0, and hence, no variance. The input variables that have been excluded from the analysis as a result of transformation or lack of variance are tagged as 'NA' (i.e. '*not analysed*') in Table 4-2 and Table 4-3. Predictor variables that are absent in the data are tagged as 'ND' (i.e. '*not present in data subset*'; Table 4-2 and Table 4-3).

A critical feature that affects the discussion of the results is to do with the transformation of the predictor variables, as depicted in the framework model equations 4-4 to 4-7 introduced in section 4.2.1. The transformation to natural log will lead to a zero value for some predictor variables (e.g. if the actual value of the predictor variable is 1.0, then $\text{LN}(1) = 0$). An example of this is Nb in data subset 1 which has a weight percentage of 1.0 and after the natural log transformation, is not present with the active variables available for analysis. Thus, it should be emphasised that this *zero* for the transformed variable (i.e. Nb as an example) is assumed to be equivalent to the average value of the variable in the corresponding data subset, and *not* to the absence of the predictor variable in question. A way around this is to set the application to include a

mean value for any missing data during the analysis. However, replacing missing data with mean values is generally not recommended (Pardoe, 2012). Hence, a clear distinction has been made as to which predictor variables are actually absent in the fuel and/or alloy composition, (denoted as *ND*) or excluded due to transformation (denoted as *NA*) (see also Table 4-2 and Table 4-3). It should be noted that PCA and PLS analyses for all data subsets with the original values (i.e. without transformation to natural log) forms part of the framework model discussed in section 4.2.1 (full result in Appendix D and Appendix E).

4.2 Fireside Corrosion Model Development

4.2.1 Fireside Corrosion Framework Models

The corrosion models were built using the statistical techniques, PCA and PLS, on a standardised $m \times n$ matrix. The input parameters of the corrosion dataset consist of the alloy elemental compositions (wt %), the fuel compositions (wt %), the metal temperature (expressed as 1000/metal temperature, 1000/K), the gas temperature or the temperature difference (K) and the position of tubes (superheaters and reheaters) in the leading or non-leading position. The base metal (i.e. Fe; and in some data subsets, Ni, for nickel-based alloys) was not included in the analysis. For PCA, the base element (Fe or Ni) and the corrosion rates were inputted as supplementary variables which were projected onto the vector subspace generated by the PCs. The input variables (*X*) and the dependent variable (*Y*, fireside corrosion rate) were standardised to have a mean of zero and a standard deviation of 1. Standardising provides a new centre of origin for the PCA and PLS coordinates.

The fireside corrosion model is structured after the Arrhenius equation linearised as shown in equation 4-1:

$$\begin{array}{c}
 \text{Gas temperature (K)} \\
 \underbrace{\hspace{1.5cm}} \\
 \ln y = \ln(\beta_o) + \beta_1 x_{1i} + \beta_2 x_{2i} + \beta_3 x_{3i} \dots + \beta_k x_{ki} + \varepsilon_i \quad \text{4-1} \\
 \underbrace{\hspace{1.5cm}} \quad \underbrace{\hspace{1.5cm}} \quad \underbrace{\hspace{1.5cm}} \\
 \text{1000 / Metal temperature} \quad \text{Alloy elements} \quad \text{Fuel elements} \\
 \text{(1000 / K)} \quad \text{(wt \%)} \quad \text{(wt \%)}
 \end{array}$$

Different framework models derived from the general structure in equation 4-1 were tested to determine which was better suited to explain the data (designated A – F, equations 4-2 to 4-7).

Framework model A

$$\ln \text{corr rate} = \ln A + B.1000/T_m + c.T_g + d.M_{(\text{alloy})} + e.N_{(\text{fuel})} \quad 4-2$$

Framework model B

$$\ln \text{corr rate} = \ln A + B.1000/T_m + c.(T_g - T_m) + d.M_{(\text{alloy})} + e.N_{(\text{fuel})} \quad 4-3$$

Framework model C

$$\ln \text{corr rate} = \ln A + b.\ln T_m + c.\ln T_g + d.\ln M_{(\text{alloy})} + e.\ln N_{(\text{fuel})} \quad 4-4$$

Framework model D

$$\begin{aligned} \ln \text{corr rate} = \ln A + b.\ln T_m + c.\ln(T_g - T_m) + d.\ln M_{(\text{alloy})} \\ + e.\ln N_{(\text{fuel})} \end{aligned} \quad 4-5$$

Framework model E

$$\ln \text{corr rate} = \ln A + B.1000/T_m + c.\ln T_g + d.\ln M_{(\text{alloy})} + e.\ln N_{(\text{fuel})} \quad 4-6$$

Framework model F

$$\begin{aligned} \ln \text{corr rate} = \ln A + B.1000/T_m + c.\ln(T_g - T_m) + d.\ln M_{(\text{alloy})} \\ + e.\ln N_{(\text{fuel})} \end{aligned} \quad 4-7$$

Where;

$\ln \text{corr rate}$ = fireside corrosion rate (micron/1000 hrs or $\mu\text{m}/\text{hr}$)

$1000/T_m$ = 1000 / metal temperature (1000/K)

$\ln.T_m$ = metal temperature in natural log form (equations 4-4 and 4-5)

T_g = gas temperature (K)

$\ln.T_g$ = gas temperature in natural log form (equations 4-4 and 4-6)

$(T_g - T_m)$ = temperature difference (K).

$\ln.(T_g - T_m)$ = temperature difference in natural log form (equations 4-5 and 4-7)

$M_{(alloy)}$ = alloy elements selected for model building

$N_{(fuel)}$ = fuel elements selected for model building

$\ln.M_{(alloy)}$ = alloy elements in natural log form selected for model building

$\ln.N_{(fuel)}$ = fuel elements in natural log form selected for model building

The temperature difference parameter, $(T_g - T_m)$ K, was considered in lieu of gas temperature (T_g) K in the case frameworks B, D and F (equations 4-3, 4-5, and 4-7). Ultimately it is the temperature difference that provides one of the driving forces for deposition reactions to occur that could then lead to the formation of the corrosive alkali iron trisulphate on the SH/RH (tube) surface. The framework models 4-4 and 4-5 were used where the predictive performances of the Arrhenius models were poor. The predictive ability and model performance for each model case were evaluated using statistical measures such as the coefficient of determination (R^2), and the root mean square error of prediction (RMSE) detailed in chapter 6. The results from framework model F (equation 4-7) will be presented in this chapter and in subsequent chapters for discussion. Table 4-1 summarises the models that have been developed. PCA derived models are designated A, and PLS derived models, B.

Table 4-1: Model suite derived from PCA (designated A) and PLS (designated B). Tube positions not specified are assumed to be in the leading position

MODEL TITLE	MATERIALS	TUBE POSITION	FUEL
Model 1A, 1B	Austenitic alloys	Leading tubes	Midland and North Eastern Region UK coals
Model 2A, 2B		Non-leading tubes	
Model 3A, 3B	Ferritic alloys	Leading tubes	
Model 4A, 4B		Non-leading tubes	
Model 5A, 5B	Austenitic alloys	Position not specified	US Coal – Illinois, Ohio, Eastern and Western coal etc.
Model 6A, 6B	Nickel-based alloys		
Model 7A, 7B	Coatings and claddings		
Model 8A, 8B	Austenitic alloys	Position not specified	World-traded coal
Model 9A, 9B	Coatings and claddings	Position not specified	World-traded coal
Model 10A, 10B	Austenitic alloys	Position not specified	Biomass - clean wood pellets, waste wood and forestry waste wood
Model 11A, 11B	Nickel-based alloys		
Model 12A, 12B	Ferritic alloys		
Model 13A, 13B	Coatings and claddings		
Model 14A, 14B	TP312, HR3C	Position not specified	Co-firing fuel (Daw mill coal and biomass fuel)
Model 15A, 15B	TP312	Position not specified	
Model 16A, 16B	T22	Position not specified	

4.2.2 Variables Selected (Input Parameters) for Model Building

Input parameters used for model building are determined from the outcome of PCA and PLS data analysis. To recap, for the PCA technique, the selection is done in two steps:

- Performing a stepwise regression to eliminate PCs (initially selected by retaining PCs with eigenvalues > 0.5) that do not correlate with the dependent variable Y , i.e. the corrosion rate.
- Inspecting the rotated loadings plot table aka varimax plots to select input variables that have high loadings (> 0.5) on the selected PCs.

In PLS model building, the number of PLS components can be determined by inspecting the summary chart (e.g. Figure 3-5) to give a rough idea of the optimal number of components to retain (which can be verified or supported from a univariate test of significance) or via cross-validation and then using the outcome of the PRESS statistic to ascertain the number of PLS components to retain. The important input variables are obtained via an independent calculation, i.e. estimating VIP scores (see equation 3-24) and then selecting predictor variables with VIP scores > 0.8 . The concept behind the VIP variable selection procedure is to reveal the importance of each variable as reflected by the loading weights from each selected PLS component (Mehmood *et al.*, 2012; Farres *et al.*, 2015).

To conform to the Arrhenius model structure (equation 4-1), the inverse metal temperature parameter will remain a constant feature in the model equation. This is because the metal temperature plays a significant role in the fireside corrosion mechanism. High (metal) temperatures will sustain the corrosive deposits in the molten state, thus enabling reactions that flux the protective scale from the SH/RH, and accelerates the corrosion process (left hand side of the bell shape corrosion behaviour, section 2.6.2, Figure 2-11) (Simms, 2011a; Wright and Shingledecker, 2015). Thus, it is imperative that this parameter is retained in the model equation. In the rare event where the inverse metal temperature was eliminated for model building, the PC selection procedure was revised either by lowering the eigenvalue threshold in PCA (e.g. from 0.5 to 0.2) or forcing some PCs to remain in the stepwise regression module. In the

same way, to retain the inverse metal temperature in PLS models, the number of PLS components or the VIP selection threshold was adjusted.

The variables selected for model building and the parameter estimates from PCA and PLS are outlined in tabular form (Table 4-2 and Table 4-3) for comparison and discussion.

Table 4-2: Estimated standardised regression coefficients for the predictor variables in PCA models 1A-16A. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant.

VAR	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A
1000/T _m	-0.20	-0.31	-0.36	-0.22	0.13	-0.123	0.38	-0.055	-0.10	0.072	0.12	-0.21	-0.23	-0.052	0.10	-0.79
(T _g -T _m)	0.095	0.19	0.38	-0.076	0.34	0.023	ND	-0.056	ND	-0.19	0.09	0.041	-0.067	ND	ND	ND
ALLOY ELEMENTS																
C	-0.087	-0.14	-0.0096	NS	NS	0.065	-0.10	NS	0.075	0.11	NS	NS	-0.035	0.0032	NA	NA
Mn	-0.0086	-0.023	-0.0096	NS	-0.04	0.016	-0.034	0.079	NA	NS	0.024	0.015	-0.024	NA	NA	NA
P	0.0086	0.023	-0.0096	NS	-0.16	0.019	-0.039	0.17	-0.044	0.25	NS	NS	-0.007	ND	ND	ND
S	0.0086	0.023	-0.0096	NS	-0.10	0.019	-0.064	0.16	-0.044	0.19	-0.082	NS	-0.038	ND	ND	ND
Si	-0.093	-0.078	-0.0096	NS	-0.12	-0.062	0.10	-0.033	-0.084	-0.003	-0.052	0.037	0.13	0.0032	NA	NA
Cr	-0.048	-0.11	0.0096	NS	0.012	-0.043	NS	NS	0.075	-0.12	NS	0.017	0.11	0.0032	NA	NA
Ni	-0.017	-0.11	-0.0096	NS	-0.016	Base	NS	NS	NS	-0.051	Base	-0.047	0.14	0.0032	NA	ND
Mo	0.12	0.040	0.0096	NS	NS	-0.092	0.011	0.15	-0.050	-0.073	NS	0.034	0.028	-0.0032	NA	NA
Nb	NA	NA	ND	ND	0.0034	-0.099	0.14	-0.030	ND	0.18	-0.016	ND	-0.084	-0.0032	NA	ND
Ti	-0.068	-0.033	ND	NS	0.055	-0.066	-0.07	-0.021	ND	-0.30	-0.026	ND	0.18	ND	ND	ND
V	0.0086	0.023	ND	NS	NS	ND	0.078	-0.15	ND	-0.19	NS	NS	-0.12	ND	ND	ND
Cu	ND	ND	-0.0096	NS	0.052	0.013	0.057	0.078	-0.044	-0.022	ND	0.019	0.29	ND	ND	ND
N	ND	ND	ND	ND	0.067	ND	0.034	-0.023	ND	NS	-0.026	ND	-0.16	-0.0032	NA	ND
Ce	ND	ND	ND	ND	-0.063	ND	-0.0048	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ta	ND	ND	ND	ND	0.027	ND	-0.31	NS	ND	ND	ND	ND	ND	ND	ND	ND
Al	ND	ND	ND	ND	NS	0.041	0.11	-0.067	NS	-0.0084	NS	ND	NS	ND	ND	ND
W	ND	ND	ND	ND	NS	0.083	-0.16	NS	-0.058	0.0089	ND	ND	0.11	ND	ND	ND
B	ND	ND	ND	ND	NS	0.10	NS	-0.051	ND	0.15	0.0001	ND	NA	ND	ND	ND
Co	ND	ND	ND	ND	NS	-0.040	ND	NS	-0.044	0.0084	NS	ND	0.29	ND	ND	ND

VAR	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A
Fe	Base	Base	Base	Base	Base	-0.059	0.076	Base	NS	Base	NS	Base	-0.045	Base	Base	Base
(Nb + Ta)	ND	ND	ND	ND	ND	ND	ND	ND	0.13	ND	ND	ND	ND	ND	ND	ND
O	ND	ND	ND	ND	ND	ND	ND	ND	0.085	ND	ND	ND	0.16	ND	ND	ND
Y	ND	ND	ND	ND	ND	ND	ND	ND	NS	ND	ND	ND	NS	ND	ND	ND
FUEL ELEMENTS																
Na	0.12	-0.034	0.057	NS	0.082	0.034	0.01	NA	NA	0.012	0.059	NS	0.046	-0.092	-0.088	NS
K	0.041	-0.022	0.052	NS	0.084	0.0086	0.021	NA	NA	0.078	NS	-0.13	-0.12	0.11	0.12	NS
Mg	NS	0.11	-0.017	NS	0.081	0.0632	-0.016	NA	NA	-0.0082	0.076	NS	0.011	0.096	0.11	NS
Ca	NS	0.022	-0.047	NS	0.15	0.12	-0.027	NA	NA	0.11	0.077	NS	0.074	-0.10	-0.11	NS
Al	0.022	0.13	NS	NS	NS	-0.027	NS	NA	NA	0.043	0.058	NS	0.060	-0.092	-0.11	NS
Fe	0.084	0.043	0.058	-0.028	0.28	0.091	0.15	NA	NA	-0.025	0.052	NS	0.027	-0.11	-0.11	NS
Si	0.021	-0.0097	NS	NS	0.052	-0.043	NS	NA	NA	0.0013	0.059	NS	0.045	-0.0092	-0.051	NS
Cl	0.29	-0.066	0.073	NS	0.14	0.024	-0.0092	NA	NA	0.075	0.066	NS	0.079	0.096	0.094	NS
S	-0.23	-0.046	0.1	-0.028	-0.013	-0.023	-0.031	NA	NA	-0.12	NS	NS	0.31	0.050	0.024	NS
Ti	0.044	0.13	-0.03	0.027	0.06	0.059	0.090	NA	NA	0.03	-0.08	NS	-0.013	-0.097	-0.11	NS
P	ND	ND	ND	ND	-0.40	-0.33	-0.30	NA	NA	-0.13	0.085	-0.11	-0.082	0.11	0.11	NS
Mn	ND	ND	ND	ND	0.28	0.057	0.15	NA	NA	-0.19	NS	-0.13	-0.17	-0.11	-0.11	NS
Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.030	0.072	NS	0.025	-0.088	-0.11	NS

VAR – Predictor variables (in natural log, except T_m)

1000/T_m - Metal temperature, 1000/K

(T_g-T_m) – The temperature difference (K)

Yellow cells – most influential variable (highest standardised regression coefficient)

Orange cells – positively correlated with the corrosion rate

Blue cells – negatively correlated with the corrosion rate

NS – Not selected for model building (grey cells)

NA – Not analysed but present in the data subset (grey cells)

ND – Not present in data subset (white cells)

Base – Base metal

Table 4-3: Estimated standardised regression coefficients for the predictor variables in PLS models 1B-16B. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant.

VAR	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13B	14B	15B	16B
1000/T _m	-0.30	-0.50	-0.37	-0.39	0.078	-0.14	0.28	-0.0008	-1.00	0.37	0.086	-0.11	-0.2	-0.052	0.027	-0.82
(T _g -T _m)	0.12	0.28	0.38	0.19	0.37	NS	ND	0.0015	ND	-0.011	-0.051	0.085	NS	ND	ND	ND
ALLOY ELEMENTS																
C	-0.099	-0.12	NS	NS	NS	NS	NS	0.070	NS	0.46	NS	NS	NS	0.0032	NA	NA
Mn	NS	NS	NS	NS	NS	NS	NS	0.070	NA	0.10	NS	NS	NS	NA	NA	NA
P	NS	NS	NS	NS	NS	NS	-0.026	0.15	NS	0.14	-0.064	NS	NS	ND	ND	ND
S	NS	NS	NS	NS	NS	NS	-0.11	0.16	NS	0.17	NS	NS	NS	ND	ND	ND
Si	-0.074	NS	NS	NS	NS	-0.056	NS	-0.034	-0.084	0.12	NS	0.022	0.16	0.0032	NA	NA
Cr	-0.059	-0.098	NS	NS	NS	-0.079	-0.19	-0.080	NS	-0.14	NS	NS	NS	0.0032	NA	NA
Ni	NS	-0.14	NS	NS	NS	Base	-0.20	-0.0039	NS	NS	Base	-0.039	0.20	0.0032	NA	ND
Mo	0.061	-0.069	NS	NS	0.13	-0.097	NS	0.14	NS	0.033	NS	NS	NS	-0.0032	NA	NA
Nb	NA	NA	ND	ND	NS	-0.10	0.086	0.010	ND	NS	-0.051	ND	NS	-0.0032	NA	ND
Ti	NS	NS	ND	ND	NS	-0.081	NS	-0.025	ND	-0.18	NS	ND	0.17	ND	ND	ND
V	NS	NS	ND	ND	NS	ND	NS	-0.14	ND	0.095	ND	NS	-0.17	ND	ND	ND
Cu	ND	ND	NS	NS	NS	NS	NS	0.056	NS	NS	ND	NS	0.25	ND	ND	ND
N	ND	ND	ND	ND	NS	ND	0.11	-0.0070	ND	-0.64	NS	ND	NS	-0.0032	NA	ND
Ce	ND	ND	ND	ND	NS	ND	NS	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ta	ND	ND	ND	ND	NS	ND	-0.29	ND	ND	ND	ND	ND	ND	ND	ND	ND
Al	ND	ND	ND	ND	NS	NS	0.18	-0.057	NS	NS	NS	ND	NS	ND	ND	ND
W	ND	ND	ND	ND	NS	-0.0016	NS	0.054	NS	NS	ND	ND	NS	ND	ND	ND
B	ND	ND	ND	ND	NS	0.085	NS	-0.028	ND	NS	NS	ND	NA	ND	ND	ND
Co	ND	ND	ND	ND	NS	NS	NS	0.054	NS	NS	-0.079	ND	0.26	ND	ND	ND
Fe	Base	Base	Base	Base	Base	NS	-0.0007	Base	NS	Base	0.080	Base	NA	Base	NA	NA

VAR	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13B	14B	15B	16B
(Nb + Ta)	ND	ND	ND	ND	ND	ND	ND	ND	NS	ND	ND	ND	ND	ND	ND	ND
O	ND	ND	ND	ND	ND	ND	ND	ND	NS	ND	ND	ND	0.096	ND	ND	ND
Y	ND	ND	ND	ND	ND	ND	ND	ND	NS	ND	ND	ND	NS	ND	ND	ND
FUEL ELEMENTS																
Na	0.065	NS	0.015	NS	0.11	0.034	NS	NA	NA	NS	0.060	NS	0.035	-0.092	-0.098	NS
K	NS	-0.048	0.018	NS	0.072	NS	NS	NA	NA	0.078	0.080	-0.13	-0.12	0.11	0.12	NS
Mg	NS	NS	NS	-0.032	0.025	0.058	NS	NA	NA	NS	0.076	NS	NS	0.096	0.11	NS
Ca	-0.13	NS	NS	-0.056	0.13	0.12	NS	NA	NA	0.24	0.077	NS	0.10	-0.10	-0.11	NS
Al	NS	0.049	-0.12	NS	NS	NS	0.34	NA	NA	NS	0.059	NS	0.061	-0.092	-0.11	NS
Fe	NS	0.019	0.099	0.085	0.30	0.088	0.11	NA	NA	NS	0.054	NS	NS	-0.11	-0.12	NS
Si	NS	-0.090	0.13	NS	0.069	NS	0.14	NA	NA	NS	0.060	NS	0.049	NS	-0.037	NS
Cl	0.42	0.092	-0.026	NS	0.20	-0.0005	-0.12	NA	NA	NS	0.066	NS	0.079	0.097	0.1	NS
S	-0.1	-0.019	0.19	-0.024	-0.0068	NS	NS	NA	NA	-0.16	NS	NS	0.35	0.050	0.039	NS
Ti	NS	0.074	NS	0.11	0.062	NS	NS	NA	NA	NS	-0.081	NS	NS	-0.097	-0.11	NS
P	ND	ND	ND	ND	-0.40	-0.36	-0.39	NA	NA	-0.39	0.085	-0.11	-0.095	0.11	0.12	NS
Mn	ND	ND	ND	ND	0.34	0.050	NS	NA	NA	-0.15	-0.083	-0.13	-0.16	-0.11	-0.12	NS
Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND	NS	0.073	NS	NS	-0.088	-0.11	NS

VAR – Predictor variables (in natural log; except T_m)

1000/T_m - Metal temperature, 1000/K

(T_g-T_m) – The temperature difference (K)

Yellow cells – most influential variable (highest standardised regression coefficient)

Orange cells – positively correlated with the corrosion rate

Blue cells – negatively correlated with the corrosion rate

NS – Not selected for model building (grey cells)

NA – Not analysed but present in the data subset (grey cells)

ND – Not present in data subset (white cells)

Base – Base metal

4.3 Coal Models

This section presents results from data subsets featuring the UK, the US and world-traded coal; i.e. data subsets 1-9. Initial statistics include the correlation matrix of the variables to determine the relationship between the predictor variables and the fireside corrosion rate for each data subset (this correlation matrix is derived independently and not from the matrix $(X^T X)$ described in section 3.2.2.1.1 which forms the basis of PCA). This is important as it serves as a preliminary guess as to which variables are most likely to have an impact on the corrosion rate and might be retained in the model. A subset of the matrix table is presented (section 4.3.1) with a focus on the correlation of the corrosion rate (i.e. the model dependent variable, Y) with selected predictor variables: namely the inverse metal temperature, Cr (alloy), Cl (fuel), S (fuel), and the alkali metals (fuel), as these are active parameters in the deposition and/or the fireside corrosion mechanisms. The complete correlation table for the data subset is contained in Appendix B.

The results of models 1A (PCA) and 1B (PLS) (for data subset 1) are outlined in section 4.3.1 followed by a discussion on the results (section 4.3.2). Other (coal) model results will follow suit in section 4.3.3 with the discussion centred on the selection of important alloy and fuel elements, and taking into account the different metallic alloys and coal type studied and the different range of boiler conditions. The PCA/PLS results derived using framework model F are presented and discussed in sections 4.3.1 to 4.5 (with occasional references to the other framework models). The results for framework models A-E are presented in Appendices C to E.

4.3.1 Austenitic Leading Tubes/UK Coal (PCA/PLS Models 1A and 1B)

This data subset (subset 1) represents UK coal data with austenitic alloys in the leading position. PCA and PLS were performed on a standardised 51×23 matrix. The correlation values are shown in Table 4-4. There are statistically significant correlations between the $\ln$ corrosion rate and the inverse of metal temperature ($1000/K$), Cr (alloy), Cl (fuel) and S (fuel). Note that there are also significant correlations between the predictor variables; for instance, Cl (fuel) and the inverse of metal temperature, Cl and S (fuels), Na and K (fuels), Cr (alloy), K (fuel) and S (fuel).

Table 4-4: Correlation matrix for selected variables in data subset 1 (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the element in full is from the metal/alloy)

Variable	1000 / Metal Temp (1000 / K)	Chromium wt %	Na wt %	K wt %	Cl wt %	S wt %	ln corr rate ($\mu\text{m}/\text{hr}$)
1000 / Metal Temp (1000 / K)	1.000	-0.261	0.208	0.139	0.313	0.059	-0.289
Chromium wt %	-0.261	1.000	0.223	0.325	-0.085	0.365	-0.363
Na wt %	0.208	0.223	1.000	0.902	0.554	0.295	0.066
K wt %	0.139	0.325	0.902	1.000	0.278	0.551	-0.118
Cl wt %	0.313	-0.085	0.554	0.278	1.000	-0.360	0.589
S wt %	0.059	0.365	0.295	0.551	-0.360	1.000	-0.493
ln corr rate ($\mu\text{m}/\text{hr}$)	-0.289	-0.363	0.066	-0.118	0.589	-0.493	1.000

With an emphasis on the direction of the correlation between the corrosion rate and the predictor variables (positive or negative), it is observed that the *ln* corrosion rate increases with an increase in the inverse of metal temperature (1000/K) and Cl (fuel). Sulphur is negatively correlated with the *ln* corrosion rate, as is Cr (alloy element). The observation of the *ln* corrosion rate trend with Cr suggests that increased levels improve corrosion resistance due to the formation of a Cr_2O_3 layer. The correlation between the *ln* corrosion rate and S takes an interesting turn as there is a negative correlation with the corrosion rate even though S is an active variable in the fireside corrosion mechanism.

4.3.1.1 PCA Model 1A

The eigenvalue criterion was used to select 8 out of 16 PCs (which together explains 95% variation in the input data: - this table is shown in chapter 3, Table 3-20). Further dimension reduction involved selecting the PCs that were most correlated with the *ln* corrosion rate using the *best subset* stepwise regression module (Table 4-5). Hence PC 2 was excluded from further analysis following results from the stepwise regression. Table 4-6 shows the rotated loading plots obtained from PCA. The selection criterion was used to retain variables with loadings equal to and greater than 0.5.

Table 4-5: The best (PC) subset stepwise regression module highlighting the PCs retained for model building (data subset 1)

Subset No.	Summary of best subsets of PCs									
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
1	0.79	7	0.27		0.29	0.24	0.41	-0.56	0.25	0.25
2	0.79	8	0.27	-0.051	0.29	0.24	0.41	-0.56	0.25	0.25
3	0.73	6	0.27		0.29		0.41	-0.56	0.25	0.25
4	0.73	6	0.27		0.29	0.24	0.41	-0.56		0.25
5	0.73	6	0.27		0.29	0.24	0.41	-0.56	0.25	
6	0.72	7	0.27	-0.051	0.29		0.41	-0.56	0.25	0.25
7	0.72	7	0.27	-0.051	0.29	0.24	0.41	-0.56		0.25
8	0.72	7	0.27	-0.051	0.29	0.24	0.41	-0.56	0.25	
9	0.71	6			0.29	0.24	0.41	-0.56	0.25	0.25
10	0.71	7		-0.051	0.29	0.24	0.41	-0.56	0.25	0.25

Table 4-6: PC/variable correlation (varimax rotated loadings table). Highlighted (yellow)

PCs are used for fireside corrosion model building. Variables with loadings > 0.5 are marked in red and selected for model building (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	Factor Loadings (Varimax normalised) - Data subset 1 Marked loadings are > 0.5							
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
1000/Metal Temp (1000 / K)	-0.137	0.108	-0.151	0.012	-0.075	0.147	0.215	0.916
(Tg-Tm) K	-0.159	0.052	0.119	0.135	0.213	-0.053	-0.780	-0.336
Alloy								
Carbon (wt %)	-0.129	0.119	0.962	0.155	0.057	-0.043	-0.089	-0.066
Manganese (wt %)	-0.991	-0.037	-0.104	-0.012	0.026	0.011	-0.049	0.030
Phosphorus (wt %)	0.991	0.037	0.104	0.012	-0.026	-0.011	0.049	-0.030
Sulphur (wt %)	0.991	0.037	0.104	0.012	-0.026	-0.011	0.049	-0.030
Silicon (wt %)	0.561	0.157	0.782	0.123	0.026	-0.062	-0.112	0.031
Chromium (wt %)	0.519	0.098	0.823	0.144	-0.092	-0.042	-0.004	-0.093
Nickel (wt %)	0.578	0.058	0.728	0.088	0.242	0.006	0.056	-0.213
Molybdenum (wt %)	0.428	-0.144	-0.467	-0.153	0.591	0.120	0.226	-0.300
Titanium (wt %)	-0.155	0.079	0.155	-0.085	0.930	0.041	-0.147	-0.023
Vanadium (wt %)	0.991	0.037	0.104	0.012	-0.026	-0.011	0.049	-0.030
Fuel								
Na (wt %)	0.094	0.478	0.079	0.662	0.079	0.433	0.316	0.061
K (wt %)	0.045	0.377	0.196	0.848	0.048	0.168	0.186	0.076
Mg (wt %)	0.004	0.949	0.159	-0.008	-0.003	0.084	-0.035	0.002
Ca (wt %)	0.152	0.901	0.102	0.142	0.069	0.017	0.225	0.117
Al (wt %)	0.010	0.684	0.116	0.637	-0.093	0.120	0.174	0.025
Fe (wt %)	-0.064	-0.045	0.100	0.907	-0.190	-0.083	-0.137	-0.141
Si (wt %)	-0.020	-0.550	0.045	-0.327	-0.058	-0.079	-0.704	0.011
Cl (wt %)	-0.009	0.117	-0.052	0.075	0.062	0.943	0.095	0.167
S (wt %)	0.170	-0.051	0.214	0.662	0.002	-0.541	0.197	0.195
Ti (wt %)	-0.007	-0.484	0.047	-0.356	-0.056	-0.011	-0.681	-0.008

The variables nominated for model building were extracted from the highlighted PCs in Table 4-6; i.e. PC 1, and PCs 3-8. Thus, the alkaline earth metals in PC 2 are not included for the fireside corrosion model building. However, Al and Si (fuel elements), which are marked in PC 2 also have high loadings in PCs 4 and 7 respectively and are thus retained in the final model variant derived from PCA. Principal component regression (PCR) produces the parameter estimates for these variables, which are transformed back to unstandardized form in the final step of model building (see section 3.2.2.2).

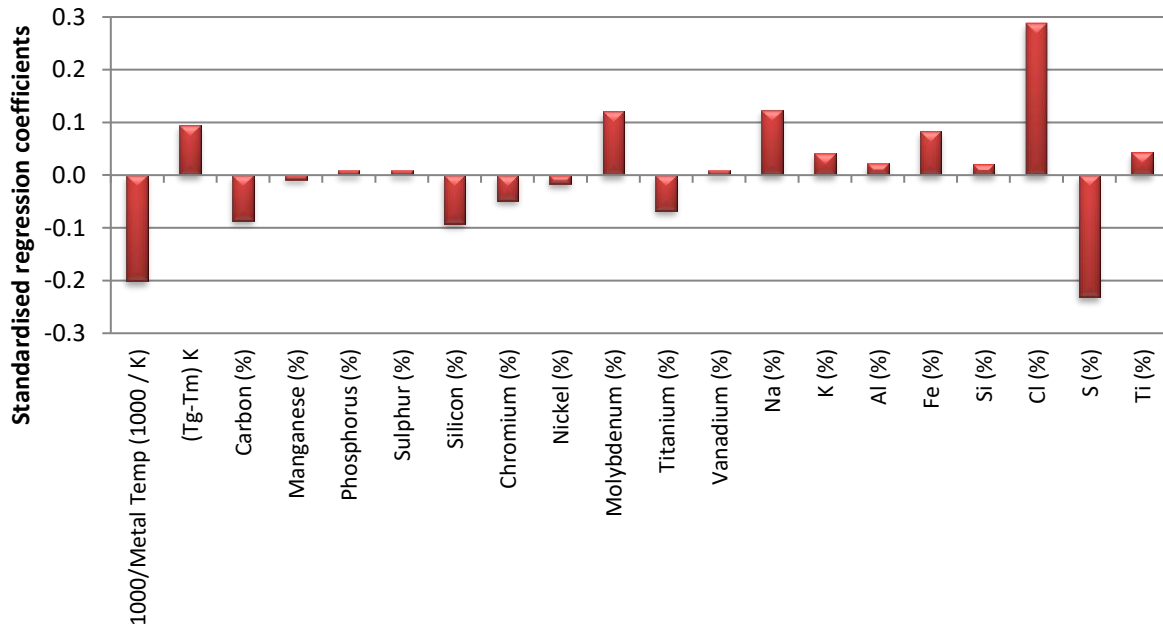


Figure 4-2: Variables selected and retained in PCA model 1A plotted using standardised regression coefficients (the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

The predictor variables selected and retained in the PCA model 1A have been plotted using the standardised regression coefficient values to visualise the extent of their association with the dependent variable (Figure 4-2). The length of the bars highlights the extent of influence an input variable has on the $\ln$ corrosion rate, and the position of the bars depicts positive or negative correlation with the $\ln$ corrosion rate. The longest bar in Figure 4-2 is the fuel element Cl and it sits on the positive axis of the chart,

implying that it has both the highest influence on the $\ln$ corrosion rate and is positively correlated with the $\ln$ corrosion rate. As such the inference is that increased Cl levels in the coal would result in an increase in the corrosion rate. The other significant correlations are S (fuel), Na, (fuel), Mo (alloy), metal temperature (1000/K), and the temperature difference, ($T_g - T_m$). However, whilst the fuel elements, K, Al, Si and Ti have been selected for PCA model building, their impact is almost negligible (Figure 4-2), a common feature and limitation of PCA.

For the austenitic alloy elements; the results show that C, Cr, Si, Ti and to a comparatively smaller extent, Mn and Ni are negatively associated with the corrosion rate implying more resistant effects (Figure 4-2).

4.3.1.2 PLS Model 1B

The PLS analysis proceeds by determining the ideal number of PLS components to use for model building. The number of PLS components correlates to the variation in the response (dependent) variable explained by the input data and is summarised in Table 4-7.

Table 4-7: The increase in R^2 values and average R^2 values for the predictor (X) and dependent (Y) variables (data subset 1)

	Summary of PLS (Data subset 1)			
	Increase R^2 of Y	Average R^2 of Y	Increase R^2 of X	Average R^2 of X
Comp 1	0.480	0.480	0.234	0.234
Comp 2	0.300	0.780	0.154	0.389
Comp 3	0.062	0.842	0.118	0.506
Comp 4	0.014	0.856	0.144	0.650
Comp 5	0.011	0.867	0.120	0.770
Comp 6	0.011	0.877	0.056	0.826
Comp 7	0.008	0.885	0.046	0.872
Comp 8	0.006	0.892	0.037	0.909
Comp 9	0.005	0.897	0.024	0.933
Comp 10	0.003	0.900	0.032	0.965
Comp 11	0.004	0.904	0.016	0.980
Comp 12	0.006	0.910	0.004	0.984
Comp 13	0.002	0.911	0.009	0.993
Comp 14	0.000	0.912	0.005	0.998
Comp 15	0.000	0.912	0.001	1.000
Comp 16	0.000	0.912	0.000	1.000

Nine PLS components were initially selected for model building, which following the univariate test of significance (p-value) was reduced further to 6 (Table 4-8). As the table shows, only the X scores 1-6 are statistically significant at $p < 0.05$ (see computation of X scores in section 3.2.3, equation 3-15).

Table 4-8: The X scores (1-9) corresponds to the number of PLS components selected. The X scores 1-6 are statistically significant at $p < 0.05$ (numbers in red) and thus 6 PLS components were used to build the corrosion model for data subset 1

Effect	Univariate Tests of Significance for Ln Corr Rate ($\mu\text{m}/\text{hr}$) Std. Error of Estimate: 0.2320
	p
Intercept	0.000000
X SCORE1	0.000000
X SCORE2	0.000000
X SCORE3	0.000013
X SCORE4	0.023722
X SCORE5	0.042630
X SCORE6	0.046842
X SCORE7	0.080863
X SCORE8	0.123840
X SCORE9	0.159872

Hence 6 PLS components were selected indicating that approximately 88% variation in the response variable (Y) is explained by 83% variation in the predictor variable data (X) (see Table 4-7). The number of predictor weights used for model building corresponds to the number of PLS components selected. Thus using 6 predictor weights (Table 4-9) and the average R^2 of Y values for components 1 to 6 from Table 4-7, VIP scores (using equation 3-24) were calculated for the input variables. Variables that meet the selection criteria of >0.8 VIP score were advanced to the PLS corrosion model building stage which was computed on a spreadsheet. The VIP scores and variables selected for model building are displayed in Table 4-10. The variables selected for PLS model building include the inverse metal temperature, the temperature difference, C, Si, Cr, Mo from the alloy elements; and Na, Ca, Cl and S from the fuel (Table 4-10). A significant observation is that fewer predictor variables were nominated by PLS than PCA. The main advantage of the PLS technique over PCA is that it eliminates input variables that have a negligible association with the corrosion rate.

Table 4-9: Predictor weights corresponding to the number of PLS components used for variable selection and model building

	Predictor weights (Data subset 1)																					
	1000/Metal Temp (1000 /K)	(Tg-Tm) °C	Carbon (%)	Manga nese (%)	Phosph orus (%)	Sulphur (%)	Silicon (%)	Chromium (%)	Nickel (%)	Molyb denum (%)	Titanium (%)	Vanadium (%)	Na (%)	K (%)	Mg (%)	Ca (%)	Al (%)	Fe (%)	Si (%)	Cl (%)	S (%)	Ti (%)
Comp 1	-0.228	0.169	-0.331	0.038	-0.038	-0.038	-0.301	-0.287	-0.188	0.312	0.026	-0.038	0.052	-0.093	-0.125	-0.223	-0.144	-0.051	0.132	0.466	-0.390	0.104
Comp 2	-0.351	0.219	-0.149	-0.158	0.158	0.158	-0.043	-0.013	0.063	0.269	-0.022	0.158	0.327	0.189	0.036	-0.056	0.104	0.146	-0.011	0.618	-0.253	-0.055
Comp 3	-0.452	0.360	0.180	0.147	-0.147	-0.147	0.017	0.089	-0.014	-0.274	-0.215	-0.147	0.122	0.166	-0.020	-0.245	0.045	0.326	0.186	0.413	-0.024	0.031
Comp 4	-0.418	-0.089	-0.012	-0.126	0.126	0.126	0.072	0.136	-0.042	-0.287	-0.523	0.126	-0.200	-0.144	-0.042	-0.280	-0.229	-0.086	0.155	0.317	0.152	-0.154
Comp 5	-0.296	-0.238	-0.068	0.038	-0.038	-0.038	-0.056	-0.032	-0.194	-0.305	-0.390	-0.038	-0.092	-0.035	0.192	-0.076	-0.081	-0.187	-0.098	0.440	0.234	-0.455
Comp 6	-0.488	-0.043	0.058	0.031	-0.031	-0.031	0.091	-0.016	-0.032	-0.120	0.211	-0.031	-0.278	-0.077	0.302	-0.088	-0.163	-0.329	0.015	0.350	0.332	-0.367

Table 4-10: Variable importance in projection (VIP) scores (red text indicates variables above a threshold of 0.8 and selected for inclusion in the PLS fireside corrosion model 1B; the fuel elements are in symbols, alloy elements are written in full)

	VARIABLES	VIP SCORES
	1000/Metal Temp (1000 / K)	1.421
	(T _g -T _m) (K)	0.961
Alloy Elements	Carbon (wt %)	1.241
	Manganese (wt %)	0.494
	Phosphorus (wt %)	0.494
	Sulphur (wt %)	0.494
	Silicon (wt %)	1.055
	Chromium (wt %)	1.006
	Nickel (wt %)	0.682
	Molybdenum (wt %)	1.374
	Titanium (wt %)	0.482
	Vanadium (wt %)	0.494
Fuel Elements	Na (wt %)	0.947
	K (wt %)	0.652
	Mg (wt %)	0.482
	Ca (wt %)	0.862
	Al (wt %)	0.600
	Fe (wt %)	0.630
	Si (wt %)	0.524
	Cl (wt %)	2.424
	S (wt %)	1.539
	Ti (wt %)	0.506

4.3.1.3 Summary of Results: PCA/PLS Models (Data Subset 1)

Table 4-11 shows the standardised regression estimates obtained from PCA and PLS (extracted from Table 4-2 and Table 4-3). It should be noted that Nb (alloy element), although present in the data subset, was excluded from PCA (and PLS) analysis for reasons outlined in section 4.1.1.

The analysis from PLS highlights 10 out of 23 variables for model building compared to 20 from PCA. The variables nominated from both techniques (PCA, PLS) are similar in their association with the *ln* corrosion rate, notably the inverse metal temperature, the temperature difference (T_g-T_m), Cr (alloy), S (fuel) and Cl (fuel). Note that these variables are also statistically significant, as shown in the correlation matrix in Table 4-4.

Table 4-11: Standardised regression coefficients for the predictor variables in data subset 1 derived from PCA and PLS (shaded cells indicate predictor variables not selected for model building; the fuel elements are in symbols, alloy elements are written in full)

	VARIABLES	PCA Model 1A	PLS Model 1B
	1000/Metal Temp (1000 / K)	-0.20	-0.30
	(Tg-Tm) (K)	0.095	0.12
Alloy Elements	Carbon (wt %)	-0.087	-0.099
	Manganese (wt %)	-0.0086	
	Phosphorus (wt %)	0.0086	
	Sulphur (wt %)	0.0086	
	Silicon (wt %)	-0.093	-0.074
	Chromium (wt %)	-0.048	-0.059
	Nickel (wt %)	-0.017	
	Molybdenum (wt %)	0.12	0.061
	Titanium (wt %)	-0.068	
	Vanadium (wt %)	0.0086	
Fuel Elements	Na (wt %)	0.12	0.065
	K (wt %)	0.041	
	Mg (wt %)		
	Ca (wt %)		-0.13
	Al (wt %)	0.022	
	Fe (wt %)	0.084	
	Si (wt %)	0.021	
	Cl (wt %)	0.29	0.42
	S (wt %)	-0.23	-0.10
	Ti (wt %)	0.044	

4.3.2 Discussion on PCA Coal Model 1A and PLS Coal Model 1B Results

Influence of alloy compositions on the fireside (ln) corrosion rate: The chemical composition of the alloys is important with respect to fireside corrosion for determining the presence of a protective and stable oxide scale. In this regard, the discussion on the alloy elements nominated for model building will be centred on their role in producing effective resistant oxide scales or in impeding the formation of one, or of having no effect. Reviewing the alloying parameters selected for PCA/PLS model building and their possible influence on the fireside corrosion rate; C, Cr, Si and, to a smaller extent, for PCA only, Ni and Ti, shows negative correlation with the corrosion rate implying an enhanced corrosion resistance with an increase in these alloying elements. Mo is positively correlated with the corrosion rate suggesting that it could be detrimental in coal ash environments under the range of combustion conditions considered, possibly due to its increased volatility (Patel *et al.*, 2013). As detailed in the literature from Weele (1991), it is also possible that Mo may flux into the molten sulphate and thus

increase its acidity which could enhance corrosion as deposit more aggressive. The inclusion in the predictive models of alloy elements P, S and V by PCA even with small (positive) associations with the corrosion rate is noted but not statistically significant (see full correlation table in Appendix B for data subset 1; i.e. Table B-1). The main alloying effect of V is to stabilise carbides and also reduce creep ductility (Sourmail, 2004; Higgins, 2006). On the other hand, high levels of S and P can induce brittleness in steels (Higgins, 2006). However, with fireside corrosion resistance being the main objective, the impact of these elements may be deliberated based on the extent of their association with the fireside corrosion rate, and of note is their exclusion from the PLS model (as they show negligible significance). The retention of these input alloy elements in the PCA model may likely be indicative of their potential impact, which depending on the exact levels available, may increase the susceptibility of boiler tube materials to fireside corrosion. This is an important consideration, as the levels of the alloying elements could be beneficial or detrimental. Mo is a good example, as levels between 2 and 4 wt % is considered ideal for improving corrosion resistance (Schade *et al.*, 2008) while S and P levels in steel grades are usually maintained below 0.05 wt %. V is usually used in very small quantities to stabilise carbides in steel materials thus the potential volatility of VO₂ carries little concern in alloys' oxidation responses (Lai, 2007). In this regard, the corrosion dataset may largely contain industrially relevant alloys which are pre-selected to have alloying levels confined to a degree that they do not cause significant fireside corrosion problems.

Influence of fuel variables on the fireside (ln) corrosion rate: Assessing the nominated fuel variables, there is a clear indication that Cl has a controlling influence on the corrosion rate, followed by S albeit in the opposite direction. The explanation for the negative correlation of the corrosion rate with S is linked to observations in the literature (Wright and Krause, 1997b) which attributes the negative correlation to the excess levels present in UK coals (Figure 4-3). For this reason, S appears not to have a controlling influence on fireside corrosion rates although it is required for the corrosion mechanism to proceed.

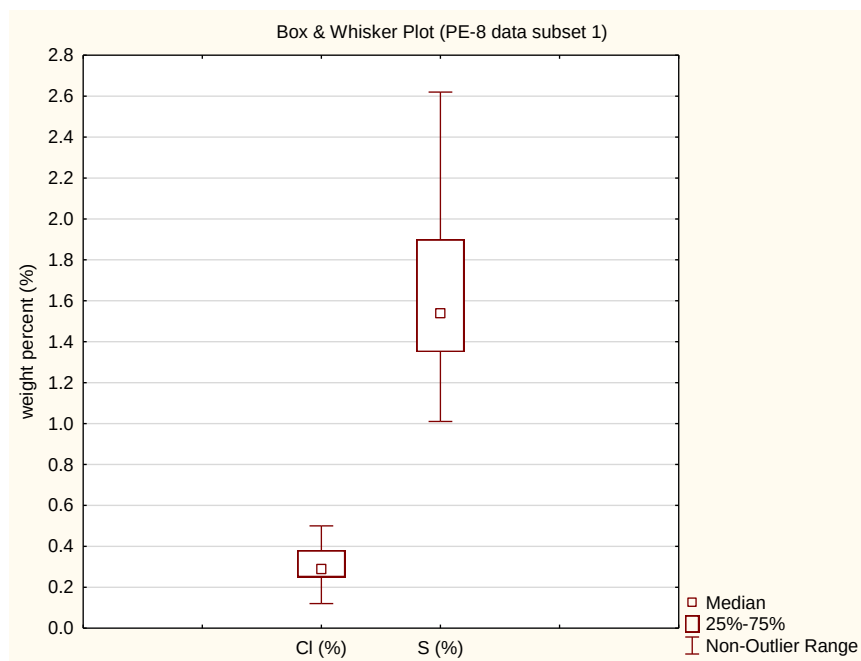


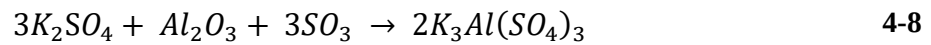
Figure 4-3: Box and whisker plot showing the median, range and 25th-75th percentile for the Cl and S content (in the fuel) from data subset 1

Focusing on the alkali metals, PCA nominated Na and K for model building; while the PLS selection excludes K. The alkali metals are active in the corrosion mechanism but their levels in the coal and thus availability to take part in gas phase reactions are equally important. Other corrosion studies showed that the average percentage of Na released to the combustion gas (following bomb combustion studies) and thus available to participate in the reaction was approximately 21% (wt %) compared to 12% for K despite there being higher levels of K in the coal (Wright and Krause, 1997b). It is also established in the literature that K occurs primarily within micaceous mineral matter in UK coals and so is not readily released during combustion (Wright *et al.*, 1997). Hence it appears in this scenario that K plays a limited role in the corrosion process, possibly due to the fact that a major portion of it may be tied to the clay mineral.

The alkaline earth metals were not included for consideration in model building in PCA, but PLS, however, included Ca. The correlation matrix (Table B-1 in Appendix B) reveals that the correlation between the corrosion rate and Ca is statistically significant; hence its inclusion by PLS is justified. The alkaline earth compounds generally have

higher melting temperatures than alkali metal compounds. As such, and under the conditions represented in this data subset; the presence of Ca is not detrimental to the tube operating life.

The other fuel elements nominated by PCA; i.e. Al, Fe, Si and Ti, have negligible association with the corrosion rate (Figure 4-2) but are also not statistically significant as indicated in Table B-1 (Appendix B). These elements are not generally thermodynamically stable in the gas phase under the prevailing flue gas temperatures in coal combustion and thus occur mainly as solids (Wright and Krause, 1997b). However, they are capable, under the right conditions, of reacting with other species to form deposits that may induce corrosive attack. In a very high-temperature combustion environment, Al_2O_3 (from the coal ash) may react with alkali sulphates in the deposit and SO_3 in the gas to form alkali Al trisulphates (equation 4-8) with a melting point of 654 °C (Lutz *et al.*, 2015).



Fe, in the form FeS_2 , can be reduced to FeS, FeO or metallic Fe with lower melting temperatures and can form deposits or react with SO_x in the gas resulting in the formation of a lower melting /eutectic temperature deposit (Laumb, 2008; Lutz *et al.*, 2015). Regarding the corrosive potential of Si, it has been suggested in the literature that Si from SiO_2 can form lower melting species that can be deposited on the superheater and reheaters (more so than Al_2O_3) (Lai, 2007b). However, Wright and Kung (2018) contend that complex compounds with SiO_2 and Al_2O_3 hardly exist for the alkali species and the alkali metals in coal are more inclined to react with S to form low melting sulphates that can interact with other low-melting compounds in the coal deposit. Thus the inclusion of Al, Si and Ti as important predictor variables from PCA is arguable given the negligible association with the corrosion rate, but not dismissed because high levels of Al, Fe, or Si in the entrained ash could indicate a propensity to form a molten phase complex.

The fuel element, Ti, was nominated for model building in PCA coal model 1A. Titanium (from the fuel) was also retained in corrosion models 2A (PCA) and 2B (PLS), model 3A, models 4A and 4B, models 5A and 5B, models 6A, and model 7A,

suggesting a pattern that is hard to ignore (see section 4.3.3; also Table 4-2 and Table 4-3). There is a chance Ti may be indicative of the presence of some other fuel component which could be potentially corrosive. This was initially looked in to by examining the loadings plot from PCA depicted in Figure 4-4.

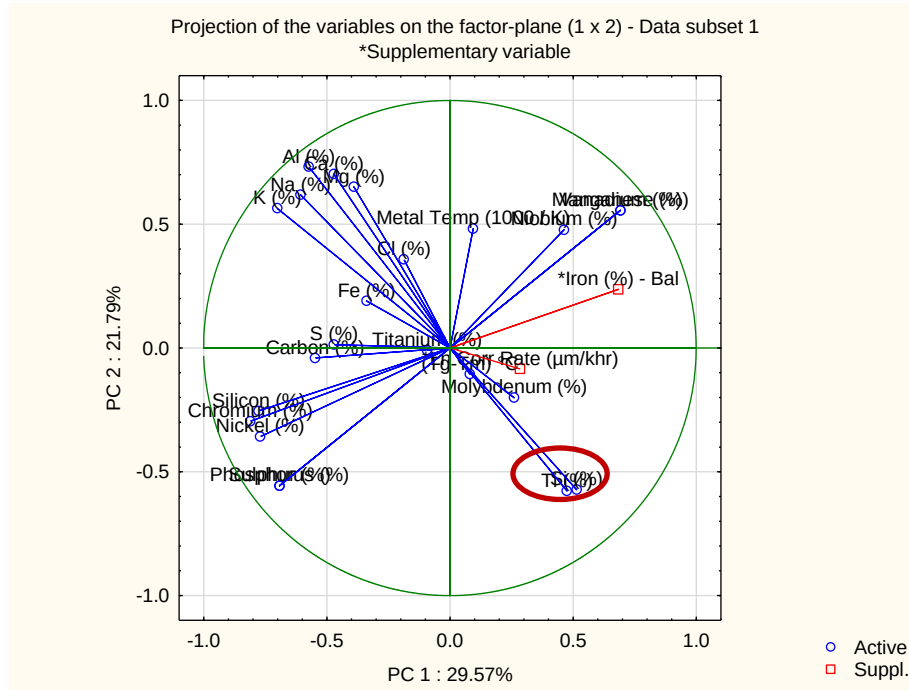


Figure 4-4: PCA loadings plot (PC 1 vs PC 2) for data subset 1 showing the PC-variable relationship and the correlation between the predictor variables (fuel elements are in symbols and the alloy elements in full; circled region indicates fuel elements Ti and Si)

The loadings plot shows the relationship between the PCs and the input variables. Input variables that span a longer length load highly on the PCs and represent the largest source of variability in the data. In Figure 4-4, Ti and Si load highly on the first two PCs hence only the plot between PC 1 and PC 2 is displayed (this is different from the varimax rotated plots which are reserved for variable selection). Two (or more) components are positively (and highly) correlated if they appear in the same quadrant, e.g. Si and Ti (the circled region in Figure 4-4), and negatively correlated if they are in diametric positions. For the former case, the closely positioned variables behave in the same manner and if a regression analysis is to be done, one of the highly correlated variables can be substituted for the other. Whether the presence of one is indicative of the other is at best hypothetical without further studies. However, the loadings plot for

the PE-8 dataset in general (i.e. subsets 2, 3 and 4) shows a similar pattern (i.e. proximity of Ti and Si). There is also a chance that the selection of Ti is purely statistical because the output from PLS analysis excluded Ti from consideration in models 1, 3, 6 and 7, hence eschewing the selection of ‘spurious’ variables prevalent in PCA. It has not been established if Ti directly contributes to the formation of low melting eutectics, as there has been no indication in the literature and from previous field investigations. However, Watt (1969) citing a previous study considered the possibility of formation of other volatile suboxides and inferred that under suitable conditions, TiO, as well as AlO, BO, VO etc., might all exist in amounts sufficient to play an important role in the failure of refractories and the chemistry of slags.

In summary, the only fuel species revealed to be correlated with the corrosion rate corresponding to results from the PLS models are Cl and Na. The impact on the corrosion rate is likely due to the variable concentration of chloride species at the temperature range of interest which assists in the formation of corrosive molten alkali iron trisulphate in coal combustion. At gas temperatures below 1000 °C, the only alkali bearing species present in significant quantities is Cl (Rosendahl, 2013). On the other hand, alkali sulphates form at much higher gas temperatures (> 1100 °C) (Broström *et al.*, 2013). Thus, the mechanism could be controlled by chloride species before stable alkali sulphates are formed.

The next subsection will review the results for the other coal models (models 2-9).

4.3.3 Discussion on PCA/PLS Coal Corrosion Models 2-9

Model 2 is derived from the data subset for austenitic tube materials in the non-leading position (UK coals). PCA and PLS were done on a standardised 28×23 matrix, and the resulting correlation matrix is detailed in the appendix (Appendix B, Table B-2). The initial results from PCA with this data subset was poor and also knocked out metal temperature and thus would not conform to the Arrhenius form. Hence the PC selection criteria had to be adjusted to eigenvalues > 0.2 to improve the result (as opposed to > 0.5). Using PLS, there was more user freedom in the algorithm to build the regression model. The results for PCA /PLS shows that the inverse metal temperature (1000/K) is the input parameter with the highest influence on the corrosion rate (Table 4-2 and

Table 4-3), followed by the temperature difference ($T_g - T_m$, K). There is some variation in the selection of alloy components from PCA and PLS; the common input alloy elements highlighted from both were C, Cr, Ni and Mo. On the fuel side, Cl comes up as an important predictor variable for model building with varying directions for PCA and PLS (with respect to the $\ln$ corrosion rate; positive for PLS model 2B). The results show the alkali metals have a negative association with the corrosion rate and the more potentially damaging influence of fuel elements have been attributed to Al, Fe, Cl (PLS only), Ti, and, for the PCA model, the alkaline earth metals. This presents a relatively tame combustion atmosphere compared to model 1 (discussed in section 4.3.2) as the non-leading positioned superheater and reheaters will be impacted by the aggressive onslaught of ash deposits to a lesser degree than the leading tubes which are more accessible to condensing vapours. As discussed in section 4.3.2, the participation of Ti in the formation of molten complex specific to fireside corrosion is not evident from past investigations, but its selection warrants further investigation.

Models 3 and 4: The analysis of the data subset associated with ferritic tubes (data subsets 3 and 4) posed a challenge. The composition of the variables was too similar (mainly on the alloy side) and thus many were *almost* perfectly correlated (see Appendix B, Table B-3 and Table B-4). The set criteria for variable selection had to be adjusted numerous times to devise a model that had a close fit to the data. The (inverse of) metal temperature was included for model building and was projected as the most influential input parameter in the corrosion models 3 and 4. The positive coefficient of the alkali metals, Fe, Si and S in models 3A (PCA) and 3B (PLS) suggests an increase in the corrosion rate with these fuel elements. None of the alloy components were nominated for model building in PCA model 4A (Table 4-2) and PLS models 3B and 4B (Table 4-3). The loadings plot from PCA revealed the problems with the structure of both data subsets. As an example, Figure 4-5 shows the loadings plot for data subset 3. Assessing the plot, it is apparent that the alloy elements are clustered and loads highly on PC 1. The analysis from PLS suggests, however, that these clustered variables; i.e. the alloy elements, are not needed to explain the variation in the corrosion rate and thus were all excluded from PLS model building. PCA focuses on the variation in the input data only, which might explain the selection of these alloys. Notably, alloy elements, Cr and Mo, included in PCA model 3 correlates positively with the corrosion rate

suggesting insufficient protection from fireside corrosion. Due to the poor performance of models 3 and 4, other model equation formats were attempted (i.e. framework models C and D; equations 4-4 and 4-5) but the model performance was not improved. It is very likely that additional data involving other ferritic alloys may improve the prediction model for data subsets 3 and 4.

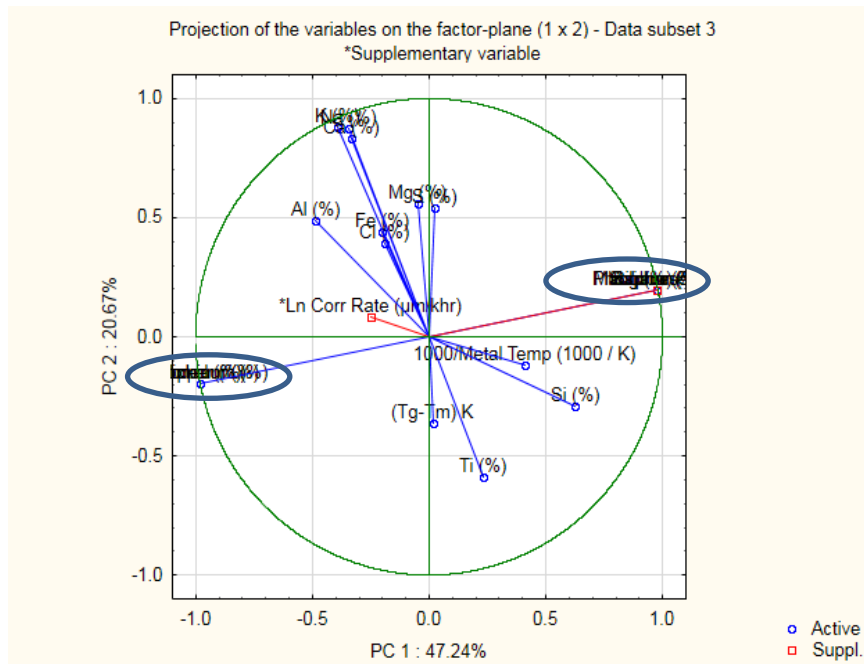


Figure 4-5: PCA loadings plot (PC 1 vs PC 2) for data subset 3 showing the PC-variable correlation and the relationship between the predictor variables (circled portion shows the highly correlated alloy elements)

Models 5-7 are coal models based on US (coal) data. Model 5 is for the data subset with austenitic alloys, model 6 is for nickel-based alloys, and model 7 is the coatings data. The data subset is a combination of subcritical and ultra-supercritical (USC) conditions with metal temperatures up to 800 °C. The combustion environment is different from the UK environment. The correlation matrix (displayed in Appendix B, Tables B-5, B-6 and B-7) shows interesting features, notably the positive correlation of *ln* corrosion with the metal temperature (data subsets 5 and 7), which, because it is input in the inverse (i.e. 1000/K), implies an opposite correlation with the corrosion rate. There are varying correlations on the corrosion rate with the fuel elements for all three US data subsets. The PCA and PLS US coal models bear some similarities in terms of the variables selected (see Table 4-2 and Table 4-3).

Although the analysis from PLS model 5B excluded all the alloy components except Mo, PCA model 5A highlighted alloy elements Mn, P, S, Si, Cr, Ni, Nb, Ti, Cu, N, Ce and Ta. All the fuel elements except Al were selected and added to the PCA and PLS models. In a similar fashion to the UK coal data subset 1, S was nominated for PCA/PLS model building but acted in the negative direction. It appears the S levels, as represented in this data subset were always sufficient to form a low melting complex and hence this fuel specie was not considered a rate controlling influence. For the PLS model 5B, however, the association of S and Cl with the corrosion rate was very sensitive to the number of PLS components retained for model building (Table 4-12) but was stable for the other predictor variables. Selecting four PLS components (which explained 84% variation in *Y*, the *ln* corrosion rate) produced a better fit to the data (data subset 5) than just two PLS components (which explained 77% variation in *Y*, the *ln* corrosion rate). A consistent feature in the PLS model was that the association of both fuel elements, S and Cl, with the *ln* corrosion rate acted in opposite directions (Table 4-12) while the other predictor variables remained constant (i.e. in the same direction).

Table 4-12: Standardised regression coefficients of Cl and S (fuel) depending on the number of PLS components selected for analysis (PLS model 5B)

Number of PLS Component Selected	Regression Coefficient (Cl)	Regression Coefficient (S)
2 PLS Components	-0.0097	0.12
4 PLS Components	0.20	-0.0068

On the influence of the fuel elements for data subset 5, the alkali metals (Na, K) as well as Mg, Ca, Fe, Cl, and Si selected showed a positive correlation with the corrosion rate, implying a potentially aggressive combustion environment (only if they are present) as it appears these elements influences the corrosion rate.

The influence of the inverse of metal temperature in data subset 5 (austenitic tube materials, US coal) and 7 (coatings, US coal), has steadily remained in the positive

direction relative to the *ln* corrosion rate in both the PCA and PLS models. It is possible that the range of fireside metal temperature from all three US data subsets lies at two extremes (see Table 3-19). This might explain the positive association of the Cr alloy element with the corrosion rate for PCA model 5A (PLS model 5B excludes Cr), suggesting the Cr content may not be as effective in forming protective oxide scales in these conditions.

PCA model 6A and PLS model 6B (Ni-based alloys, US coal), however, yielded poor predictions. There are two deductions from this outcome. First is that the variation in *Y* (*ln* corrosion rate) explained by the input data, *X*, has always consistently remained at or below 40% (PLS analysis, Figure 4-6). This phenomenon clearly showed that only about 42% of the variance in *Y* can be explained by 100% of the variation in the *X* data, hence the R^2 (coefficient of determination) value for this model has consistently been low. It appears that more data may be needed to improve this model.

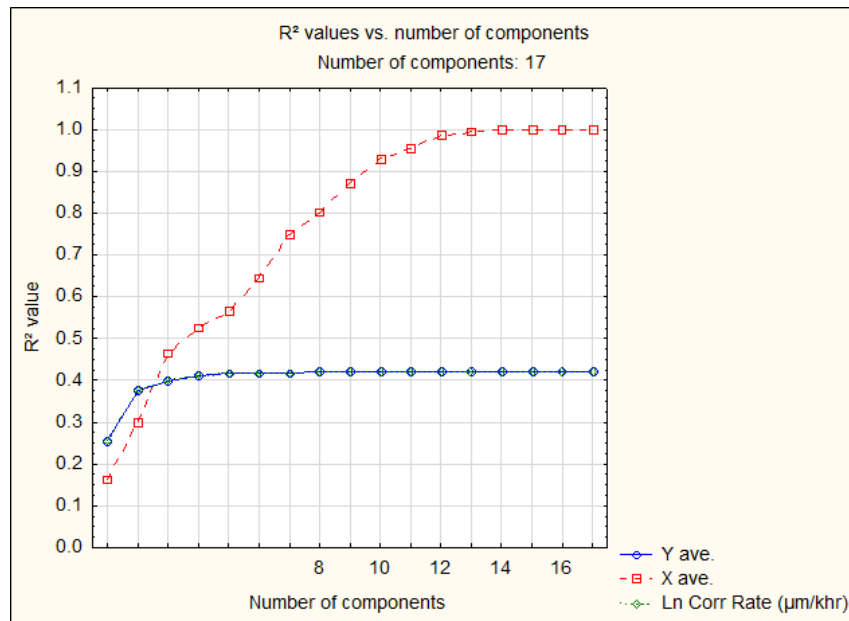


Figure 4-6: Average R^2 values of *Y*, the corrosion rate (blue) and *X*, input data (red) plotted against the number of PLS components (PLS model 6B)

The second observation is on the structure of the data subset. The corrosion rate measurements for this data subset had almost similar (low) values regardless of increasing temperatures (600 °C to 750 °C), except for two extremely high rates at 714 °C and 737 °C for the alloy HR6W (Figure 4-7). It is possible the lower temperature

region of the bell-shaped curve association may not be the ideal model format for this data subset, possibly because the extreme data points may be due to the occurrence of parallel (corrosion inducing) reactions with different dependencies on temperature.

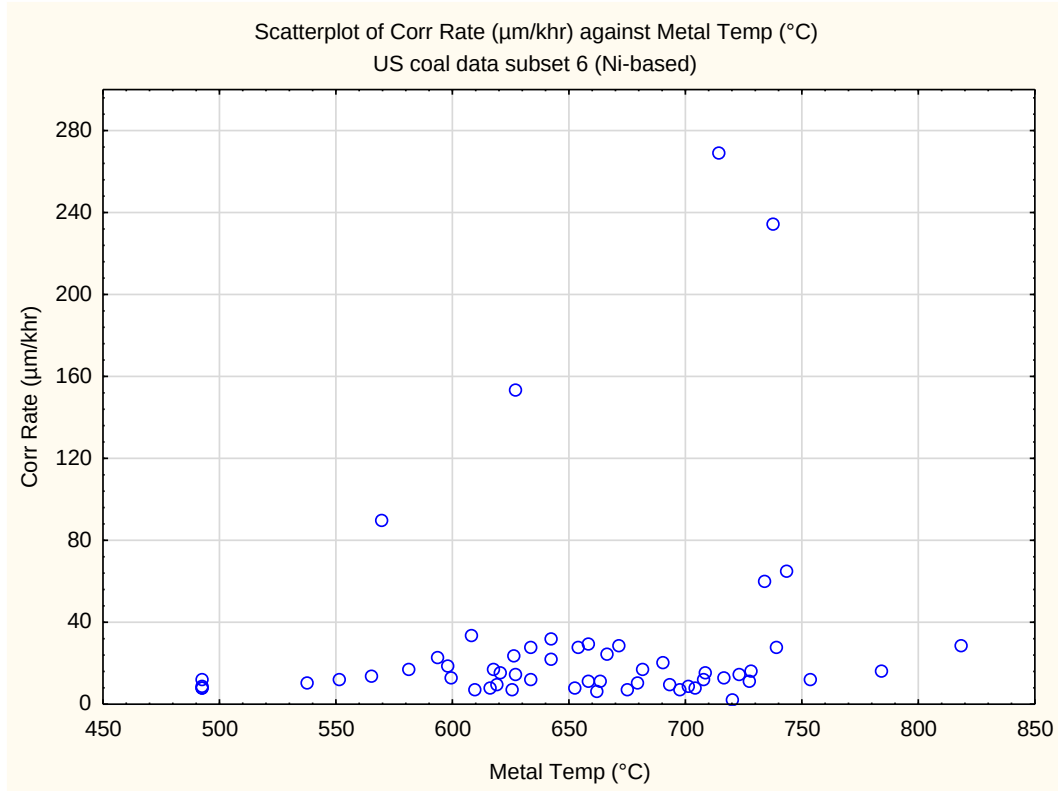


Figure 4-7: Plot of corrosion rates measured against metal temperature, US coal data subset 6.

Models 8 and 9 were derived from world-traded coal data for austenitic alloys and coatings respectively. The coal parameters were averaged over the plant life and could not be used in the statistical analysis as there was no variation in the data. Hence only the alloy components were analysed. The results show the influence of increased metal temperatures in both cases. The most influential, but least protective alloy variables in model 8 that were considered rate controlling were P and S, followed by Mo (Table 4-2 and Table 4-3). By contrast, the elements Si, Ti, V, Cr, Ni, N, Al and B (the last five were highlighted by PLS only) are negatively correlated with the $\ln$ corrosion rate implying a more resistant or beneficial impact under the range of operating conditions studied.

The most influential predictor variable highlighted in PCA model 9A (coatings data) was the coating element (Nb + Ta), while PLS model 9B presented the inverse of metal temperature as the most influential variable and on the alloy side, only Si was included for PLS model building (negative correlation with *ln* corrosion rate). Beyond highlighting important variables from the coating composition that may influence the corrosion rate, further speculation on the performance of the coatings material, which largely depends on the coating composition, method of application and the exposure location (Epelbaum *et al.*, 2010), is outside the scope of this study.

4.4 Biomass Models (Corrosion Models 10-13)

The correlation matrix for data subset 10 (mainly woody biomass) is shown in Table 4-13. A significant relationship exists between the *ln* corrosion rate and the inverse of metal temperature, Cr (alloy), and fuel elements K, and S. Although Cl is positively associated with the corrosion rate, the correlations are not significant.

Table 4-13: Correlation matrix for selected variables in data subset 10 (red text indicates significant correlation judged from reliability index i.e. $p < 0.05$; elements in symbols are the fuel elements)

Variable	1000/Metal Temp (1000 / K)	Chromium (wt %)	Na (wt %)	K (wt %)	Cl (wt %)	S (wt %)	Ln Corr Rate ($\mu\text{m}/\text{hr}$)
1000/Metal Temp (1000 / K)	1.000	-0.063	0.658	0.758	0.707	-0.102	0.303
Chromium (wt %)	-0.063	1.000	0.160	0.116	0.133	0.077	-0.298
Na (wt %)	0.658	0.160	1.000	0.343	0.988	0.529	-0.015
K (wt %)	0.758	0.116	0.343	1.000	0.434	-0.592	0.366
Cl (wt %)	0.707	0.133	0.988	0.434	1.000	0.423	0.110
S (wt %)	-0.102	0.077	0.529	-0.592	0.423	1.000	-0.398
Ln Corr Rate ($\mu\text{m}/\text{hr}$)	0.303	-0.298	-0.015	0.366	0.110	-0.398	1.000

A comparison of the PCA and PLS results shows major differences in the predictor variables selected for model building and in the direction of association with the *ln* corrosion rate. Although the input fuel variable, Cl, was nominated for the PCA model 10A, the exclusion of Cl from PLS model 10B is not unexpected given its low concentration averaging 0.03 wt (%) from the source data (Uniper Technologies, 2016a). In general, wood-derived fuels show lower values of ash, Cl, K, N, S and Si,

and higher concentrations of C and Ca compared to other biomass varieties (Vassilev *et al.*, 2009). The biomass species in this data subset were predominantly wood pellets, which are considered a benign fuel with respect to fireside corrosion (E.ON Technologies, 2015b).

Although the fuel S content is low in this data subset compared to the coal data, S was selected for model building and correlates in the negative direction with the $\ln$ corrosion rate, underscoring its suppressive effect on the more damaging chlorides. Potassium was included for model building in PCA and PLS analysis suggesting its susceptibility in promoting the corrosion rate. Potassium is highly volatile in biomass fuels (Vassilev *et al.*, 2009), forming KCl in the combustion gas. High levels of KCl in the gas phase enhances the formation of deposits that can lead to the corrosion of SH/RH tubes in a biomass-fired environment (Antunes and de Oliveira, 2013). The inclusion of K in the corrosion model aligns with findings from the plant investigation that indicated a deposit consisting mainly of solid K_2SO_4 (Uniper Technologies, 2016c) which, as alluded earlier, suggests a benign environment. In addition to K, the PCA model (10A) includes Na, Ca, Al, Si, Ti and Ba as potentially corrosive and thus capable of promoting the formation of complex deposits that could impact boiler tube materials. However, except for K and Ca, the PLS model excludes these fuel variables. The selection of Ca suggests the possibility of forming low melting phases with other coal minerals, as Ca sulphates are also present in the condensed phase in most biomass-fired systems (Antunes and de Oliveira, 2013). The corrosion environment can be characterised as induced by Cl with deposits consisting of mainly alkali and alkaline earth metals (primarily Ca). The addition of P for model building supports test conclusions from the fireside corrosion investigation by Uniper Technologies (2016a), that a thin layer rich in P was deposited on top of the outer corrosion scale layer on many test coupons. However, P was not implicated in the corrosion process, and this is backed up by the results, which show a negative association with the corrosion rate for the PCA and PLS models.

Input parameters in models 10 and 11 that behave counter-intuitively are the inverse of metal temperature ($1000/K$) and the temperature gradient ($T_g - T_m$, K), as the results suggest these predictor variables do not necessarily increase the corrosion rate although

both were selected for model building. One possible explanation for this could be that the corrosion reactions may be enhanced at lower temperatures and gradually diminished at higher temperatures (Uniper Technologies, 2016a), hence increased metal temperature may have the opposite effect especially when alkali sulphates replaces the more corrosive chlorides (the opposite side of the bell curve). Concluding remarks from the original authors of the source data corroborates this trend with respect to the metal temperature (E.ON Technologies, 2015b, 2015a; Uniper Technologies, 2016a). The authors inferred that, as deposition of the alkali chloride (via a condensation mechanism) was driven by the temperature difference between the gas and the tube surface, the coolest surface will attract a greater flux or deposition rate of alkali chloride. However, with increasing metal temperature, the proportion of chloride in the deposited ash is decreased, being replaced with the less damaging sulphate (E.ON Technologies, 2015b). Another observation regarding the effect of temperature was remarked by Antunes and de Oliveira (2013) in their study of corrosion in biomass boilers. The authors concur that severe corrosion occurs when the fuel chemistry is characterised by high Cl, low S, and moderate amounts of Na and K, however, the extent of condensed alkali metals is chiefly influenced by the flue gas temperature (T_g) and remains unchanged with an increase in tube wall temperature.

For the *PCA and PLS models 11* (Ni-based alloys, biomass data), the important alloy elements included P, S, Si, Nb, Ti, Co, and N. Taking into consideration the results from PLS model 11B, only P, Nb and Co were nominated and these acted in the opposite direction to the $\ln$ corrosion rate; while Fe was positively associated with the $\ln$ corrosion rate. Niobium is a refractory metal (Johannesen and Anderson, 1989) which enhances oxidation resistance and promotes strength for high-temperature utilisation of the alloys (The European Stainless Steel Development Association, 2000; Maalekian, 2007). The most creep resistant steels contain Co as well as N, Cu, Cr, Ni and W. With regards to Fe selection (PLS model 11B), in an oxidising environment, Fe diffusion is much faster in magnetite (Fe_3O_4) and haematite (Fe_2O_3) hence likely to form oxides that can participate in the corrosion reaction (Johannesen and Anderson, 1989). Ultimately, it is the mobile species that determine the corrosion behaviour of the alloy (Johannesen and Anderson, 1989). On the fuel side, all the fuel elements nominated were deemed

potentially corrosive except Ti and Mn. Sulphur was not included for model building, although the result suggests Cl enhances the corrosion rate.

Following results from the analysis of biomass data subset 12 (ferritic tube materials), important variables positively correlated with the $\ln$ corrosion rate include the inverse of metal temperature, the temperature difference ($T_g - T_m$, K), and Si (alloy). The fuel elements are considered benign in this study with similar outcomes from both PCA and PLS models. PCA and PLS models nominated K, P and Mn for the model building but with a negative correlation with respect to the $\ln$ corrosion rate. It is possible that, because the metal temperature range in this data subset falls on the lower band of values compared to the other data subsets (Figure 4-8), the temperature is not sufficiently high to induce deposit melting thus the deposits may predominantly remain as solid phases, and this means slower reaction rates.

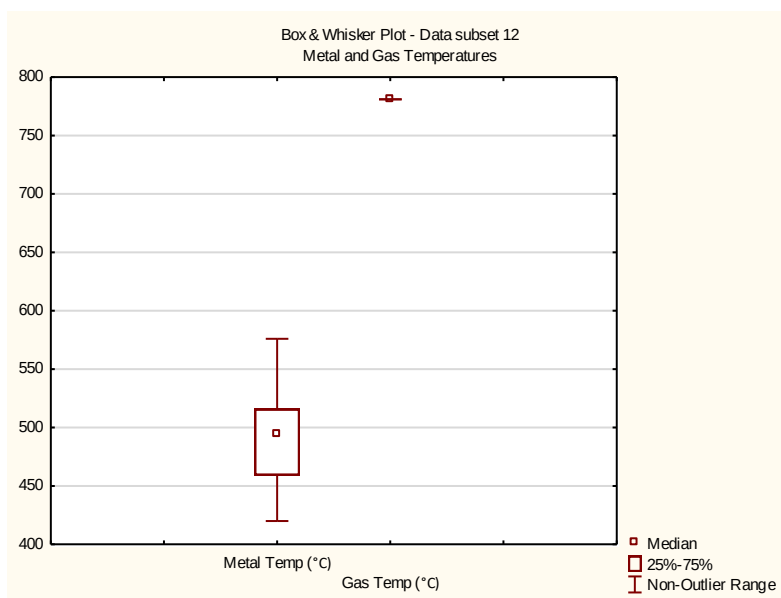


Figure 4-8: Box and whisker plot showing the median, range and 25th-75th percentile of data for metal and gas temperatures (in degrees C) for biomass data subset 12

The normally protective alloy element levels in ferritic tube materials are too low to ascribe any significance to their impact; hence notably Cr is excluded from PLS model 12B. The results (Table 4-2 and Table 4-3) suggests Si (alloy element) does not form stable oxides in this combustion environment but Ni, if present at all in ferritic tube alloys, albeit in small amounts, may improve the corrosion resistance.

Model 13 represents coating data in biomass-fired systems. The influential variables nominated for the PCA model include the inverse of metal temperature, and for the coating materials, C, Mn, P, S, Si, Cr, Ni, Mo, Nb, Ti, V, Cu, N, Co, O and Fe. Sulphur from the fuel was highlighted as the most influential variable in this data subset (Table 4-2). PLS model 13B nominated fewer and slightly different alloying elements (Si, Ni, Ti, V, Cu, Co and O) (Table 4-3) but similar fuel variables compared to the PCA model (Table 4-2).

4.5 Co-firing Models (Corrosion Models 14-16)

Data subsets 14-16 were amongst the smallest, with only 12 data points for data subset 14, 9 data points for data subset 15, and 23 data points for data subset 16; comprising two austenitic materials (TP316 and HR3C) for data subsets 14 and 15, and one ferritic material (T22) for data subset 16. The source data provided no information on the gas temperature; hence this parameter was omitted. The correlation matrix in Table 4-14 shows a significant relationship between the *ln* corrosion rate and the fuel elements Na, K and Cl.

Observations from the correlation matrix (Table 4-14, for data subset 14) show that the inverse of metal temperature is not significant, and this was evident during model building as the inverse of metal temperature was initially excluded but was forced in the stepwise regression step in PCA so it aligns with the Arrhenius model structure. For the same reason, the VIP selection criteria in PLS analysis had to be adjusted to 0.3 to include the inverse of metal temperature. It is interesting to note that this adjustment to include metal temperature did not significantly improve or alter the model performance (judged by the R^2 value; see also PLS framework model A result in Appendix D; i.e. Table D-4, and Table E-2 and Table E-4 in Appendix E).

Table 4-14: Correlation matrix for selected variables in data subset 14 (red text indicates significant correlation judged from reliability index i.e. $p < 0.05$; elements in symbols are the fuel elements)

Variable	1000/Metal Temp (1000 / K)	Chromium (wt %)	Na (wt %)	K (wt %)	Cl (wt %)	S (wt %)	Ln Corr Rate ($\mu\text{m}/\text{hr}$)
1000/Metal Temp (1000 / K)	1.000	0.361	-0.527	0.196	0.494	0.641	0.195
Chromium (wt %)	0.361	1.000	-0.485	0.195	0.457	0.577	0.232
Na (wt %)	-0.527	-0.485	1.000	-0.794	-0.996	-0.846	-0.788
K (wt %)	0.196	0.195	-0.794	1.000	0.843	0.349	0.944
Cl (wt %)	0.494	0.457	-0.996	0.843	1.000	0.798	0.830
S (wt %)	0.641	0.577	-0.846	0.349	0.798	1.000	0.388
Ln Corr Rate ($\mu\text{m}/\text{hr}$)	0.195	0.232	-0.788	0.944	0.830	0.388	1.000

The species nominated from the fuel elements (as contaminants) include K, P, Mg, Cl and S. Considering the fuel blend (i.e. coal/wood, coal/CCP); these selections (the fuel elements) were expected. There was a positive correlation between the (*ln*) corrosion rate and the alloy elements C, Si, Cr, and Ni. On evaluation of the original data subset, it was apparent from a statistical viewpoint that higher corrosion rates were observed with increasing amounts of the alloying elements C, Si, Cr, and Ni (mainly from HR3C). However, more data is needed to generate a viable model.

Data subset 15 is an excerpt of data subset 14 that excludes the HR3C alloy as it appeared from the initial analysis that the alloy elements do not correlate significantly with the *ln* corrosion rate (unless the inverse of metal temperature is forced in the model and thus the selection criteria results in the selection of the alloy elements). For this reason, the data analysed in this subset does not include the chemical composition of TP316, as it is the only austenitic alloy present and so there is no variation. The fuel variables selected for model building matches the selection in data subset 14. However, metal temperature (1000/K) appears to act in the opposite direction suggesting the fuel elements (mainly K, Mg, Cl, S and P) pose a significant risk in a co-fired environment.

Data subset 16 contains one ferritic alloy (T22); thus, the alloy composition was excluded from the analysis as there was no variation. The inverse of metal temperature is the only input parameter nominated for model building for the PCA and PLS models. This selection has been consistent for all the ferritic data analysed (i.e. models 3, 4 and

12; see Table 4-2 and Table 4-3) implying that the metal temperature is the most influential parameter for combustion systems employing ferritic materials regardless of the fuel type, as there are insufficient corrosion-resistant alloy elements available (mainly Cr) to form protective oxides. As with data subsets 14 and 15, more co-firing corrosion data is needed to reach a definite conclusion on the impact of the fuel elements and alloying elements in co-firing conditions.

4.6 Summary of PCA, PLS Fireside Corrosion Models

This approach to modelling uses statistical data analysis techniques (PCA, PLS) to reduce the dimensionality of large datasets and maximise variability of the data to produce fireside corrosion prediction models. This study underscores the importance of the alloying compositions such as the Cr content for the formation of resistant oxide scales, and the fuel species; such as the alkali metals, alkaline earth metals and other fuel-derived elements, which will react to form the deposits required for fireside corrosion. The crucial input parameters subsequently used for model building are unique to the combustion environment studied. The UK coal corrosion models for the leading position of SH and RH tubes are dependent mainly on the boiler operating conditions (metal temperature, temperature difference), the alloy contents, Cr and Mo, and the fuel's alkali levels, Cl and S. There are slightly different input parameters for the UK coal corrosion models for the non-leading position of the SH/RH tubes. On the other hand, the US coal models rely mostly on the fuel elements with PCA and PLS showing variation as to the important alloy parameters. The biomass corrosion models have highlighted K and Ca as rate controlling parameters more so than the operating conditions; except for the models derived from the ferritic and coating data, where the corrosion rate is impacted more by the metal temperature under biomass-firing. The PCA/PLS derived corrosion models from co-firing data (austenitic alloys) suggest an aggressive combustion environment dependent on the fuel content. A notable exception is the co-firing data under ferritic materials where the corrosion rate is solely dependent on the metal temperature.

There has been considerable success in the use of statistical techniques (PCA and PLS) to build corrosion models to predict the degree of fireside corrosion for different combustion conditions, tube materials, tube positions, and fuel types. The different

framework models employed have ultimately produced consistent results with respect to the key variables selected for model building (presented in Appendices C and D). The predictor variables retained in the models are in line with conclusions from previous investigations, for instance; Cl has a rate controlling influence particularly for UK coals, but different results were observed for US coals.

With respect to the techniques, PLS on average produced good predictive models and with fewer variables compared to PCA. The analysis from PCA tends to incorporate more variables even for those with smaller magnitudes, as noted on the bar chart in Figure 4 3. However, those variables of less significance, retained in PCA models, were in most cases excluded from PLS models, and in effect (for PCA) it increases the chances of overfitting the data.

More details on the modelling approach including guidance on the steps devised to build the corrosion models are outlined in Appendix G.

5 VARIATION IN CORROSION MODEL BUILDING

This chapter examines different variations of the corrosion model including a data sensitivity analysis. Section 5.1 presents the results for a different framework model with a change in the expression of the metal temperature. Section 5.2 presents the results of a re-analysis based on combined variables from the loadings plot (PCA) and a discussion on the model results. Section 5.3 analyses PCA and PLS models with interaction terms included as input parameters. Section 5.4 focuses on sensitivity analysis to assess the robustness of the corrosion model when experiencing small variations in an input parameter (Cr data modified).

5.1 Variations in Model Structure

5.1.1 Change in Model Parameters Represented as Framework Model C: Metal Temperature (K) and Gas Temperature (K)

This section focuses on the modification in the expression of the metal temperature and the use of the gas temperature instead of the temperature difference ($T_g - T_m$, K) as input parameters for the fireside corrosion model. The framework model C (equation 5-1) which captures these changes is used to illustrate the result for data subset 1 (UK coal, austenitic materials).

$$\ln \text{corr rate} = \ln A + b. \ln T_m + c. \ln T_g + d. \ln M_{(\text{alloy})} + e. \ln N_{(\text{fuel})} \quad 5-1$$

Where;

$\ln \text{corr rate}$ = fireside corrosion rate (microns/1000 hrs or μ_m/KHR)

$\ln T_m$ = metal temperature in natural log form

$\ln T_g$ = gas temperature in natural log form

$\ln M_{(\text{alloy})}$ = alloy elements in natural log form selected for model building

$\ln N_{(\text{fuel})}$ = fuel elements in natural log form selected for model building.

The PCA and PLS results are shown in Table 5-1. The ensuing discussion will be based on the variables nominated for model building. The model performances compared to

the other frameworks are detailed in the appendix section (Appendix D, Table E-1 to Table E-4).

Table 5-1: Estimated standardised regression coefficients for the predictor variables in PCA and PLS models for equation framework C. The shaded cells signify variables not selected for model building (elements in symbols are the fuel elements and the elements in full are from the metal/alloy; *fc* is short for ‘framework C’)

	VARIABLES	PCA Model 1A (fc)	PLS Model 1B (fc)
	Metal Temperature (K)	0.18	0.20
	Gas Temperature (K)	0.13	0.16
Alloy Elements	Carbon (wt %)	-0.087	-0.10
	Manganese (wt %)	-0.0085	
	Phosphorus (wt %)	0.0085	
	Sulphur (wt %)	-0.0085	
	Silicon (wt %)	-0.092	-0.079
	Chromium (wt %)	-0.047	-0.057
	Nickel (wt %)	-0.020	
	Molybdenum (wt %)	0.11	0.092
	Titanium (wt %)	-0.077	
	Vanadium (wt %)	0.0085	
Fuel Elements	Na (wt %)	0.13	0.10
	K (wt %)	0.037	
	Mg (wt %)	-0.055	
	Ca (wt %)	-0.099	-0.12
	Al (wt %)	0.0090	
	Fe (wt %)	0.066	
	Si (wt %)		
	Cl (wt %)	0.30	0.35
	S (wt %)	-0.22	-0.15
	Ti (wt %)		

The result for the PCA model (framework model C) is similar to the framework model F version discussed in chapter 4, except that the alkaline earth metals have been nominated for model building, while Ti from the fuel has been eliminated. However, their association with the corrosion rates are similar, and so are the estimated (standardised) regression coefficients (i.e. compared to model 1A in Table 4-2). The results from the PLS model (framework model C) also features similar selections and association with the corrosion rate as seen in the framework model F, thus showing some consistency. Note that the association is positive for the metal temperature as it is not expressed as the inverse (i.e. increasing temperature increases the corrosion rate). Using the gas temperature in lieu of the temperature difference positively affects the

corrosion rate and has not changed the initial deductions arrived at for the framework case F version discussed in chapter 4. Therefore, utilising the same number of PCs as case F, and PLS components as case F, and employing framework model C; the selected variables, sign of selected variables and the coefficient for the models did not considerably change although R^2 was improved for PCA (see Appendix D.2.3 and, Table E-1). Hence a change in the expression of the input parameters does not appear to alter the prevailing conclusion discussed in section 4.3.2, i.e. with respect to the alloy and fuel parameters that impact the fireside corrosion rate, the input parameters for the UK coal model (SH/RH in leading tube position) are indeed the same.

5.2 PCA Using Combined Variables from Loadings Plot

The loadings plot gives insight into the data structure (Cox, 2013). It shows the correlation between the variables and the PCs in the new subspace defined by the PCs. The loadings are obtained by multiplying the elements in the weight vector (the eigenvector) by the square root of the variance (the eigenvalue) of the associated PC and are expressed as equation 5-2.

$$r_{\alpha k} = U_{\alpha k}(\lambda)^{1/2} \quad 5-2$$

Where;

$r_{\alpha k}$ = the loading of the k_{th} variable on the α_{th} PC (i.e. the correlation between the α_{th} PC and the k_{th} variable)

U = the eigenvector of the k_{th} variable for the α_{th} PC

λ = the eigenvalue of the α_{th} PC.

Highly correlated variables appear as clusters in the loadings plot, and one way to deal with this is to either exclude one (Jolliffe, 2002; Pardoe, 2012) or to combine these correlated variables and analyse as a pair (2) or group (> 2) (Camperos, 2016). The latter option involves a close examination of the loadings plot to find variables that simultaneously load highly on a PC and are clustered, combining those variables and re-analysing following the same steps as outlined in section 3.2.2.1. The PCs with

maximum variability are usually the first two or three PCs; hence the focus will be on PC 1 and PC 2.

5.2.1.1 PCA Loadings Plot Analysis, Data Subset 1

The loadings plot derived from data subset 1 (UK coal, austenitic tubes, leading position) was examined for clusters or (high) correlations within the variables and re-analysed to develop PCA corrosion models. Only clusters that show strong correlations are combined, as illustrated in the circled regions in Figure 5-1. The supplementary variables include the *ln* corrosion rate (*Y*) and the base alloy (iron) which are projected onto the subspace generated by the PCs but are not active variables in the analysis.

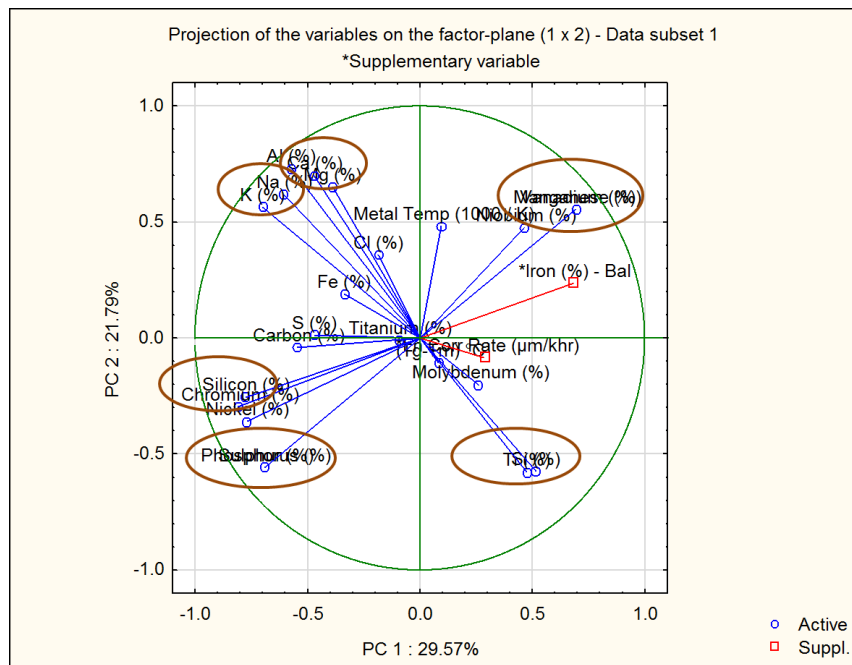


Figure 5-1: Loadings plot for PC 1 vs PC 2 from PE-8 data subset 1 showing highly correlated variables combined for re-analysis (circled regions). Fuel elements are indicated with symbols; alloy elements are written in full. The supplementary variables are in red.

The loadings plot (Figure 5-1) features highly correlated variables which indicate similar weights in the loading vectors and thus influence the PCA model in similar ways (Li, 2001; Wehrens and Mevik, 2007). All the variables located in the same quadrant are positively correlated (to different degrees) and are negatively correlated to the variables located diametrically. On the fuel side, there is an overlap of Na and K, Ca

and Mg (and arguably Al), Si and Ti; and on the alloy side, P and S, Si, Cr and Ni, Mn and V. For simplicity, only the variables with maximum variability, i.e. spanning a longer length, are considered for pairing. The justification is that the further the variable is away from the origin, the more influential the variable is in defining the PCA model (Statistica Documentation, 2012). Na and K are strongly (and positively) correlated (Figure 5-1), and an obvious choice to pair as alkali metals; likewise, for Ca and Mg (alkaline earth metals). However, Al has been excluded even though it lies in close proximity with Ca and Mg. This was a contentious decision as Al is not chemically similar to Ca and Mg (more on this in section 5.2.1.3). That being said, Si (group 14 in the periodic table) and Ti (a transition metal, group 4) clearly overlap in the plot and, due to its selection for model building as discussed in section 4.3.2, Ti was paired with Si for more understanding on its role (if any) in the corrosion process. On the alloy side, Si and Cr, Mn and V, and P and S were paired. These paired variables were re-analysed with the other separate (input) variables to derive the PCA (corrosion) model (using framework model F).

The results displayed in Table 5-2 are the standardised regression coefficients for the variables nominated and used for model building. Table 5-3 compares the performance statistics of the combined version (R^2) with the current PCA model results.

Table 5-2: Results showing the standardised regression estimates from the PCA model using combined variables from the loading plots (elements in symbols are the fuel elements and the elements in full are from the metal/alloy)

Variables Nominated	PCA Standardised Coefficients
1000/Metal temp (1000/K)	-0.19
(T _g – T _m) (K)	0.10
Carbon (wt %)	-0.12
Phosphorus + Sulphur (wt %)	0.019
Silicon + Chromium (wt %)	-0.072
Nickel (wt %)	-0.032
Molybdenum (wt %)	0.14
Titanium (wt %)	-0.062
Manganese + Vanadium (wt %)	-0.019
Na + K (wt %)	0.082
Mg + Ca (wt %)	-0.13
Al (wt %)	0.021
Fe (wt %)	0.12
Cl (wt %)	0.33
S (wt %)	-0.24
Si + Ti (wt %)	0.050

Table 5-3: Performance statistics (R²) from the combined variables PCA version (PCA model 1A combined) and the initial PCA derived model (PCA model 1A)

Performance Statistics	PCA Model 1A	PCA Model 1A (combined)
R ²	0.77	0.83

Examining Table 5-3, there is an improvement in the model performance for the combined version of PCA. The variables selected in the combined version are similar to the variables chosen for model building in the current version of PCA model 1A (framework model F). While combining input variables have dealt with the multicollinearity issues from a statistical viewpoint, the results (variables selected, sign of variables selected) were similar in both versions (i.e. the combined version discussed here and the original version discussed in section 4.3.1.1), and as such it does not augment the current conclusions on the corrosion behaviour presented in this data subset.

The following sub-section considers the loading plots of data subset 1 (Figure 5-1), but the paired variables are used to develop a PLS corrosion model.

5.2.1.2 Loadings Plot Analysis with PCA and Model Building with PLS, Data Subset 1

The strategy here was to use loadings plot from PCA, combine highly correlated variables and build the fireside corrosion model using PLS. The loadings plot in Figure 5-1 was the starting point in developing the model. The variables combined are the same as in section 5.2.1.1. The results are tabulated in Table 5-4 and the performance statistic in Table 5-5.

Table 5-4: Results showing the standardised regression estimates from PLS analysis using combined variables from the loading plots (elements in symbols are the fuel elements and the elements in full are from the metal/alloy)

Variables Nominated	PLS Standardised Coefficients
1000/Metal temp (1000/K)	-0.34
Carbon (wt %)	-0.19
Silicon + Chromium (wt %)	-0.13
Molybdenum (wt %)	0.19
Cl (wt %)	0.57
S (wt %)	-0.25

Table 5-5: Performance statistics (R^2) from the PLS derived model (PLS model 1B), the revised versions of PLS model 1B (combined) and PCA model 1A (combined)

Performance Statistics	PLS Model 1B	PLS Model 1B (combined)	PCA Model 1A (combined)
R^2	0.85	0.75	0.83

There is a reduced performance of the PLS combined model compared to the PCA combined version. This outcome underscores the limitation in expanding the loading plot output from PCA to other statistical analyses such as PLS. The clusters obtained from PCA loadings plot (X space) are structured differently from PLS (X in relation to Y). Ultimately, the best performing model judged by the R^2 value is the (original) PLS fireside corrosion model 1B.

5.2.1.3 The Limitations on the use of Loadings Plot as a Basis for the Fireside Corrosion Model

This discussion will focus only on the effectiveness of this technique (i.e. combining variables from the loadings plot) in fireside corrosion prediction and if it is worth pursuing further. Performing PCR through this route reveals the association of the variables. The multicollinearity issues can be resolved by either discarding one of the highly correlated variables or pairing the variables and analysing alongside other (unpaired) input variables. This provides a space to reveal patterns in the data such as the association of these elements in the same combustion conditions, for instance, the association of S or Cl, indicating whether the presence of one is independent of the other as the loadings plot in Figure 5-1 appears to suggest (i.e. almost 90° apart).

The main issue with the loadings plot is the structure of the data in its totality; i.e. the corrosion data subsets in this study have input parameters comprising alloy elements, fuel elements, and boiler conditions (metal and gas temperatures). This could potentially reveal clusters consisting of variables from the same category (e.g. fuel) especially when the variation in the data is not much (e.g. biomass data subset with only three woody biomass species analysed, see Figure 5-2); or clusters of input variables from different groups such as an alloy element and a fuel element (Figure 5-3).

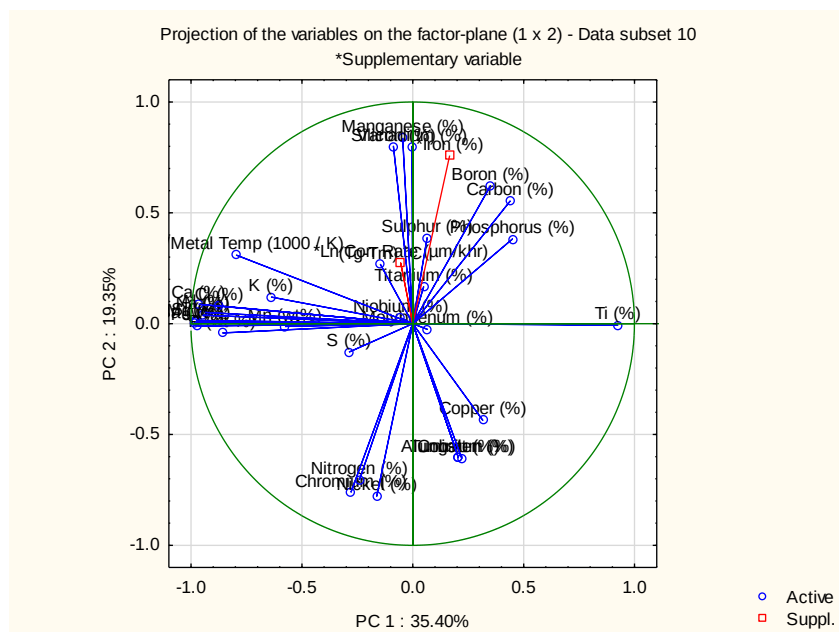


Figure 5-2: Loadings plot for PC 1 vs PC 2 from biomass data subset 10 showing correlated fuel variables

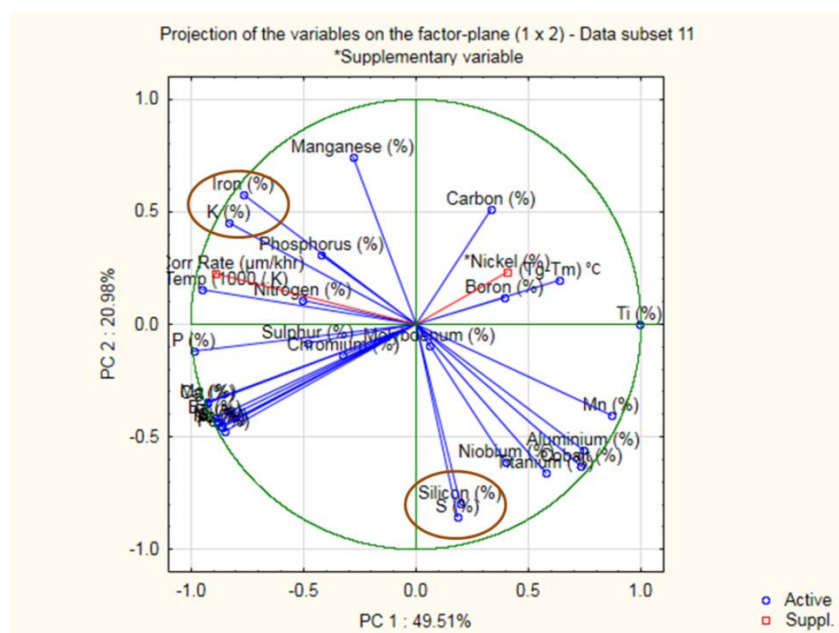


Figure 5-3: Loadings plot for PC 1 vs PC 2 from biomass data subset 11 (Ni-based tubes) showing correlated variables (focus is on the circled region; silicon from the alloy and S from the fuel; iron from the alloy and K from the fuel)

Camperos (2016) explored this route as well; however, the pairing of correlated variables (and subsequent inferences made) was easier in that scenario because the data employed for model building were grouped in different categories and analysed separately; i.e. steam conditions, alloy compositions and fuel (ash) data were grouped and analysed separately (Camperos *et al.*, 2015; Camperos, 2016). Hence there were fewer constraints in interpretations of the results.

There were some other concerns with adapting this route for PCR and PLS models, one of which was the tendency to pair non-chemically similar elements particularly, on the fuel side (e.g. Ca+Mg+Al in Figure 5-1, and majority of the fuel elements in Figure 5-2). From a statistical standpoint, clustered parameters reveal constructs in the data that could explain the inclusion of certain variables for the PCA models derived. However, in interpreting the plots and considering underlying relationships, there needs to be a careful evaluation of the variables to be paired or grouped; for instance, only Ca and Mg, but not Al, were paired as the latter (Al) is not an alkaline earth metal.

On the alloy side, a different argument ensues; hence looking back at Figure 5-1, it should be noted that while the alloy elements Cr, Ni and Si are in close proximity, only Cr and Si were combined because an increase in these alloying elements increases corrosion resistance through the formation of a protective oxide scale. This is an example where scientific reasoning governs the decision on the selection of paired variables from the loadings plot to be used for model building. Hence there is no one rule that can be suitably adapted for all scenarios in the context of grouping/combining inputs.

In addition to the issues above, the only PCs that can be conveniently examined in the loadings plot are always the first two PCs, PC 1 and PC 2, (depicting maximum variability), and sometimes the third and fourth PCs, but rarely the fifth, sixth PCs and beyond. This is because the variables are almost always so clustered from PC 3 onwards that attempting to group variables proved futile, even though the $\ln$ corrosion rate (inputted as a supplementary variable) loads highly on that PC. An extreme example of a loadings plot from PC 5 and PC 6 is shown in Figure 5-4.

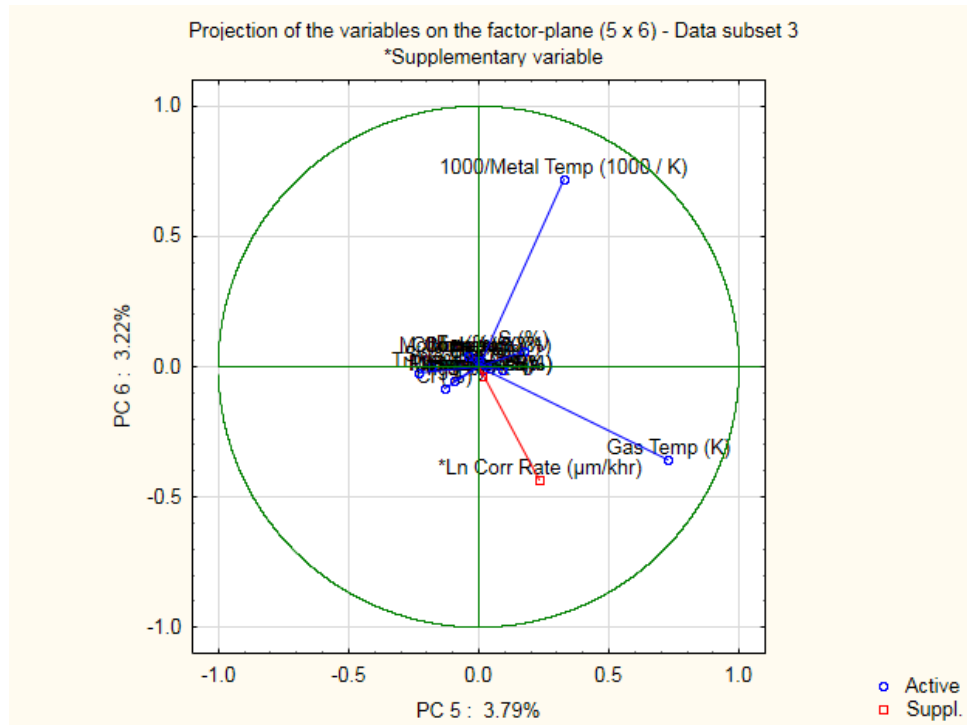


Figure 5-4: Loadings plot for PC5 vs PC6 from data subset 3 showing correlated variables

Finally, with respect to the PLS performance, pre-processing the data in this way (i.e. observing and combining correlated input variables from the loadings plot) can provide insight into the data structure and can be used for classification, but as Table 5-5 reveals, it does not improve the PLS model. The reason for this is tied to the main difference between PCA and PLS as PCA only considers the variation in the input (X) data, which is portrayed in the loadings plot. However, these highly correlated variables in the loadings plot may not be significantly correlated with the dependent variable, i.e. the $\ln$ corrosion rate.

5.3 PCA/PLS Interaction (Fireside Corrosion) Models

Fireside corrosion experienced by superheaters and reheaters involves the interaction of many parameters and complex reactions of which several operate in parallel depending on the boiler conditions. Although the derived statistical models do not address individual chemical reactions, important statistical correlations over a specific operational range are revealed. An interaction model, however, was considered to assess whether the association of specific input parameters on the corrosion rate depends on the value of another input variable. For instance, in coal combustion, the concentration

of SO₂ in the gas controls the extent to which the corrosive alkali sulphate (molten) complex could occur (Antunes and de Oliveira, 2013). As such, the correlation between the alkali metals and the corrosion rate may vary according to the levels of S present. In coal combustion environments, sulphidation is the main fireside corrosion mechanism that leads to the formation of the damaging molten alkali iron trisulphate that attacks SH/RH tube materials. Thus, a simple model interaction has been attempted by including the interaction term $S \times (Na+K)$ and re-analysing the dataset including this term and then using PCA and PLS to develop coal corrosion models. In biomass boilers, the corrosion reactions involve the more damaging alkali chlorides; hence the interaction term included in biomass modelling is the alkali metals and Cl, i.e. $Cl \times (Na+K)$. Three data subsets were analysed with the interaction parameter: data subsets 1 (UK coal), 5 (US coal data) and 10 (biomass data). The results are briefly discussed in the following sub-sections.

5.3.1 PCA/PLS Interaction Model for Data Subset 1

The nominated variables retained in the PCA and PLS models, and their respective standardised regression estimates are shown in Table 5-6. Note that for an interaction model to work, the concept of hierarchy must be preserved (Pardoe, 2012), i.e. the individual variables in the interaction term; i.e. (Na+K) and S, must be retained as active variables for model building.

Table 5-6: Standardised regression coefficients for the predictor variables including an interaction term for data subset 1 (shaded cells were excluded from model building; the fuel elements are in symbols, alloy elements written in full)

	VARIABLES	PCA Model 1A (Int)	PLS Model 1B (Int)
	1000/Metal Temp (1000 / K)	-0.19	-0.25
	(T _g -T _m) (K)	0.095	0.12
Alloy Elements	Carbon (wt %)	-0.087	-0.10
	Manganese (wt %)	-0.015	
	Phosphorus (wt %)	0.015	
	Sulphur (wt %)	0.015	
	Silicon (wt %)	-0.089	-0.083
	Chromium (wt %)	-0.046	-0.056
	Nickel (wt %)	-0.01	
	Molybdenum (wt %)	0.13	0.078
	Titanium (wt %)	-0.058	
	Vanadium (wt %)	0.015	
Fuel Elements	Na+K (wt %)	0.096	0.077
	Mg (wt %)	-0.044	
	Ca (wt %)	-0.1	-0.12
	Al (wt %)	0.043	
	Fe (wt %)	0.11	
	Si (wt %)	0.012	
	Cl (wt %)	0.32	0.41
	S (wt %)	-0.23	-0.14
	Ti (wt %)	0.036	
	S×(Na+K) (wt %)	-0.018	

The PCA and PLS models show Cl plays a dominant role in the fireside corrosion mechanism, followed by the metal temperature (1000/K) and it appears S does not determine the overall fireside corrosion rate nor does the interaction term, $S \times (Na+K)$ (included in PCA model but not PLS). This estimated regression coefficient is similar to the results from the current version without an interaction term (discussed in chapter 4, section 4.3.2). Unlike the PCA model, the interaction, $S \times (Na+K)$ was not highlighted for PLS model building. The conclusions arising from the interaction model ultimately aligns with the previous result obtained (section 4.3.1) as clearly Cl determines the overall reaction rate, however it does show that for the operating range considered (i.e. 605 °C – 680 °C), S, although active in the corrosion mechanism, is not rate controlling.

5.3.2 PCA/PLS Interaction Model for Data Subset 5

The resulting regression estimates for the interaction model derived from the US coal data are presented in Table 5-7. The interaction term has been included for the PLS model and is positively associated with the corrosion rate, however, the PCA model excludes the interaction term. Other influential fuel parameters indicated to promote the corrosion rate include the alkali metals, the alkaline earth metals, Fe, Si, Cl, Ti, and Mn; this is very similar to the original version (models 5A and 5B) discussed in section 4.3.3. The US corrosion models suggest an aggressive environment in which the fuel elements and the temperature difference play a more active role in determining the corrosion rate.

Table 5-7: Standardised regression coefficients for the predictor variables including an interaction term for data subset 5 (shaded cells indicate predictor variables excluded from model building; the fuel elements are in symbols, alloy elements written in full)

	VARIABLES	PCA Model 5A (Int)	PLS Model 5B (Int)
	1000/Metal Temp (1000 / K)	0.16	0.06
	(Tg-Tm) (K)	0.35	0.37
Alloy Elements	Carbon (wt %)	0.13	
	Phosphorus (wt %)	-0.16	-0.12
	Sulphur (wt %)	-0.094	
	Chromium (wt %)	-0.0063	
	Nickel (wt %)	-0.014	
	Molybdenum (wt %)	0.021	0.12
	Titanium (wt %)	0.047	
	Cerium (wt %)	-0.057	
	Tungsten (wt %)	0.065	
	Boron (wt %)	0.057	
	Tantalum (wt %)	0.0094	
	Cobalt (wt %)	0.078	
Fuel Elements	Na+K (wt %)	0.093	0.079
	Mg (wt %)	0.083	0.043
	Ca (wt %)	0.15	0.15
	Fe (wt %)	0.27	0.31
	Si (wt %)	0.067	0.082
	Cl (wt %)	0.17	0.21
	S (wt %)	-0.025	-0.037
	Ti (wt %)	0.07	0.06
	S×(Na+K) (wt %)		0.067
	P (wt %)	-0.39	-0.41
	Mn (wt %)	0.28	0.33

5.3.3 PCA/PLS Interaction Model for Data Subset 10

The results for the PCA/PLS biomass corrosion model with interaction terms are presented in Table 5-8 and reveal critical fuel species including the alkali metals and Ca, and, for the PCA model, the selection extends to fuel elements Al, Cl, Ti, Ba, and the interaction term $Cl \times (Na + K)$. The results align with the original PCA/PLS biomass model discussed in section 4.4 with the fuel element, S, shown to be less detrimental in biomass-fired systems. The fuel composition in this data subset consists mainly of woody biomass, and the literature shows that the deposits prevalent in this environment are grouped among those that contain low silica, low K and high Ca ashes with high melting points (Simms, 2011a). A similar correlation is portrayed in the interaction models, and it is worth noting that the interaction term selected for PCA model building is positively associated with the $\ln$ corrosion rate.

Table 5-8: Standardised regression coefficients for the predictor variables including an interaction term for data subset 10 (shaded cells indicate predictor variables excluded from model building; the fuel elements are in symbols, alloy elements written in full)

	VARIABLES	PCA Model 10A (Int)	PLS Model 10B (Int)
	1000/Metal Temp (1000/K)	0.074	0.37
	(Tg-Tm) (K)	-0.18	-0.0062
Alloy Elements	Carbon (wt %)	0.11	0.47
	Manganese (wt %)		0.11
	Phosphorus (wt %)	0.24	0.13
	Sulphur (wt %)	0.19	0.16
	Silicon (wt %)	-0.0028	0.13
	Chromium (wt %)	-0.12	-0.14
	Nickel (wt %)	-0.05	
	Molybdenum (wt %)	-0.08	0.034
	Niobium (wt %)	0.18	
	Titanium (wt %)		-0.18
	Vanadium (wt %)	-0.18	0.1
	Copper (wt %)	-0.018	
	Nitrogen (wt %)		-0.66
	Tungsten (wt %)	0.01	
	Boron (wt %)	0.14	
	Aluminium (wt %)	-0.01	
	Cobalt (wt %)	0.01	
Fuel Elements	Na+K (wt %)	0.089	0.09
	Mg (wt %)	-0.015	
	Ca (wt %)	0.1	0.23
	Al (wt %)	0.029	
	Fe (wt %)	-0.038	
	Si (wt %)	-0.011	
	Cl (wt %)	0.06	
	S (wt %)	-0.13	-0.18
	Ti (wt %)	0.038	
	Cl×(Na+K) (wt %)	0.07	
	P (wt %)	-0.13	-0.4
	Ba (wt %)	0.02	
	Mn (wt %)	-0.18	-0.12

5.3.4 Summary of Interaction Models

In conclusion, fireside corrosion models involving interactive variables have been developed to provide insight on the association of active fuel elements and their corresponding influence on the corrosion rate, as these elements do not act on their own in coal-fired or biomass-fired combustion systems. The final corrosion models obtained are developed with an additional (interaction) term included as an input parameter.

Similar deductions with the original PCA/PLS models have been attained and the model performance from the original and variant models are identical.

5.4 Corrosion Data Sensitivity Analysis

PCA and, to a lesser extent, PLS, can be sensitive to the structure of the dataset. This is likely to impact on the final regression models produced and as such the impact of varying the input parameters was studied to ascertain the performance of these models when there was a slight variation in the input parameters. The approach chosen in this work was to vary the alloying element, Cr, for the PE-8 data subset 1, leaving other input parameters at their original values. The maximum composition of the alloy elements was used for the analysis. For the sensitivity analysis, the Cr content was altered to its minimum/nominal value to ascertain if small changes modify the results significantly. To this end, the Cr values in data subset 1 (range 15Cr – 26Cr) were modified to minimum values (range 15Cr – 24Cr) and re-analysed. The PLS regression result is presented and discussed in section 5.4.1. The result of the PCA model is presented in Appendix F.

5.4.1 PLS Model 1B with Modified Cr Content

Six PLS components were advanced through to the model building stage; these were the same as for the original PLS model developed for data subset 1. The variables selected, and the corresponding regression coefficients estimated are compared with the original PLS models in Table 5-9.

Table 5-9: Regression coefficients for the PLS model using original Cr values and modified Cr data (alloy compositions written in full, fuel in symbols; all variables in *ln* form)

Variables selected for PLS Model Building	Regression Coefficients (Original Cr Data)	Regression Coefficients (Modified Cr Data)
1000/Metal Temp (1000/K)	18.88	19.15
(T _g -T _m) (K)	-15.70	-15.68
Carbon (wt %)	0.735	0.728
Silicon (wt %)	-0.275	-0.244
Chromium (wt %)	-0.249	-0.496
Molybdenum (wt %)	0.146	0.143
Na (wt %)	0.131	0.133
Ca (wt %)	-0.214	-0.214
Cl (wt %)	1.396	1.390
S (wt %)	-0.447	-0.454

A sensitivity index (SI) can be used to measure the change in the results (regression coefficients) with changes in the input data (Pannell, 1997) and is given by equation 5-3 (Pannell, 1997).

$$SI = (D_{max} - D_{min}) \quad 5-3$$

Where;

SI = sensitivity index

D_{max} = the output when the parameter is set at its maximum value

D_{min} = the output when the parameter is set at its minimum value

The SI value for the modified parameter (Cr) using equation 5-3 is 0.247, i.e. almost double in magnitude. The implication is that twice as much of the Cr content in the revised version is necessary for a change (reduction) in the corrosion rate, in contrast to the original values where the Cr content is slightly higher. The overall results and

variables selected for model building remain unchanged. The selected variables are oriented in the same directions (in relation to the corrosion rate), and the scatterplot in Figure 5-5 shows close R^2 values. Hence, in conclusion, it follows that minor variations in the input data do not significantly affect the results and the performance of the PLS (corrosion) models.

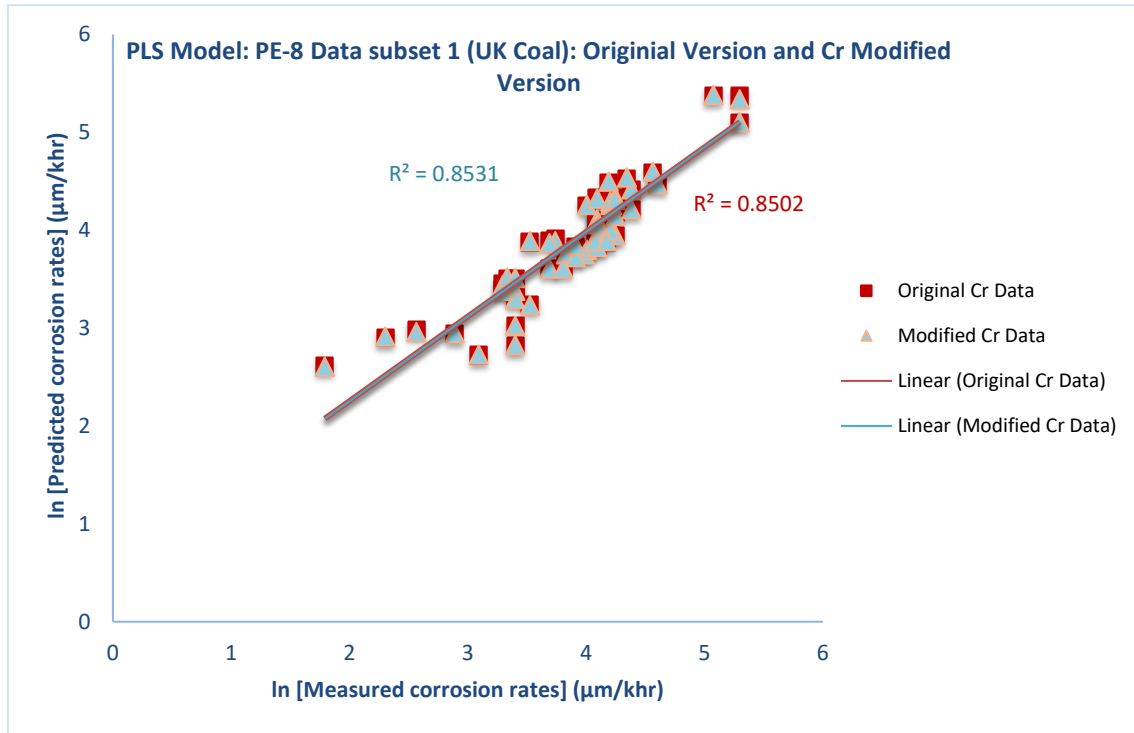


Figure 5-5: Comparison of measured corrosion rates and predicted (PLS) corrosion rates using original Cr values and modified Cr values for data subset 1

6 MODEL PERFORMANCE AND VALIDATION

This chapter documents the model performance as judged by the coefficient of determination (R^2), and the root mean square error (RMSE). The performances of framework model F for the PCA and PLS derived fireside corrosion models were assessed using the RMSE and the R^2 values (section 6.1). A comparison of the performance of PCA/PLS derived models with the measured corrosion rates is illustrated in section 6.1.1.4. An overview of the model performances with focus on framework model F is discussed in section 6.2. Graphical residual plots were used to validate the models (section 6.3). The PE-8 fireside corrosion model from literature applied to the UK and US data and compared with the PCA/PLS derived fireside corrosion models are discussed in section 6.4.

6.1 Assessment of Model Performance

Two measures of performance have been chosen for this research, the coefficient of determination (R^2), and the root mean squared error of prediction (RMSE).

6.1.1.1 The coefficient of determination, R^2

The coefficient of determination (R^2) shows the proportion of variance in the dependent variable, Y that is explained by its linear association with the independent or predictor variable(s), X (Pardoe, 2012). Larger values of R^2 indicate a better fit for the model. It is calculated using the expression:

$$1 - \frac{\sum_{i=1}^n (Y_o - \hat{Y}_p)^2}{\sum_{i=1}^n (Y_o - m_Y)^2} \quad \mathbf{6-1}$$

Where;

Y_o = observed (or measured) Y values

$\hat{Y}_p$ = fitted (or predicted) Y values

m_Y = the sample mean (of observed Y values)

n = total number of cases or observations.

6.1.1.2 The Root Mean Square Error of Prediction (RMSE)

The RMSE is a measure of differences between predicted values and observed values; i.e. the residuals. The RMSE is calculated by squaring and averaging each residual, and then taking the square root of the result as shown in equation 6-2 (Cox, 2013). The value is always between 0 and 1, and the smaller the RMSE, the better the model's predictive ability (Kumar and Goyal, 2011; Cox, 2013).

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (y_p - y_o)^2}{n}} \quad 6-2$$

Where;

y_p = predicted values

y_o = measured values

n = total number of observations.

6.1.1.3 Performance of PCA/PLS Corrosion Models (RMSE)

Table 6-1 shows the RMSE values for PCA and PLS corrosion models derived from data subsets 1-16 (framework model F). The models with a high RMSE value also exhibit low R^2 value, notable exceptions being PLS models 2B and 5B, and PCA models 5A and 11A (Table 6-1 and Figure 6-1). This can be attributed to the occurrence of a few high error predictions for these data subsets. PCA model 4 had the highest RMSE value reflecting the issues with this data subset. The complete RMSE values for the other framework models are displayed in the appendix (Table E-3 and Table E-4). Dimension reduction overall was better served with PLS than PCA. Ultimately, the performance on average for both models shows a relatively good performance thus providing a reasonable approximation to the corrosion data.

Table 6-1: Comparison of PCA/PLS RMSE values for data subsets 1-16 (framework model F)

RMSE	PCA Models	PLS Models
Model 1	0.31	0.25
Model 2	0.26	0.67
Model 3	0.57	0.56
Model 4	0.78	0.72
Model 5	0.73	0.76
Model 6	0.66	0.68
Model 7	0.66	0.54
Model 8	0.33	0.29
Model 9	0.44	0.50
Model 10	0.56	0.55
Model 11	0.71	0.55
Model 12	0.27	0.25
Model 13	0.55	0.58
Model 14	0.34	0.34
Model 15	0.32	0.33
Model 16	0.57	0.58

6.1.1.4 Comparison of Predicted Corrosion Rates with Measured Corrosion Rates

Figure 6-1 and Figure 6-2 presents a sequence of scatterplots for the PCA/PLS models derived from framework model F and the measured corrosion rates. The R^2 value displayed shows the proportion of variance in the dependent variable (fireside corrosion rate) explained by the derived models.

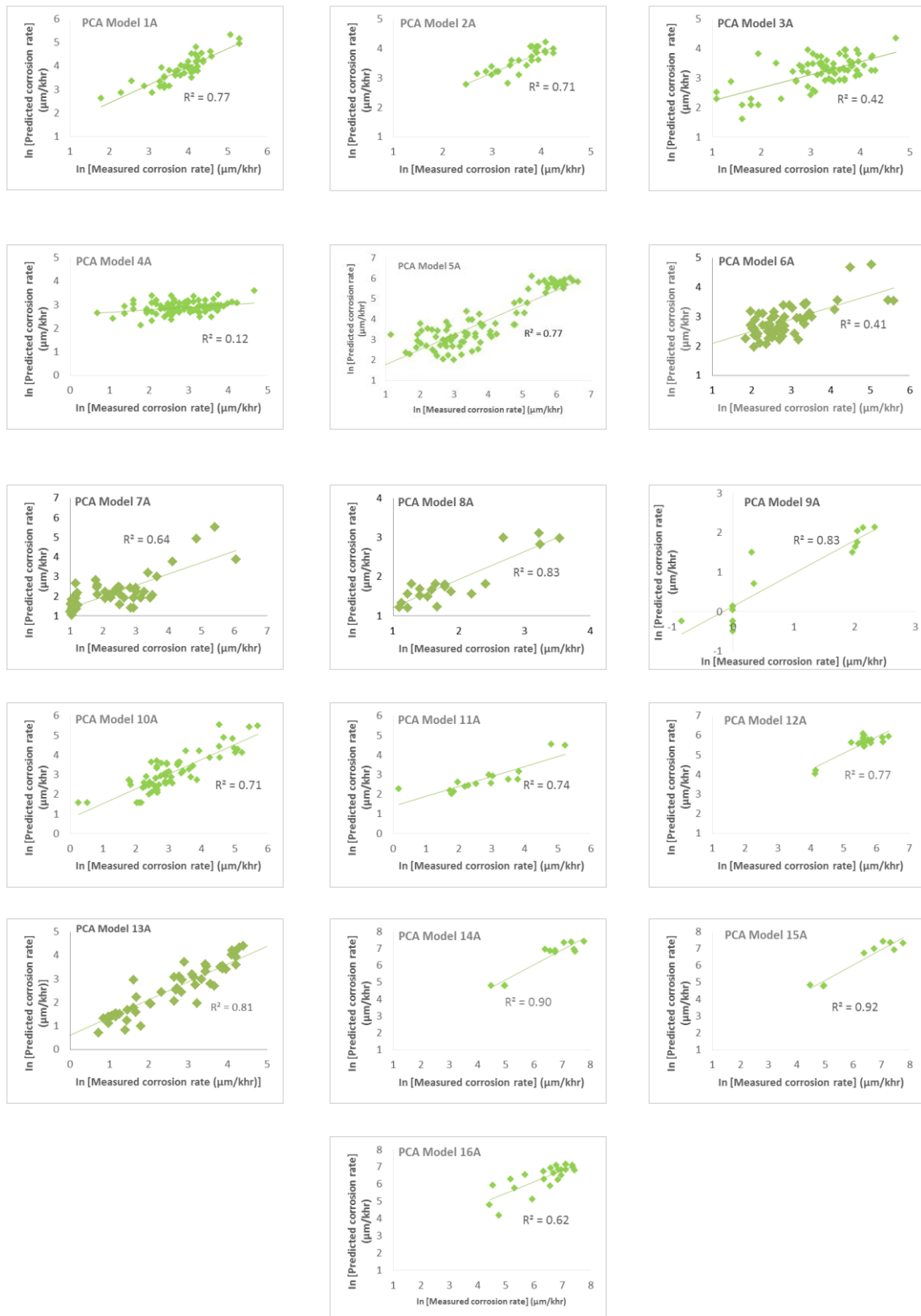


Figure 6-1: Scatterplot of the PCA models against the measured corrosion rates for data subsets 1A-16A

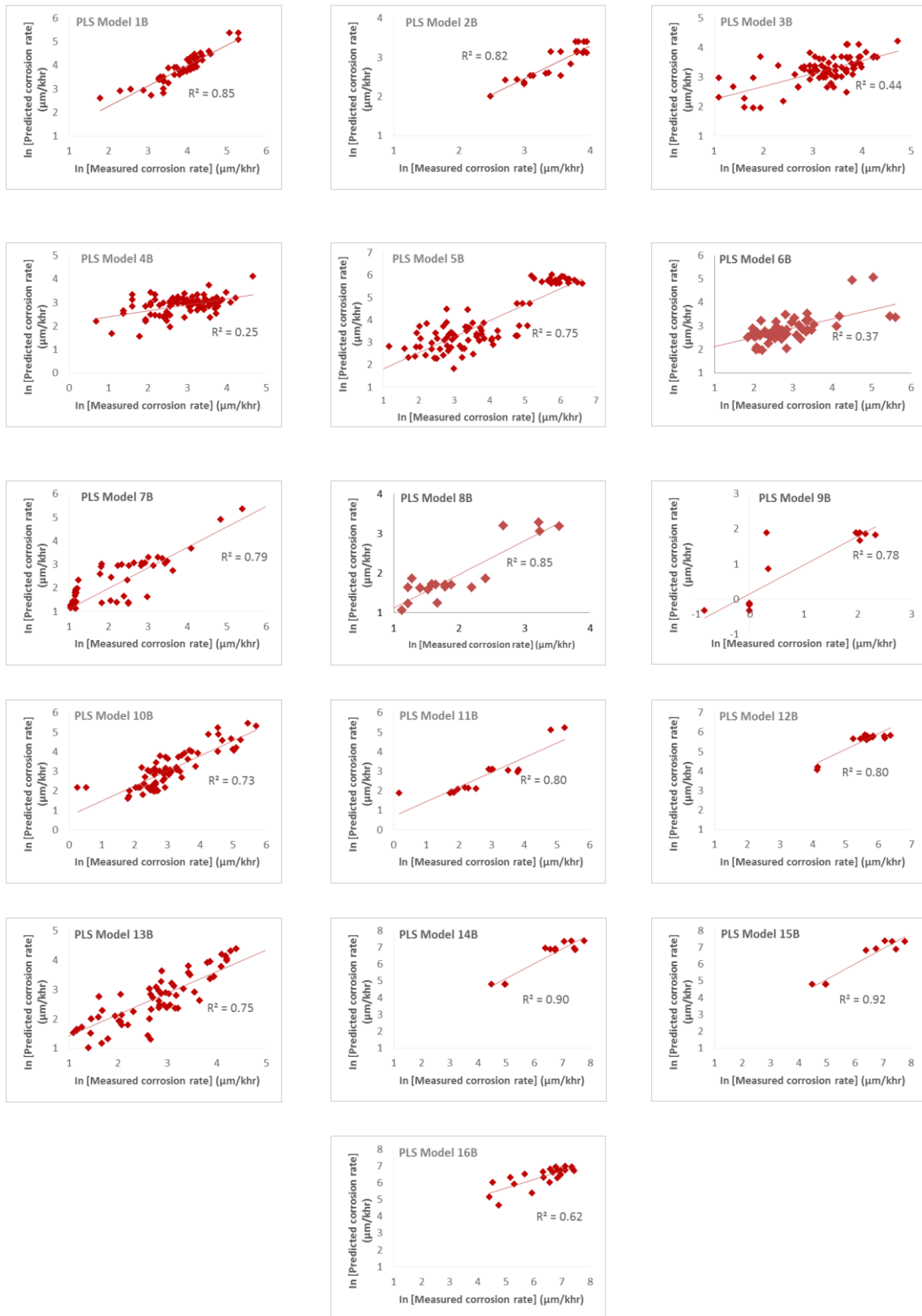


Figure 6-2: Scatterplot of the PLS models against the measured corrosion rates for data subsets 1B-16B

6.2 Summary and Discussion of Model Predictive Performances for PCA vs PLS

The fireside corrosion models developed using PCA and PLS had varying degrees of success. There were good prediction performances from PCA and PLS models 1, 2, 5, and 7-16 with R^2 value ≥ 0.7 . By contrast, the predictive performances from models 3, 4 and 6 were particularly poor. The lack of variation in the range of ferritic alloys for data subsets 3 and 4 is the most plausible reason for the weak performance. However, the reason for the poor predictive performances of PCA and PLS derived corrosion model 6 is not completely understood. Other model cases (i.e. equations 4-3 and 4-4) attempted for this data subset were unsuccessful (see Table D-7 and Table D-8). It appears the Arrhenius format may not be the right model structure for this data. The issue with the PCA/PLS corrosion model 6 has been addressed in section 4.3.3

The PLS corrosion models show a more reliable predictive performance than PCA even with few input parameters. However, there were three cases where the predictive performance of PCA was slightly improved compared to PLS; i.e. model 5A (US coal data), model 9A (UK data, world traded coal for coated materials), and model 13A (biomass coatings data). The reason for this is inherently statistical. Reviewing the number of variables used for model building in all three cases, it is evident that PCA tends to nominate more input variables which invariably increases the R^2 value sometimes more so than necessary, whilst PLS, as has consistently been the case, highlights only a few variables from the same data subset with equally good model performance. There is an argument to be made, thus, that the PCA models are more susceptible to modelling ‘noise.’ The variables selected for PLS model building, on the other hand, are mostly associated with the corrosion rate as the analysis from PLS maximises variance in the Y space that is explained by the X (input) data.

6.3 Model Adequacy and Validation

The most reliable method to validate the corrosion model developed is to apply the model to a new set of data that was not used for model building because it is not enough to use the R^2 value to assess the capability of the model to approximate real conditions. The hold-out method of cross-validation is the easiest choice for validating the PLS model, as the feature is included in the application (STATISTICA) and can be easily

applied. Using cross-validation, the data subset can be split in half where a portion is used for training (the learning or training sample) and the other half not used for model building is used for prediction (the test data). However, there were a couple of issues encountered mainly due to the nature of the data subset. First the choice of data cases (rows of observations or measurements) employed as the learning or training set has been random, and in most cases, the model building process was impeded when one or more predictor variable(s) in the training data had no variance. In this scenario, the analysis will simply not proceed and re-ordering the training sample could lead to a reduction in the data set aside for building the model which is not ideal. In other cases, the data subsets were too small to be validated; e.g. UK world-traded coal (coatings) model 9, biomass nickel-based model 11 and, co-firing models 14-16. Hence a larger dataset (preferably over a 100 entries) is best suited for the cross-validation hold-out technique. The largest dataset used for model development in this work contains 102 data entries, which is the ferritic (UK coal) data subset with minimal variation on the alloy side. There are two alloys present in this data subset (i.e. data subsets 3 and 4), and one of the alloy types dominates a major portion of the data resulting in the no-variance scenario if cross-validation is used.

Despite these limitations, cross-validation was attempted with data subset 1 with the framework model F to assess the robustness of the technique in model building and validate the model. The PE-8 data subset 1 is the UK coal data for austenitic tube materials in the leading position and consists of 51 measured data and 23 variables including the corrosion rate. The data subset was split in half, the top 26 data entries or cases served as the training set and the lower half (25 cases) as the test data. PLS was thus performed on a 26×23 matrix. 6 PLS components were selected thus 90% variation in the input data; X , explains 92% variance in Y (the corrosion rate). Six PLS weights were used to select the variables for model building (see Table 6-2).

Table 6-2: Variable importance in projection (VIP) scores (red text indicates variables above a threshold of 0.8 and selected for inclusion in the PLS corrosion model; the fuel elements are in symbols, alloy elements are written in full)

	VARIABLES	VIP SCORES
	1000/Metal Temp (1000 / K)	1.29
	(T _g -T _m) (K)	0.78
Alloy Elements	Carbon (wt %)	1.17
	Manganese (wt %)	0.65
	Phosphorus (wt %)	0.65
	Sulphur (wt %)	0.65
	Silicon (wt %)	1.11
	Chromium (wt %)	1.16
	Nickel (wt %)	0.96
	Molybdenum (wt %)	0.93
	Titanium (wt %)	0.42
	Vanadium (wt %)	0.65
Fuel Elements	Na (wt %)	1.06
	K (wt %)	0.46
	Mg (wt %)	0.55
	Ca (wt %)	0.97
	Al (wt %)	0.47
	Fe (wt %)	0.53
	Si (wt %)	0.61
	Cl (wt %)	2.24
	S (wt %)	1.65
	Ti (wt %)	0.98

Table 6-3: Estimated regression coefficients for the training data (data subset 1; the fuel elements are in symbols, alloy elements are written in full)

Variables/Intercept	Regression Coefficients	Standardised Coefficients
Intercept	20.47	-
1000 / Metal Temp (1000 / K)	-14.93	-0.30
Carbon (wt %)	-0.25	-0.10
Silicon (wt %)	-0.22	-0.07
Chromium (wt %)	-0.36	-0.06
Nickel (wt %)	-0.17	-0.04
Molybdenum (wt %)	0.22	0.09
Na (wt %)	0.08	0.04
Ca (wt %)	-0.33	-0.20
Cl (wt %)	1.06	0.36
S (wt %)	-0.92	-0.21
Ti (wt %)	-0.65	-0.07

Eleven variables were selected and used for model building and the estimated regression coefficients for the training data obtained in the PLS model (Table 6-3) were used to predict the values of the test data. The predictions for the test data are shown in Table 6-4. A scatterplot of predicted and measured values for the test data is shown in Figure 6-3.

Table 6-4: Measured and predicted corrosion rates from the training data and test data obtained via cross-validation (data subset 1)

	DATA	Measured Ln Corr rate ($\mu\text{m}/\text{hr}$)	Predicted Ln Corr rate ($\mu\text{m}/\text{hr}$)
TRAINING DATA	Case 1	3.401	3.223
	Case 2	1.792	2.397
	Case 3	3.738	4.039
	Case 4	4.094	4.131
	Case 5	3.689	4.131
	Case 6	4.248	4.312
	Case 7	3.989	3.669
	Case 8	4.007	4.025
	Case 9	3.689	3.847
	Case 10	3.829	3.669
	Case 11	3.807	3.847
	Case 12	4.248	4.354
	Case 13	4.007	4.426
	Case 14	4.248	4.109
	Case 15	4.205	4.426
	Case 16	4.220	4.426
	Case 17	3.401	3.329
	Case 18	3.526	3.282
	Case 19	5.075	5.246
	Case 20	5.298	5.232
	Case 21	5.298	4.940
	Case 22	4.094	3.998
	Case 23	4.205	4.342
	Case 24	2.303	3.149
	Case 25	4.564	4.946
	Case 26	4.094	4.180
TEST DATA	Case 27	4.382	3.994
	Case 28	4.382	4.250
	Case 29	4.605	4.267
	Case 30	3.296	3.151
	Case 31	3.296	3.169
	Case 32	3.401	3.430
	Case 33	4.094	4.180

	DATA	Measured Ln Corr rate ($\mu\text{m}/\text{hr}$)	Predicted Ln Corr rate ($\mu\text{m}/\text{hr}$)
TEST DATA	Case 34	4.094	4.008
	Case 35	4.094	3.875
	Case 36	4.094	4.167
	Case 37	4.248	4.439
	Case 38	4.190	4.581
	Case 39	4.344	4.614
	Case 40	3.332	3.614
	Case 41	2.565	3.255
	Case 42	3.912	3.498
	Case 43	3.912	4.003
	Case 44	4.205	4.215
	Case 45	4.078	4.215
	Case 46	3.526	4.215
	Case 47	4.174	4.215
	Case 48	3.401	4.034
	Case 49	3.401	2.814
	Case 50	2.890	2.999
	Case 51	3.091	2.594

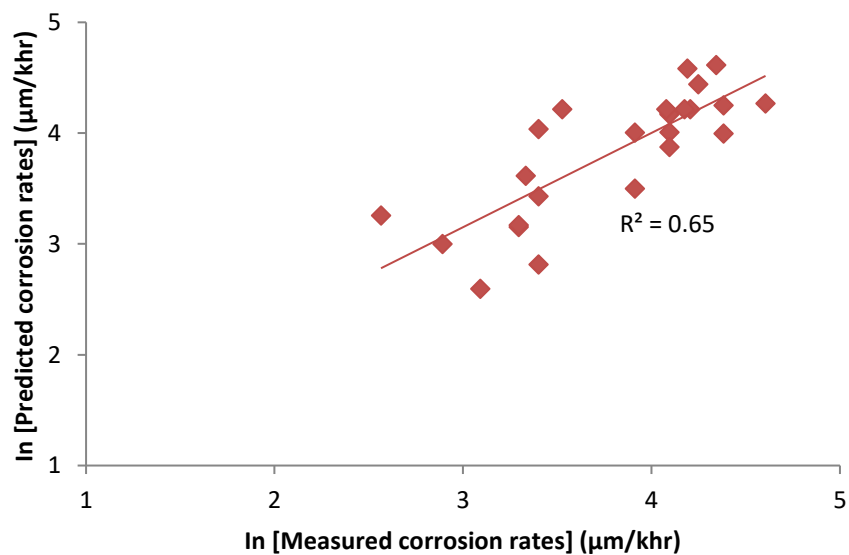


Figure 6-3: Scatterplot showing the predicted corrosion rates versus the measured corrosion rates and the R^2 value for the test data (data subset 1B)

The PLS model developed from the training sample was applied to the test data and the performance was judged by the predicted values from the test data, the R^2 value (Figure 6-3) and the RMSE which was calculated as 0.34. Except for the exclusion of the temperature difference parameter ($T_g - T_m$, K), and the inclusion of Ni (alloy) and Ti (fuel) for model building (Table 6-2 and Table 6-3), the deductions are similar to that from the PLS model built with the whole data subset (result in section 4.3.1.2). This essentially validates the model and demonstrates the reliability of the technique and its applicability to other (similar) data subsets.

Having demonstrated that the corrosion model derived can be applied to other (corrosion) datasets in similar combustion conditions (UK coal, austenitic materials), the hold-out technique of cross-validation, however, works effectively with large datasets. In the absence of additional plant data suitable for use as a test sample to validate the model and prevent the issues previously outlined, a statistical procedure, graphical residual testing (Shardt, 2015), was implemented to validate the model.

6.3.1 Graphical Residual Testing

The assumptions that must be satisfied in a regression analysis to ensure that the model developed is adequate is that the errors (residuals) must have a zero mean, must be independent and homoscedastic (i.e. the errors must have constant variance) (Shardt, 2015). A scatterplot of the residuals is a way of testing if these assumptions have been met. The residuals from the fitted model are the differences between the predicted values of the corrosion rate and the measured values. If the model is the right fit for the data, the residuals would approximate the random errors and will be dispersed around the horizontal (zero) axis (Shardt, 2015). The residuals are plotted against the predicted values as shown in Figure 6-4 and Figure 6-5.

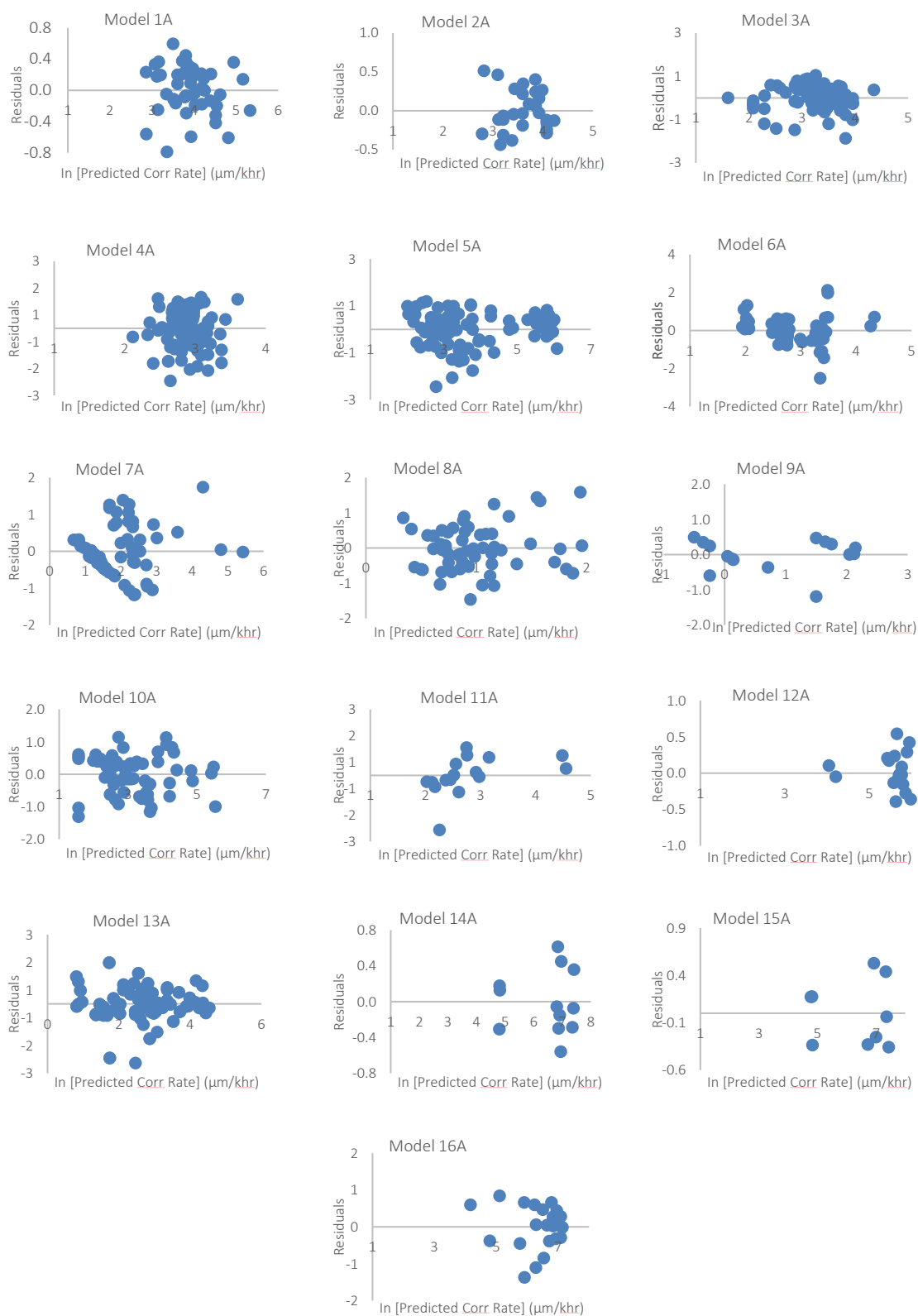


Figure 6-4: Residual plots for PCA models 1A-16A

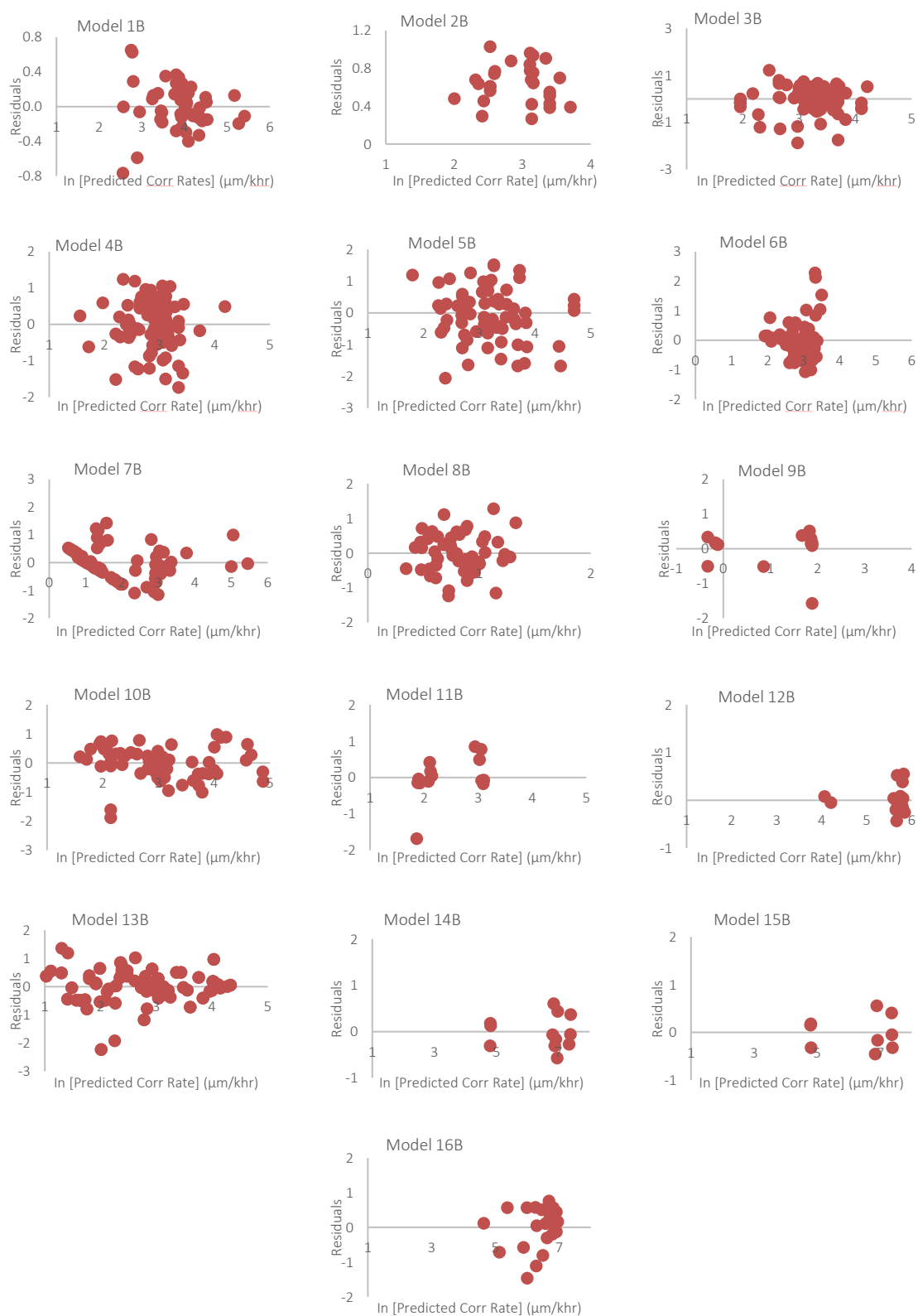


Figure 6-5: Residual plots for PLS models 1B-16B

The residual plots which do not display any orderly or discernible pattern signify that the fireside corrosion model is a good fit to the data. To this end, most of the models appear to be randomly dispersed except PCA and PLS models 7A and 7B (US coatings data), PCA model 9A (UK coatings data) and PCA/PLS model 16A and 16B (ferritic co-firing data). PLS Model 2B, and PCA/PLS models 6A and 6B shows the residuals at points high above the x-axis (although no discernible pattern in the residuals).

Assessing the residual plot for PCA model 6A (Figure 6-4), some of the residuals appear at points high above and below the x-axis. PLS models 2B and 6B shows some scatter around zero, but there are still points on the graph where the residuals are higher (Figure 6-5). The plot for PCA/PLS models 7 shows the residuals in a somewhat decreasing pattern. Although the graph for PCA/PLS model 11 shows the residuals at each point scattered around zero, there is a lone point on the graph that is much further away from the others. The graph for PCA model 9A (Figure 6-4) appears to form a repeating pattern; and there is a slight, almost curved-like form in the residual plots for PCA/PLS models 16.

Data subsets 9, 11, and the co-firing data subsets 14-16 range from 9-23 data entries which are not enough to properly validate the model. For models 7A and 7B however, the residuals on the left-hand region of the plot (Figure 6-4 and Figure 6-5) appears to form a decreasing pattern while the residuals on the right side of the plot are more randomly dispersed. The implication is that a linearized model may not be suitable for this data. The scatterplots for model 7 in Figure 6-1 and Figure 6-2 also showed clustered points on the left-hand side hence prompting scrutiny on the structure of this data subset. The coatings material for data subset 7 is displayed in Table 3-7. It was observed that these clustered data points are mainly from the measured rates obtained from supercritical conditions and consist of welded overlay (WO) materials, i.e. 52WO/72WO / 50-50 LC and 622WO / 230 with very low corrosion rates measured/predicted for this portion of data. A radical approach would entail excluding the data points from the left-hand portion of the graph (although in doing so, a significant portion of the data was excluded). This was tested using PLS for the modified data excluding entries from supercritical conditions and the outcome produced the residual plot shown in Figure 6-6.

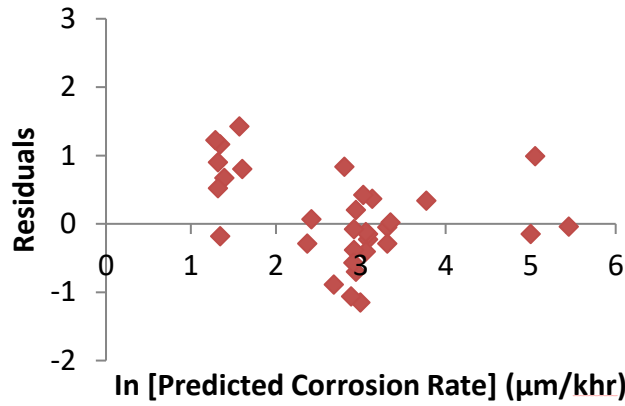


Figure 6-6: Residual plot for modified PLS model 7B (v2) excluding the supercritical portion of the corrosion data (US coatings data with coal)

The R^2 for the modified version is still very good (i.e. $R^2 = 0.77$; previously 0.79 as shown in Figure 6-2), and the RMSE value for the modified PLS model is slightly lower (i.e. 0.49, as opposed to 0.54 in the original version, see Table 6-1). As the US coal data is a combination of subcritical and supercritical conditions, a different, perhaps non-linear model may be appropriate for this data subset.

6.4 Comparison between PCA, PLS and PE-8 Models for PE-8 Data (UK Data subset 1) and US Data

6.4.1 PE-8 vs PCA, PLS Models (UK data subset 1)

The scatterplot in Figure 6-7 compares the performance of the newly derived models (PCA, PLS) superimposed on the original PE-8 (UK) fireside corrosion model reported in the literature for UK coals (detailed in chapter 2, section 2.8). The PE-8 model (equation 6-3) and the derived PCA and PLS models (equations 6-4 and 6-5) for the UK coal data are outlined below

$$\text{Corrosion rate} = AB \left(\frac{T_g}{G} \right)^m \left[\frac{(T_m - C)}{M} \right]^n (\%Cl - D) \quad 6-3$$

Where;

corrosion rate = fireside corrosion rate in $\mu\text{m/k.hr}$

A = tube position factor (leading or non-leading);

B = material factor for austenitic steels

T_g = average flue gas temperature (range: 870 - 1200°C)

T_m = tube metal temperature (range: 605°C - 680°C)

%Cl = average fuel chlorine composition (wt %).

The alloy and fuel variables expressed in equations 6-4 and 6-5 are in natural log form (framework model F). To construct the scatterplot and compare with the PE-8 version, the predicted values of the corrosion rate for the PCA/PLS models have been converted from natural log to original values.

$$\begin{aligned} \text{Corrosion rate (PCA)} = & 16.55 - 10.47 \frac{1000}{T_{\text{metal}} \cdot (K)} + 0.61 \cdot (T_g - T_m)(K) \\ & - 0.24 \cdot C_{\text{alloy}}(\text{wt}\%) - 0.02 \cdot Mn_{\text{alloy}}(\text{wt}\%) + 0.10 \cdot P_{\text{alloy}}(\text{wt}\%) + 0.04 \cdot S_{\text{alloy}}(\text{wt}\%) \\ & - 0.31 \cdot Si_{\text{alloy}}(\text{wt}\%) - 0.33 \cdot Cr_{\text{alloy}}(\text{wt}\%) - 0.08 \cdot Ni_{\text{alloy}}(\text{wt}\%) + 0.29 \cdot Mo_{\text{alloy}}(\text{wt}\%) \\ & - 0.54 \cdot Ti_{\text{alloy}}(\text{wt}\%) + 0.02 \cdot V_{\text{alloy}}(\text{wt}\%) \\ & + 0.25 \cdot Na_{\text{fuel}}(\text{wt}\%) + 0.09 \cdot K_{\text{fuel}}(\text{wt}\%) + 0.05 \cdot Al_{\text{fuel}}(\text{wt}\%) \\ & + 0.18 \cdot Fe_{\text{fuel}}(\text{wt}\%) + 0.08 \cdot Si_{\text{fuel}}(\text{wt}\%) + 0.97 \cdot Cl_{\text{fuel}}(\text{wt}\%) \\ & - 0.99 \cdot S_{\text{fuel}}(\text{wt}\%) + 0.21 \cdot Ti_{\text{fuel}}(\text{wt}\%) \end{aligned} \quad \mathbf{6-4}$$

$$\begin{aligned} \text{Corrosion rate (PLS)} = & 18.88 - 15.70 \frac{1000}{T_{\text{metal}} \cdot (K)} + 0.73 \cdot (T_g - T_m)(K) \\ & - 0.27 \cdot C_{\text{alloy}}(\text{wt}\%) - 0.25 \cdot Si_{\text{alloy}}(\text{wt}\%) - 0.41 \cdot Cr_{\text{alloy}}(\text{wt}\%) + 0.15 \cdot Mo_{\text{alloy}}(\text{wt}\%) \\ & + 0.13 \cdot Na_{\text{fuel}}(\text{wt}\%) - 0.21 \cdot Ca_{\text{fuel}}(\text{wt}\%) + 1.40 \cdot Cl_{\text{fuel}}(\text{wt}\%) \\ & - 0.45 \cdot S_{\text{fuel}}(\text{wt}\%) \end{aligned} \quad \mathbf{6-5}$$

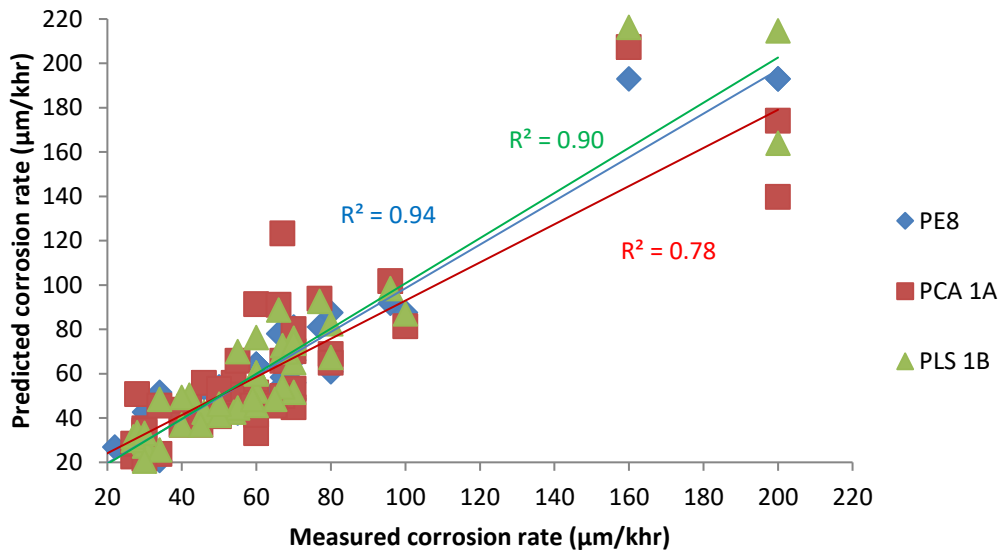


Figure 6-7: Comparison of measured corrosion rate with predicted rates from PE-8 model, PCA model 1A, and PLS model 1B (PE-8 UK data subset 1)

The scatterplot in Figure 6-7 shows a good predictive performance (high R^2) for all three models for the UK data; i.e. PE-8, PCA and PLS models. The PE-8 model ties with the PLS model as the best performing model judging from the high percentage of variation it explains (i.e. R^2). It follows that the fuel element, Cl, does have a controlling rate in the corrosion mechanism for UK coals for the range of boiler operating conditions considered in this data and with austenitic steels as established in chapter 4. To ascertain if this translates to US coal and operating conditions, the PE-8 model was applied to the US coal data and plotted on a scatterplot alongside the derived PCA and PLS US model (section 6.4.2).

6.4.2 PE-8 vs PCA, PLS Models (US data subset 5)

This subsection shows the PE-8 model (equation 6-3), PCA model 5A (equation 6-6), and PLS model 5B (equation 6-7), for the US coal data subset 5. The leading tube (SH/RH) position was assumed for the US data. The scatterplots for all three (i.e. predicted corrosion rates against the measured corrosion rates) are displayed in Figure 6-8.

$$\begin{aligned}
\text{Corrosion rate (PCA)} = & -2.29 + 2.04 \frac{1000}{T_{\text{metal}} \cdot (K)} + 0.78 \cdot (T_g - T_m)(K) \\
& - 0.08 \cdot Mn_{\text{alloy}}(\text{wt}\%) - 0.09 \cdot P_{\text{alloy}}(\text{wt}\%) - 0.05 \cdot S_{\text{alloy}}(\text{wt}\%) - 0.21 \cdot Si_{\text{alloy}}(\text{wt}\%) \\
& + 0.09 \cdot Cr_{\text{alloy}}(\text{wt}\%) - 0.04 \cdot Ni_{\text{alloy}}(\text{wt}\%) + 0.005 \cdot Nb_{\text{alloy}}(\text{wt}\%) \\
& + 0.05 \cdot Ti_{\text{alloy}}(\text{wt}\%) + 0.11 \cdot Cu_{\text{alloy}}(\text{wt}\%) + 0.04 \cdot N_{\text{alloy}}(\text{wt}\%) \\
& - 0.17 \cdot Ce_{\text{alloy}}(\text{wt}\%) + 0.37 \cdot Ta_{\text{alloy}}(\text{wt}\%) \\
& + 0.04 \cdot Na_{\text{fuel}}(\text{wt}\%) + 0.05 \cdot K_{\text{fuel}}(\text{wt}\%) + 0.04 \cdot Mg_{\text{fuel}}(\text{wt}\%) \\
& + 0.07 \cdot Ca_{\text{fuel}}(\text{wt}\%) + 0.23 \cdot Fe_{\text{fuel}}(\text{wt}\%) + 0.11 \cdot Si_{\text{fuel}}(\text{wt}\%) \\
& + 0.11 \cdot Cl_{\text{fuel}}(\text{wt}\%) - 0.02 \cdot S_{\text{fuel}}(\text{wt}\%) + 0.05 \cdot Ti_{\text{fuel}}(\text{wt}\%) \\
& - 0.25 \cdot P_{\text{fuel}}(\text{wt}\%) + 0.12 \cdot Mn_{\text{fuel}}(\text{wt}\%)
\end{aligned}
\tag{6-6}$$

$$\begin{aligned}
\text{Corrosion rate (PLS)} = & -1.26 + 1.19 \frac{1000}{T_{\text{metal}} \cdot (K)} + 0.84 \cdot (T_g - T_m)(K) \\
& + 0.24 \cdot Mo_{\text{alloy}}(\text{wt}\%) \\
& + 0.06 \cdot Na_{\text{fuel}}(\text{wt}\%) + 0.05 \cdot K_{\text{fuel}}(\text{wt}\%) + 0.01 \cdot Mg_{\text{fuel}}(\text{wt}\%) - 0.06 \cdot Ca_{\text{fuel}}(\text{wt}\%) \\
& + 0.25 \cdot Fe_{\text{fuel}}(\text{wt}\%) + 0.15 \cdot Si_{\text{fuel}}(\text{wt}\%) + 0.15 \cdot Cl_{\text{fuel}}(\text{wt}\%) \\
& - 0.01 \cdot S_{\text{fuel}}(\text{wt}\%) + 0.05 \cdot Ti_{\text{fuel}}(\text{wt}\%) - 0.26 \cdot P_{\text{fuel}}(\text{wt}\%) \\
& + 0.14 \cdot Mn_{\text{fuel}}(\text{wt}\%)
\end{aligned}
\tag{6-7}$$

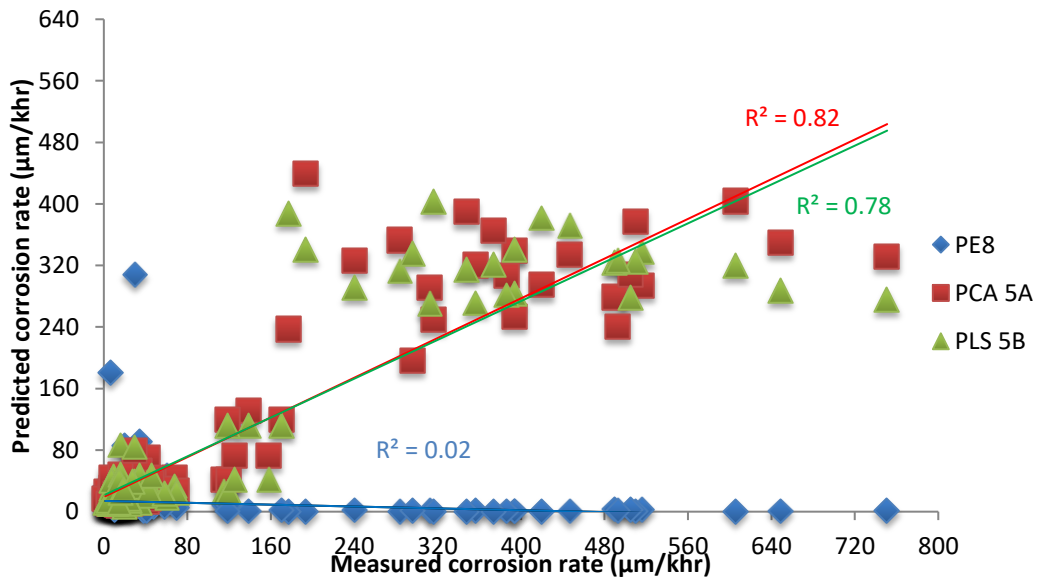


Figure 6-8: Comparison of measured corrosion rate with predicted rates from PE-8 model, PCA model 5A, and PLS model 5B (US data subset 5)

The CEGB derived PE-8 model has been observed to outperform the current PCA model in data subset 1 (UK data; Figure 6-7). However, the PE-8 model performed poorly when applied to US (coal) data (Figure 6-8) compared to the PCA and PLS models. This is an example where the assumption of Cl as a marker for the fuel corrosivity was deemed inaccurate as the PE-8 model did not fit the US data. There are differences in the coals and in the boiler operating practices in different regions that may invalidate, say, a direct translation of the UK experience with the US boiler/fuel conditions (James *et al.*, 1997; Wright and Krause, 1997a). Hence other (different) input parameters may be required to model (fireside) corrosion conditions for UK coal, US coal and biomass-fired combustion systems

6.5 Applicability of PCA/PLS Fireside Corrosion Models

The main feature in this research is the use of corrosion data generated from plant investigations to derive PCA/PLS prediction models. Plant tests offer more credible corrosion rate measurements as the tube materials are subjected to longer exposure times, which reflect real life plant conditions. Although laboratory tests allow for more controlled conditions, the exposure time is usually around 1000 hours, while field exposures can be up to 20,000 hours providing a more realistic representation of actual boiler conditions. Also, field exposures allow for the evaluation of important environmental parameters that cannot be fully replicated in the laboratory (Wright and Krause, 1997b; Simms, 2011a). Therefore, as the data used in this research represents more realistic plant conditions, the corrosion models developed will potentially enable plant lifetime extensions as conventional assumptions can be identified. This would allow for the assessment of the potential impacts of an increasingly wide range of fuels on superheater and reheater materials based on their compositions. The prediction models derived would also enable the identification of key aspects of the fireside corrosion-resistant materials which could provide a basis for the selection of alternative material that could be used in future plants or form the basis for the development of protective coating systems.

7 CONCLUSIONS

This PhD research has developed a suite of corrosion models that will predict the degree of fireside corrosion of superheaters and reheaters as a function of the fuel, boiler operating conditions and the boiler tube (SH/RH) materials. The approach to modelling uses statistical data analysis techniques (PCA, PLS) to reduce the dimensionality of large datasets and maximise variability of the data to produce predictive models. Different modelling parameters were selected from sixteen data subsets. This chapter provides a summary of the outcome of this research.

Data Collection and Gathering:

A corrosion database has been formed linking datasets from various plant investigations on materials' fireside corrosion performance. Plant data was exclusively used in this research which affords the benefit of relying on credible corrosion rate data to develop fireside corrosion models. The issues in utilising the corrosion datasets (e.g. assumptions for missing data, transformation of variables etc.) have been addressed during the development of the corrosion models and in their evaluation (section 4.1.1).

Data Analysis and Model Development:

The input parameters strongly associated with the corrosion rate were established using the PCA and PLS statistical techniques and these variables have been used to build the predictive models.

The corrosion models derived from data subsets 1 (UK coal data, austenitic tubes, leading tube position), and data subset 10, (woody biomass data, for austenitic tubes) culled from plant investigations in the UK, closely align with the literature. Notably, for data subset 1, Cl has a higher influence on the ($\ln$) corrosion rate as S is in excess, but the selection process also includes other modelling parameters that represent corrosive conditions in specific coal/biomass combustion environments. The woody biomass data subset represents a relatively benign environment and the associated fireside corrosion model suggests the metal temperature does not have the expected increasing effect on the corrosion rate as discussed in chapter 4, except where ferritic materials or coatings are employed (i.e. biomass corrosion models 12 and 13).

Comparing model 1 (from UK coal data for austenitic tubes, leading position) and model 5 (from US coal data for austenitic tubes); there are similarities in the corrosive potential of the fuel derived elements, but significant differences on the impact of alloying elements. This is particularly apparent in the PLS model 5B (US coal data), which shows zero association of the corrosion rate with the alloying elements (except Mo). The implication is that fireside corrosion is impacted more by the fuel composition than the alloying composition for the range of conditions presented in data subset 5 and that alloy variations are not likely to significantly alter the degradation of these heat exchanger materials. However, it is important to note that the UK and US plants exposed different heat exchanger tube materials (see Table 3-2 and Table 3-5).

The co-firing models (for data subsets 14 and 15) indicate a non-protective influence from the alloy compositions including Cr; instead the corrosion potential is enhanced by the presence of fuel species particularly K, Mg, Cl, S and P. The model for ferritic steels in a co-firing environment (model 16), however, appears to be strongly impacted by the metal temperature and no other predictor variables defines that model. The strong influence of the metal temperature on the corrosion rate for ferritic alloys is a common feature for the combustion environments studied in this work.

The coatings model spans across three fuel types, and exposure conditions – US coal, world traded coal and biomass data (models 7, 9 and 13 respectively); hence the results are varied. The US (fireside corrosion) model 7 ascribed more importance on the fuel element, P; and the metal temperature exhibits a higher influence in corrosion model 9. For the biomass coatings model 13, S (fuel) is revealed as more rate controlling, even more so than the coatings material which suggests that coatings may not be beneficial in this biomass-fired environment.

Variation of PCA/PLS derived models:

Different model variants were tested, a sensitivity analysis on the Cr content was performed, and the effects on the model parameters and performance were reviewed. A summary conclusion is presented below:

- The results from the different framework models outlined in section 4.2.1 (chapter 4) were similar in terms of the variables selected for model building with some minor variations (full details in Appendices C and D).
- Data sensitivity analysis was done to establish if a slight change in the values of the input variables significantly affects the variables selected for model building and the regression estimates. The Cr content was varied from maximum to minimum values, and the results showed no change in the regression outcome underscoring the effectiveness of the technique employed.
- Following the assessment on the practicality of combining highly correlated variables from the loadings plot (PCA modelling), the result did not reveal additional insight on the corrosion behaviour in UK conditions, although the PCA model was improved. One of the main drawbacks was the need to forego combination of two different classes of variables (alloy and fuel, for instance) hence this technique may be more effective if only one group of variables; e.g. fuel elements or alloy elements but not both, are being analysed.
- Lastly, the PCA/PLS models with the interaction terms, i.e. $S \times (Na + K)$ for the coal models and $Cl \times (Na + K)$ for the biomass models; were developed to ascertain the association of the input variables and how they correlate (if at all) with the corrosion rate. The interaction parameter for coal correlates positively with the corrosion rate for the US coal data (PLS model); and for the woody biomass data, the interaction parameter correlates positively with the corrosion rate (PCA model). The results from the PLS model for the UK coal data showed no significant correlation (not selected for model building); and for the PCA model, there was a negative correlation. The main deductions, however, are similar to the original PCA/PLS derived models.

Model Performance and Validation:

Statistical measures were used to validate the model (graphical residual analysis) with satisfactory outcomes save for PCA/PLS models 7A and 7B (US coal coatings data), PCA/PLS models 9A and 9B (UK coatings data with world-traded coal) and PCA/PLS models 16A and 16B (co-firing data with ferritic steels).

The performance of the models as determined by the Root Mean Square Error (RMSE) and the coefficient of determination (R^2) shows a close fit to the measured corrosion data (with few exceptions) and confirms reliability of the technique to produce stable regression estimates. However, the values of variables in the data to be analysed must be dissimilar enough for the technique to work optimally. This is the main reason why the model performances of PCA/PLS models 3 (Ferritic data subset, leading position) and PCA/PLS models 4 (Ferritic data subset, non-leading position) have been poor.

Performance of PCA vs PLS Models:

The PLS technique produced comparatively better performing predictive models with fewer required input parameters, usually half of what is needed in PCA to build the fireside corrosion model. Thus, PCA's main problem appears to be a tendency to over-fit data.

While the PCA and PLS models show the potential impacts of alloying and fuel types on fireside corrosion, this can only be for the range of alloys and combustion conditions studied. These statistical analysis techniques (PCA, PLS), however, can be applied to other similar datasets. More information on the PCA/PLS modelling technique is detailed in Appendix G.

8 RECOMMENDATIONS FOR FUTURE WORK

This research has successfully deployed two statistical techniques, PCA and PLS, to build fireside corrosion models. While this is a good start in developing fireside corrosion models for different plant conditions, there are some recommendations for consideration to improve the application of the technique and for the development of corrosion models.

PCA/PLS Technique:

- The eigenvalue selection criteria (< 0.5) adopted in this work for PCA is based on suggestions from the literature and not a statistically justified value as there is currently little consensus on the appropriate selection criteria. A paper by Foucart (2000) addresses the PC selection criteria. On PLS, the cross-validation method for PLS component selection and model validation is better suited for large datasets (entries over 100). The k-fold cross-validation technique advocated by Bouckaert *et al* (2011) is a more complicated but effective way of selecting PLS components and should be explored further.
- The algorithm for PCA, adopted from the literature (Foucart, 2000; Fekedulegn *et al.*, 2002; Jolliffe, 2002; Liu *et al.*, 2003) and accomplished using different modules, was successfully applied albeit in a roundabout mode in STATISTICA; e.g. the varimax rotation module. This is a limitation of STATISTICA. Thus, a suitable platform that links the major steps seamlessly can be investigated.

The Corrosion Model:

- Additional co-firing data, UK coatings data (coal-fired), nickel-based (woody) biomass data, and ferritic (woody) biomass data are recommended to properly authenticate the corrosion model.
- The selection of Ti (fuel component) for model building (especially for US coal data) warrants further investigation for a better understanding of the corrosion mechanism so spurious variables can be identified and excluded.
- The PCA/PLS interaction model is a means of accounting for the interaction of the input variables and how this association affects the corrosion rate. However

only one input interaction variant has been investigated; i.e. $S \times (Na+K)$ for coal models, and $Cl \times (Na+K)$ for biomass models. It is recommended that other input variable interactions be explored.

- Variations of the Arrhenius model equation (framework models) were tested and no definite conclusion as to which framework best defines the fireside corrosion model has been established. The author has chosen to use framework model F to illustrate the results because it provided a better fit to the data for the PLS models in particular, but there have been few instances where other model cases have enhanced performance. Ultimately, the variables selected for model building for all the frameworks were similar (also dependent on the number of PCA/PLS components used); although the regression coefficients are different and as such, it is recommended that the corrosion model should be viewed on a case by case basis.
- The UK coal models involving ferritic tube material (i.e. model 3, leading tube position; and model 4, non-leading tube position) have been unsuccessful using the PCA and PLS techniques and the dataset needs to be expanded to include more variation in ferritic alloys for the technique to work. However, the outcome of the nickel-based US coal model (data subset 11) has been equally poor. It appears the Arrhenius model (lower temperature portion of the bell-shaped temperature-corrosion rate curve) is unsuitable for this data (i.e. the US nickel-based data subset 6) and a different model structure needs to be investigated for corrosion data involving nickel-based alloys in coal-fired combustion systems.
- The graphical residual analysis plot for the US coal coatings data (model 7) revealed nonconformities (i.e. patterns on the plots) especially with data entries from specific coating materials in USC conditions. It may be necessary to do a separate analysis for subcritical and USC conditions.

REFERENCES

- Abdi, H. (2003) *Partial Least Squares (PLS) Regression*. Texas.
- Abdul-Wahab, S. A., Bakheit, C. S. and Al-Alawi, S. M. (2005) 'Principal Component and Multiple Regression Analysis in Modelling of Ground-level Ozone and Factors Affecting its Concentrations', *Environmental Modelling and Software*, 20(10), pp. 1263–1271.
- Afifi, A., May, S. and Clark, V. A. (2012) *Practical Multivariate Analysis*. Fifth. Florida: Taylor & Francis Group, LLC.
- Agbor, E., Zhang, X. and Kumar, A. (2014) 'A Review of Biomass Co-firing in North America', *Renewable and Sustainable Energy Reviews*, 40, pp. 930–943. doi: 10.1016/j.rser.2014.07.195.
- Akarachantachote, N., Chadcham, S. and Saithanu, K. (2014) 'Cutoff Threshold of Variable Importance in Projection for Variable Selection', *International Journal of Pure and Applied Mathematics*, 94(3), pp. 307–322. Available at: <http://www.ijpam.eu/contents/2014-94-3/2/>.
- Ambrose, J. (2015) *Rudd Confirms Coal Closures by 2025, Utility Week*. Available at: <https://utilityweek.co.uk/rudd-confirms-coal-closures-by-2025/#.V1GVlpErLcs> (Accessed: 8 November 2015).
- Antunes, R. A. and de Oliveira, M. C. L. (2013) 'Corrosion in Biomass Combustion: A Materials Selection Analysis and its Interaction with Corrosion Mechanisms and Mitigation Strategies', *Corrosion Science*. Elsevier Ltd, 76, pp. 6–26. doi: 10.1016/j.corsci.2013.07.013.
- ATC-CES (2018) *Design - Structural - HRSG*. Available at: <https://atc-ces.com/fitness-for-service> (Accessed: 22 November 2018).
- Aung, N. N. and Liu, X. (2014) 'Effect of Temperature on Coal Ash Hot Corrosion Resistance of Inconel 740 Superalloy', *Corrosion Science*. Elsevier Ltd, 82, pp. 227–238. doi: 10.1016/j.corsci.2014.01.020.
- Babcock and Wilcox Energy Solutions (2018) *Subcritical Boilers, TBWES*. Available

at: <http://www.tbwes.com/products/subcritical-boilers/> (Accessed: 22 November 2018).

Bains, M. and Robinson, L. (2016) *Material Comparators For End-Of-Waste Decisions : Manufactured Fertilisers*. Bristol: Environment Agency.

Bair, E., Hastie, T., Paul, D. and Tibshirani, R. (2006) 'Prediction by Supervised Principal Components', *Journal of the American Statistical Association*, 101(473), pp. 119–137. doi: 10.1198/016214505000000628.

Baxter, B., Fensom, A. and Hoong, N. W. (2018) 'Coal News', *World Coal*, May, pp. 5–6. Available at: www.worldcoal.com.

Beér, J. M. (2007) 'High Efficiency Electric Power Generation; The Environmental Role', *Progress in Energy and Combustion Science*, 33(2), pp. 107–134. doi: 10.1016/j.pecs.2006.08.002.

Blakeslee, T. R. (2009) *Can Biomass Replace Coal?*, *Renewable Energy World*. Available at: <http://www.renewableenergyworld.com/articles/2009/06/can-biomass-replace-coal.html> (Accessed: 19 January 2016).

Blough, J. L. and Seitz, W. W. (no date) *Fireside Corrosion Testing of Candidate Superheater Tube Alloys, Coatings, and Claddings - Phase III*. New Jersey.

Blough, J. L., Seitz, W. W. and Girshik, A. (1998) *Fireside Corrosion Testing of Candidate Superheater Tube Alloys Coatings, and Claddings - Phase II Field Testing*, ORNL/Sub/93-SM401/02. Livingston, New Jersey.

Blough, J. L., Stanko, G. J., Bakker, W. T. and Brooks, J. B. (2000) 'Superheater corrosion in ultra-supercritical power plants', in *Corrosion 2000*. Houston, Texas: Nace International.

Borio, R. W., Hensel, R. P., Ulmer, R. C., Wilson, E. B. and Leonard, J. W. (1968) *Study of Means for Eliminating Corrosiveness of Coal to High Temperature Surfaces of Steam Generating Units - II*.

Bouckaert, R. R., Frank, E., Holmes, G. and Fletcher, D. (2011) 'A Comparison of Methods for Estimating Prediction Intervals in NIR Spectroscopy: Size Matters', *Chemometrics and Intelligent Laboratory Systems*. Elsevier B.V., 109(2), pp. 139–145.

doi: 10.1016/j.chemolab.2011.08.008.

BP PLC (2018) 'Coal', in *BP Statistical Review of World Energy*. 67th Editi. London, pp. 36–40. Available at: <https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review/bp-stats-review-2018-full-report.pdf>.

Broström, M., Enestam, S., Backman, R. and Mäkelä, K. (2013) 'Condensation in the KCl-NaCl System', *Fuel Processing Technology*, 105, pp. 142–148.

Bryant, F. B. and Yarnold, P. R. (1995) 'Principal-Components Analysis and Exploratory and Confirmatory Factor Analysis', in Grimm, L. G. and Yarnolds, P. R. (eds) *Reading and Understanding Multivariate Statistics*. Washington, DC: American Psychological Association, pp. 99–136.

Bryers, R. W. (1978) *Ash Deposits and Corrosion Due to Impurities in Combustion Gases*. Edited by R. W. Bryers. Washington: Hemisphere Publishing Corporation.

Camperos, S. (2016) *Statistical Lifetime Modeling of Fe-Ni-Cr Alloys for High Temperature Corrosion in Waste to Energy Plants and Metal Dusting in Syngas Production Plants*. Institut National Polytechnique de Toulouse (INP Toulouse).

Camperos, S., Brossard, J. M., Floquet, P. and Monceau, D. (2015) 'Statistical Lifetime Modeling of Fe-Ni-Cr Alloys Subject to High-Temperature Corrosion in Waste-to-Energy Production Units', *Corrosion*, 71(11), pp. 1360–1369.

Chattopadhyay, P. (2013) *Boiler Operation Engineering*. 3rd Editio. McGraw-Hill Education.

Chelgani, S. C., Mesroghli, S. and Hower, J. C. (2010) 'Simultaneous Prediction of Coal Rank Parameters Based on Ultimate Analysis using Regression and Artificial Neural Network', *International Journal of Coal Geology*. Elsevier B.V., 83(1), pp. 31–34. doi: 10.1016/j.coal.2010.03.004.

Chou, M. I. ., Lytle, J. M., Kung, S. C. and Ho, K. K. (1999) *Effects of Chlorine In Coal On Boiler Superheater/Reheater Corrosion*. Illinois. Available at: [https://web.anl.gov/PCS/acsfuel/preprint archive/Files/44_1_ANAHEIM_03-99_0167.pdf](https://web.anl.gov/PCS/acsfuel/preprint_archive/Files/44_1_ANAHEIM_03-99_0167.pdf).

Clapp, R. M. (1991) *Modern Power Station Practice: Boilers and Ancillary Plant*. 3rd edn. New York: Pergamon Press.

CoalTech Pty Ltd (2007) *Combustion, Coal Technology*. Available at: <http://coaltech.com.au/Combustion.html#Topic40>.

Collins, B. (2010) *Partial Least Squares Regression, LPAC Seminar*. Available at: <http://vision.cse.psu.edu/seminars/talks/PLSPresentation.pdf> (Accessed: 2 October 2018).

Comrey, A. and Lee, H. (1992) *A First Course in Factor Analysis*. Hillsdale, New Jersey: Erlbaum.

Cox, I. (2013) *Discovering Partial Least Squares with JMP*. Cary, N.C: SAS Institute.

Dean, J. (2009) *Choosing the Right Type of Rotation in PCA and EFA, Shiken: JALT Testing & Evaluation SIG Newsletter*.

Department of Energy and Climate Change (2014) *Technical Assessment of the Operation of Coal and Gas Fired Plants*. Available at: <https://www.gov.uk/government/publications/technical-assessment-of-the-operation-of-coal-gas-fired-plants>.

Dijkstra, T. K. (2010) 'Latent Variables and Indices: Herman Wold's Basic Design and Partial Least Squares', in Vinzi, V. E., Chin, W. W., Henseler, J., and Wang, H. (eds) *Handbook of Partial Least Squares*. Berlin Heidelberg: Springer-Verlag. doi: 10.1007/978-3-540-32827-8_2.

Doosan Babcock (2011) *BP-11-024*.

Dunn, K. (2016) *Process Improvement Using Data*. Edited by T. Wilson. Available at: <http://learnche.org/pid>.

Dunteman, G. H. (1989) *Principal Components Analysis*. Newbury Park: Sage Publications, INC.

E.ON Technologies (2015a) *ETG/15/ASI/MA/364/R*.

E.ON Technologies (2015b) *ETG/15/ASI/MA/837/R*.

E.ON UK (2004) *COAL R267 DTI/Pub URN 04/1795*.

ECPK (2016) *Modern Power Generation, Engineering Timelines*. Available at: <http://www.engineering-timelines.com/> (Accessed: 15 January 2016).

Energieonderzoek Centrum Nederland (ECN) Phyllis2 (2012) *Database for Biomass and Waste, Phyllis Database*. Available at: <https://www.ecn.nl/phyllis2/> (Accessed: 9 September 2016).

Epelbaum, G., Hanson, E. and Seitz, M. (2010) ‘New Generation of Tube Surface Treatments Help Improve EFW Boiler Reliability’, in *Proceedings of the 18th Annual North American Waste-to-Energy Conference*. Florida, pp. 1–12.

European Commission (2016) *Large Combustion Plants Directive, European Commission - Environment*. Available at: <http://ec.europa.eu/environment/archives/industry/stationary/lcp/legislation.htm> (Accessed: 9 January 2019).

Farres, M., Platikanov, S., Tsakovski, S. and Tauler, R. (2015) ‘Comparison of the Variable Importance in Projection (VIP) and of the Selectivity Ratio (SR) Methods for Variable Selection and Interpretation’, *Journal of Chemometrics*, 29(10), pp. 528–536.

Fekedulegn, B. D., Colbert, J. J., Hicks, R. R., Schuckers, M. E., Service, F., Fekedulegn, B. D., Colbert, J. J., Hicks, R. R. and Schuckers, M. E. (2002) *Coping with Multicollinearity: An Example on Application of Principal Components Regression in Dendroecology*, United States Department of Agriculture.

Foucart, T. (2000) ‘A Decision Rule for Discarding Principal Components in Regression’, *Journal of Statistical Planning and Inference*, 89(1–2), pp. 187–195. doi: 10.1016/S0378-3758(99)00216-5.

Francis, W. and Peters, M. C. (1980) *Fuels and Fuel Technology: A Summarized Manual (SI)*. Second. Oxford: Pergamon Press Limited.

Garson, G. D. (2014) *Partial Least Squares Regression and Structural Equation Models: 2016 Edition*. 2016 Editi. Statistical Associates Publishers.

- Gibb, W. . and Angus, J. G. (1983) ‘Release of Potassium from Coal During Bomb Combustion’, *Journal of the Institute of Energy*, 56, pp. 149–157.
- Gibb, W. H., Jones, A. R. and Wigley, F. (1993) ‘The UK Collaborative Research Programme on Slagging in Pulverised Coal Furnaces: Results of Full-Scale Plant Trials’, in Williamson, J. and Wigley, F. (eds) *The Impact of Ash Deposition on Coal Fired Plants*. Solihull: Taylor & Francis, pp. 3–18.
- Green Trade Australia (2018) *Indonesian Coal, Green Trade Australia*. Available at: http://www.greentradeaustralia.com/indonesian_coal_11.html.
- Grimwood, T. (2016) ‘Coal Plants Could Be Allowed to Run Beyond 2025: Report’, *Utility Week*, June. Available at: <http://utilityweek.co.uk/news/>.
- Harb, J. N., Munson, C. L. and Richards, G. H. (1993) ‘Use of Equilibrium Calculations to Predict the Behavior of Coal Ash in Combustion Systems’, *Energy & Fuels*, 7(2), pp. 208–214. doi: 10.1021/ef00038a008.
- Harvey, R. D. and Ruch, R. R. (1985) *Overview of Mineral Matter in U.S Coals*, ACS Fuel.
- Higgins, R. A. (2006) *Materials for Engineers and Technicians*. 4th edn. Newnes.
- Hotelling, H. (1957) ‘The Relations of the Newer Multivariate Statistical Methods to Factor Analysis’, *Journal of Statistical Psychology*, 10, pp. 69–79.
- Huang, L. Y., Norman, J. S., Pourkashanian, M. and Williams, A. (1996) ‘Prediction of Ash Deposition on Superheater Tubes from Pulverized Coal Combustion’, *Fuel*, 75(3), pp. 271–279. doi: 10.1016/0016-2361(95)00220-0.
- Huggins, F. E., Seidu, L. B. A., Shah, N., Huffman, G. P., Honaker, R. Q., Kyger, J. R., Higgins, B. L., Robertson, J. D., Pal, S. and Seehra, M. S. (2009) ‘Elemental Modes of Occurrence in an Illinois #6 Coal and Fractions Prepared by Physical Separation Techniques at a Coal Preparation Plant’, *International Journal of Coal Geology*, 78(1), pp. 65–76. doi: 10.1016/j.coal.2008.10.002.
- Hurley, J. P., Benson, S. A. and Mehta, A. K. (1993) ‘Ash Deposition at Low Temperatures in Boilers Burning High-Calcium Coals’, in Williamson, J. and Wigley,

F. (eds) *The Impact of Ash Deposition on Coal Fired Plants*. Taylor and Fancis, pp. 19–30.

Hustad, J. and Barrio, M. (2015) *What is Biomass?*, *Combustion Handbook*. Available at: <http://www.handbook.ifrf.net/handbook/cf.html?id=23> (Accessed: 30 January 2015).

IEA Clean Coal Centre (2010) *Pulverised Coal Combustion*. Available at: www.iea-coal.org.uk (Accessed: 3 December 2015).

International Energy Agency (2018a) *Energy Efficiency 2018 - Analysis and Outlooks to 2040*, IEA Publications. doi: 10.1007/978-3-642-41126-7.

International Energy Agency (2018b) *India: New Procedure to Reduce Pollution From Coal-Fired Power Plants*, Newsroom. Available at: <https://www.iea.org/newsroom/news/2018/> (Accessed: 14 August 2018).

International Energy Agency (2019) *Global Energy & CO₂ Status Report: Emissions*, IEA Publications. Available at: <https://www.iea.org/geco/emissions/>.

James, P. J., Robinson, M. T. and Gibb, W. H. (1997) ‘Effect of Fuel Chlorine on the Fireside Corrosion of Ferritic Furnace Wall and Superheater/Reheater Tubing - A U.K. Perspective’, in *Possible Effects of the Chlorine Content of Coal on Fireside Corrosion in Pulverized Coal-Fired Boilers (Volume 2)*. Nottingham, pp. 93–246.

Jeffers, J. N. . (1967) ‘Two Case Studies in the Application of Principal Component Analysis’, *Applied Statistics*, 16, pp. 225–236.

Jenkins, B. ., Baxter, L. ., Miles, T. . and Miles, T. . (1998) ‘Combustion Properties of Biomass’, *Fuel Processing Technology*, 54(1–3), pp. 17–46. doi: 10.1016/S0378-3820(97)00059-3.

Johannesen, O. and Anderson, A. G. (1989) *Selected Topics in High Temperature Chemistry - Defect Chemistry of Solids*. Edited by A. G. A. Oivind Johannesen. Amsterdam: Elsevier Science Publishers.

Joliffe, I. T. (1982) ‘A Note on the Use of Principal Components in Regression’, *Applied Statistics*, 31(3), pp. 300–303.

Joliffe, I. T. (2002) *Principal Component Analysis*. Second. New York: Springer-

Verlag.

Jolliffe, I. T. (2002) *Principal Component Analysis*. Second Edi. New York: Springer-Verlag.

Kiameh, P. (2013) *Power Generation Handbook*. Second. New Delhi: McGraw Hill Education (India) Private Limited.

Kumar, A. and Goyal, P. (2011) 'Forecasting of Air Quality in Delhi using Principal Component Regression Technique', *Atmospheric Pollution Research*. Elsevier, 2(4), pp. 436–444. doi: 10.5094/APR.2011.050.

Kumari, A., Das, S. K. and Srivastava, P. K. (2017) 'Data Driven Modeling of Fireside Corrosion Rate', *Anti-Corrosion Methods and Materials*, 64(4), pp. 397–404.

Lai, G. Y. (2007a) *High-Temperature Corrosion and Materials Applications*. Ohio, USA: ASM International. doi: 97816155030552.

Lai, G. Y. (2007b) *High Temperature Corrosion and Materials Applications*. Ohio, USA: ASM International.

Langholtz, B. M. H. J., Stokes, L. M. and Eaton (2016) *2016 BILLION-TON REPORT Advancing Domestic Resources for a Thriving Bioeconomy*, Oak Ridge National Laboratory. doi: ORNL/TM-2016/160.

Lant, T., Keefe, C., Davies, C., McGhee, B., Simms, N. and Fry, T. (2010) 'Modeling Fireside Corrosion of Heat Exchanger Materials in Advanced Energy Systems', in *6th International Conference on Advances in Materials Technology for Fossil Power Plants*. EPRI, USA.

Laumb, J. D. (2008) 'Characteristics and Behaviour of Inorganic Constituents', in Tillman, D. A. and Miller, B. (eds) *Combustion Engineering Issues for Solid Fuels*. Academic Press, p. 528.

Lengyel, A., Heberger, K., Paksy, L., Banhidi, O. and Rajko, R. (2004) 'Prediction of Ozone Concentration in Ambient Air Using Multivariate Methods', *Chemosphere*, 57(8), pp. 889–896. doi: 10.1016/j.chemosphere.2004.07.043.

Li, J. (2001) *Linear, Ridge Regression, and Principal Component Analysis*. Available

at: <http://www.stat.psu.edu/jiali>.

Lind, T., Kauppinen, E. I., Jokiniemi, J. K., Maenhaut, W. and Pakkanen, T. A. (1993) 'Alkali Metal Behaviour in Atmospheric Circulating Fluidised Bed Coal Combustion', in Jim Williamson, F. W. (ed.) *The Impact of Ash Deposition on Coal Fired Plants. Proceedings of the Engineering Foundation Conference*. Solihull: Taylor & Francis.

Liu, R. X., Kuang, J., Gong, Q. and Hou, X. L. (2003) 'Principal Component Regression Analysis with SPSS', *Computer Methods and Programs in Biomedicine*, 71(2), pp. 141–147.

Lutz, B. S., Holcomb, G. R. and Meier, G. H. (2015) 'Determination of the Initiation and Propagation Mechanism of Fireside Corrosion', *Oxidation of Metals*. Springer US, 84(3), pp. 353–381. doi: 10.1007/s11085-015-9559-y.

Maalekian, M. (2007) *The Effects of Alloying Elements on Steels*.

Maitra, S. and Yan, J. (2008) *Principle Component Analysis and Partial Least Squares : Two Dimension Reduction Techniques for Regression, Discussion Paper Program*.

Mason, R. L. and Gunst, R. F. (1985) 'Selecting Principal Components in Regression', *Statistics & Probability Letters*, 3, pp. 299–301.

McDonald, D. K. (2001) *Coal Ash Corrosion Resistant Materials Testing Program Evaluation of the First Section Removed in November 2001*. Ohio, USA.

McGrath, M. (2015) *Will Coal Be On the Dole after COP21?*, *BBC News Science and Environment*. Available at: <https://www.bbc.co.uk/news/science-environment-34904127> (Accessed: 9 January 2019).

Mechanical Engineering Lectures (2017) *Vapour Power Cycles, Blogs, Mechanical Engineering*. Available at: <https://www.mechlectures.com/vapor-power-cycles/> (Accessed: 16 July 2019).

Mehmood, T., Liland, K. H., Snipen, L. and Sæbø, S. (2012) 'A Review of Variable Selection Methods in Partial Least Squares Regression', *Chemometrics and Intelligent Laboratory Systems*. Elsevier B.V., 118(July 2017), pp. 62–69. Available at: <http://dx.doi.org/10.1016/j.chemolab.2012.07.010>.

- Michelsen, H. P., Frandsen, F., Dam-Johansen, K. and Larsen, O. H. (1998) 'Deposition and High Temperature Corrosion in a 10 MW Straw Fired Boiler', *Fuel Processing Technology*, 54(1–3), pp. 95–108. doi: 10.1016/S0378-3820(97)00062-3.
- Miller, B. G. (2011) *Clean Coal Engineering Technology*. Burlington, MA: Elsevier Inc.
- Mooney, C. and Dennis, B. (2019) *In Blow to Climate Change, Coal Plants Emitted More than Ever in 2018*, *The Washington Post*.
- Naik, G. R. (2018) *Advances in Principal Component Analysis*. Edited by A. Ganesh R. Naik (BENS Research Group, MARCS Institute, Western Sydney University. Singapore: Springer Nature Singapore Pte Ltd. doi: 10.1007/978-981-10-6704-4.
- Natesan, K., Purohit, A. and Rink, D. L. (2003) *Fireside Corrosion of Alloys for Combustion Power Plants*. Illinois.
- Nelson, W. and C. Cain, J. (1960) 'Corrosion of Superheaters and Reheaters of Pulverized Coal-fired Boilers', *Trans. ASME J. Eng. Power*, 82A, pp. 194–204.
- Ng, K. S. (2013) *A Simple Explanation of Partial Least Squares*.
- Norfolk, M. (2005) *Industry in Knottingley and Ferrybridge, Knottingley and Ferrybridge* Online. Available at: https://web.archive.org/web/20060101075703/http://knottingley.org/today/industry_today.htm#Index (Accessed: 15 January 2016).
- Northern Mine Research Society (2016) *Coal Mining In The British Isles, Mine Information*. Available at: <https://www.nmrs.org.uk/mines-map/coal-mining-in-the-british-isles/> (Accessed: 19 November 2018).
- Oh, J. and Kwak, N. (2018) 'Robust PCAs and PCA Using Generalized Mean', in Ganesh R. Naik (BENS Research Group, MARCS Institute, Western Sydney University, A. (ed.) *Advances in principal Component Analysis*. Singapore: Springer Nature Singapore Pte Ltd, pp. 71–98. doi: 10.1007/978-981-10-6704-4.
- Okoro, S. C., Niessen, F., Villa, M., Apel, D., Montgomery, M., Frandsen, F. J. and Pantleon, K. (2017) 'Complementary Methods for the Characterization of Corrosion

Products on a Plant-Exposed Superheater Tube’, *Metallography, Microstructure, and Analysis*. Springer US, 6(1), pp. 22–35. doi: 10.1007/s13632-016-0325-6.

Osborne, D. (2013) *The Coal Handbook: Towards Cleaner Production*. Edited by D. Osborne. Woodhead Publishing.

Palmer, C. A., Oman, C. L., Park, A. J. and Luppens, J. A. (2015) *The U.S. Geological Survey Coal quality (COALQUAL) Database, Data Series 975*. Available at: <http://ncrdpublic.er.usgs.gov/coalqual/> (Accessed: 9 September 2016).

Pannell, D. J. (1997) ‘Sensitivity Analysis of Normative Economic Models: Theoretical Framework and Practical Strategies’, *Agricultural Economics*, 1(16(2)), pp. 139–152. Available at: <http://www.sciencedirect.com/science/article/pii/S0169515096012170>.

Pardoe, I. (2012) *Applied Regression Modelling*. Second. Hoboken, New Jersey: John Wiley & Sons.

Partnership for Policy Integrity (2016) *DOE’s “Billion Ton” Biomass Report, PFPI Reports*. Available at: <https://www.pfpi.net/does-billion-ton-biomass-report-we-read-it-so-you-wouldnt-have-to> (Accessed: 11 April 2019).

Patel, S. J., De Barbadillo, J. J., Baker, B. A. and Gollihue, R. D. (2013) ‘Nickel base Superalloys For Next Generation Coal-fired AUSC Power Plants’, *Procedia Engineering*, 55, pp. 246–252. doi: 10.1016/j.proeng.2013.03.250.

Patra, K. C., Rautray, T. R., Tripathy, B. B. and Nayak, P. (2012) ‘Elemental Analysis of Coal and Coal Ash by PIXE Technique’, *Applied radiation and isotopes : including data, instrumentation and methods for use in agriculture, industry and medicine*. Elsevier, 70(4), pp. 612–6. doi: 10.1016/j.apradiso.2011.12.013.

Peltier, R. (2013) *AEP’s John W. Turk, Jr. Power Plant Earns POWER’s Highest Honor, POWER*. Available at: <http://www.powermag.com/aeps-john-w-turk-jr-power-plant-earns-powers-highest-honor/> (Accessed: 15 January 2016).

Pisa, I. and LazaroIU, G. (2012) ‘Influence of Co-combustion of Coal/Biomass on Corrosion’, *Fuel Processing Technology*, 104, pp. 356–364. doi: 10.1016/j.fuproc.2012.06.009.

Podbaronova, J. (2010) *Assessment of Coals From Russia and Countries of Former Soviet Union for Utility Fluidized Bed Boilers*. Lappeenranta University of Technology.

Power Technology (2017) *Coal Serves as Major Fuel for Electricity Generation, New Report Reveals*, *Power Technology Newsletter*. Available at: <http://www.power-technology.com/news/newscoal-serves-as-major-fuel-for-electricity-generation-new-report-reveals-5776629> (Accessed: 11 April 2017).

Powergen (2004) *Fireside Corrosion of Boiler Materials - Effect of Co-Firing Biomass with Coal*. Nottingham.

Purgert, R., Rawls, P. and Viswanathan, V. (2008) 'Coal-Fired Power Materials', *American Society for Metals (ASM)*, pp. 47–49.

Purgert, R., Shingledecker, J., Ganta, R., Pschirer, J., Weitzel, P., Sarver, J., Vitalis, B., Gagliano, M., Stanko, G. and Tortorelli, P. (2015) *Boiler Materials for Ultra Supercritical Coal Power Plants*, DE-FG26-01NT41175.

Reid, W. T. (1971) *External Corrosion and Deposits, Boilers and Gas Turbines*. New York.

Riley, J. T. (2007) *Routine Coal and Coke Analysis: Collection, Interpretation and use of Analytical Data*. Edited by J. T. Riley. West Conshohocken, PA: ASTM International.

Robinson, A. L., Junker, H. and Baxter, L. L. (2002) 'Pilot-Scale Investigation of the Influence of Coal-Biomass Cofiring on Ash Deposition', *American Chemical Society*, pp. 343–355.

Rod Hatt (2015) *Operational Considerations When Burning Higher Chlorine Coal, Power: Connected Plant Conference*.

Roker, S. (2018a) 'IEA Releases Annual World Energy Outlook 2018 Report', *World Coal*, November. Available at: <https://www.worldcoal.com/power/13112018/iea-releases-annual-world-energy-outlook-2018-report/>.

Roker, S. (2018b) 'World Coal Magazine Editorial', *World Coal*, April.

Roni, M. S., Chowdhury, S., Mamun, S., Marufuzzaman, M., Lein, W. and Johnson, S.

(2017) ‘Biomass Co-firing Technology with Policies, Challenges, and Opportunities: A Global Review’, *Renewable and Sustainable Energy Reviews*. Elsevier Ltd, 78(May 2016), pp. 1089–1101. doi: 10.1016/j.rser.2017.05.023.

Rosendahl, L. (2013) *Biomass Combustion Science, Technology and Engineering*. Cambridge: Woodhead Publishing. doi: 2044-9364.

Sarofim, A. F. and Helble, J. J. (1993) ‘Mechanisms of Ash and Deposit Formation’, in Williamson, J. and Wigley, F. (eds) *The Impact of Ash Deposition on Coal Fired Plants, Proceedings of the Engineering Foundation Conference*. Solihull: Taylor and Fancis.

Savolainen, K. (2003) ‘Co-firing of Biomass in Coal-fired Utility Boilers’, *Applied Energy*, 74(3–4), pp. 369–381. doi: 10.1016/S0306-2619(02)00193-9.

Schade, C. T., Schaberl, J. W. and Lawley, A. (2008) *Stainless Steel AISI Grades for PM Applications, International Journal of Powder Metallurgy (Princeton, New Jersey)*.

Seggiani, M. and Pannocchia, G. (2003) ‘Prediction of Coal Ash Thermal Properties using Partial Least-squares Regression’, *Industrial and Engineering Chemistry Research*, 42(20), pp. 4919–4926.

Shalizi, C. (2009) *The Truth about Principal Components and Factor Analysis*.

Shao, Y., Wang, J., Preto, F., Zhu, J. and Xu, C. (2012) ‘Ash Deposition in Biomass Combustion or Co-firing for Power/Heat Generation’, *Energies*, 5(12), pp. 5171–5189. doi: 10.3390/en5125171.

Shardt, Y. A. W. (2015) *Statistics for Chemical and Process Engineers - A Modern Approach*. Heidelberg: Springer International. doi: 10.1007/978-3-319-21509-9.

Sharp, S. (2010) *Superheater Corrosion in Biomass Boilers: Today’s Science and Technology*. Available at: <http://www.osti.gov/bridge>.

Shingledecker, J. P. (2012) *Metallurgical Effects on Long-Term Creep-Rupture in a New Nickel-Based Alloy, Doctoral Dissertations*. University of Tennessee, Knoxville. Available at: http://trace.tennessee.edu/utk_graddiss/1348.

Simms, N. J. (2011a) ‘Environmental Degradation of Boiler Components’, in *Power Plant Life Management and Performance Improvement*. Woodhead Publishing, pp.

143–179.

Simms, N. J. (2011b) ‘Solid Fuel Composition and Power Plant Fuel Flexibility’, in Oakey, J. (ed.) *Power Plant Life Management and Performance Improvement*. Woodhead Publishing, pp. 3–37.

Simms, N. J., Kilgallon, P. J. and Oakey, J. E. (2007) ‘Degradation of Heat Exchanger Materials under Biomass Co-firing Conditions’, *Materials at High Temperatures*, 24, pp. 333–342.

Smith, K. L. and Smoot, L. D. (1990) ‘Characteristics of Commonly Used U.S. Coals Towards a Set of Standard Research Coals’, *Progress in Energy and Combustion Science*, 16(1), pp. 1–53. doi: 10.1016/0360-1285(90)90024-W.

Smith, L. I. (2002) *A Tutorial on Principal Components Analysis, Statistics*. doi: 10.1080/03610928808829796.

Sourmail, T. (2004) *Stainless Steels*. Available at: <http://thomas-sourmail.net/stainless/> (Accessed: 20 April 2016).

Sousa, S., Martins, F., Alvimferraz, M. and Pereira, M. (2007) ‘Multiple Linear Regression and Artificial Neural Networks Based on Principal Components to Predict Ozone Concentrations’, *Environmental Modelling & Software*, 22(1), pp. 97–103. doi: 10.1016/j.envsoft.2005.12.002.

Speight, J. G. (2013) *Coal-Fired Power Generation Handbook*. John Wiley & Sons.

Speight, J. G. (2015) *Handbook of Coal Analysis*. Second. New Jersey: John Wiley & Sons.

Statistica Documentation (2012) ‘Principal Component Analysis and Partial Least Squares Technical Notes’. Statsoft.

Stringer, J. (1983) *High-Temperature Corrosion Problems in Steam Boilers*. Pennington, NJ.

Stringer, J. (1995) ‘Practical Experience with Wastage at Elevated Temperatures in Coal Combustion Systems’, *Wear*, 186–187, pp. 11–27. doi: 10.1201/9780203912782.ch3.

Taler, D. and Taler, J. (2009) ‘Simplified Analysis of Radiation Heat Exchange in Boiler Superheaters’, *Heat Transfer Engineering*, 30(8), pp. 1–9. doi: 10.1080/01457630802659953.

Tambe, S. S., Naniwadekar, M., Tiwary, S., Mukherjee, A. and Das, T. B. (2018) ‘Prediction of Coal Ash Fusion Temperatures using Computational Intelligence Based Models’, *International Journal of Coal Science and Technology*. Springer Singapore, 5(4), pp. 486–507.

Tan, K. C., San Lim, H. and Jafri, M. Z. M. (2016) ‘Prediction of Column Ozone Concentrations Using Multiple Regression Analysis and Principal Component Analysis Techniques: A Case Study in Peninsular Malaysia’, *Atmospheric Pollution Research*, 7, pp. 1–14. doi: 10.1016/j.apr.2016.01.002.

The Biomass Energy Centre (2011) *Types of Biomass System*, Directgov. Available at: <http://www.biomassenergycentre.org.uk/> (Accessed: 13 November 2015).

The British Coal Utilisation Research Association (2002) *The BCURA Coal Sample Bank: A Users Handbook*. Available at: <http://www.bcura.org/coalbank.html>.

The Carbon Brief, U. (2015) *UK Coal Use to Soon Fall Back to Lowest Level since Industrial Revolution - Carbon Brief*.

The Department for Business; Energy and Industrial Strategy (BEIS) (2012) ‘Solid Fuel and Derived Gases’, in *Digest of United Kingdom Energy Statistics (DUKES)*. BEIS.

The European Stainless Steel Development Association (2000) *Stainless Steels at High Temperatures*, *Journal of Materials Science Letters*. doi: 10.1006/bbrc.2001.6020.

The Financial Times Limited (2018) *Indonesia Keeps Faith With Coal to meet Growing Energy Demand*, *Financial Times*. Available at: <https://www.ft.com/content/0fd3ed3e-89b9-11e8-affd-da9960227309> (Accessed: 15 October 2018).

The National Council for Air and Stream Improvement (2015) *Recommendations on Biomass Carbon Neutrality*. Available at: <https://newgenerationplantations.org/multimedia/file/3229dff2-a606-11e4-9137-005056986313>.

Tillman, D. A. (2000) 'Biomass Cofiring: The Technology, The Experience, The Combustion Consequences', *Biomass and Bioenergy*, 19(6), pp. 365–384. doi: 10.1016/S0961-9534(00)00049-0.

Toporov, D. (2014) *Combustion of Pulverised Coal in a Mixture of Oxygen and Recycled Flue Gas*. Elsevier.

UK Department for Business, E. and I. S. (2018) *Imports of Steam Coal to the United Kingdom (UK) Between 2002 and 2017, By Country (in 1,000 metric tons)*. Statista. Available at: <https://www.statista.com/statistics/370664/steam-coal-imports-to-the-united-kingdom-by-country/> (Accessed: 12 September 2018).

UNEP-DTIE Energy Branch (2003) *Fluidized Bed Combustion Boiler Technology For Cogeneration, Energy*.

Uniper Technologies (2016a) *UTG/16/ASI/MA/108/R*.

Uniper Technologies (2016b) *UTG/16/ASI/MA/110/R*.

Uniper Technologies (2016c) *UTG/16/ASI/MA/235/R*.

United Nations Climate Change (2019) *What is the Kyoto Protocol, 2019 United Nations Framework Convention on Climate Change*. Available at: <https://unfccc.int/process-and-meetings/the-kyoto-protocol/what-is-the-kyoto-protocol/what-is-the-kyoto-protocol> (Accessed: 9 January 2019).

University of Illinois (2000) 'Principal Component Analysis'. Illinois.

Vassilev, S. V., Baxter, D., Andersen, L. K. and Vassileva, C. G. (2010) 'An Overview of the Chemical Composition of Biomass', *Fuel*. Elsevier Ltd, 89(5), pp. 913–933.

Vassilev, S. V., Baxter, D., Andersen, L. K. and Vassileva, C. G. (2013) 'An Overview of the Composition and Application of Biomass Ash. Part 1. Phase-mineral and Chemical Composition and Classification', *Fuel*. Elsevier Ltd, 105, pp. 40–76. doi: 10.1016/j.fuel.2012.09.041.

Vassilev, S. V., Vassileva, C. G., Baxter, D. and Andersen, L. K. (2009) 'A New Approach for the Combined Chemical and Mineral Classification of the Inorganic Matter in Coal 2', *Fuel*. Elsevier Ltd, 88(2), pp. 246–254. doi:

10.1016/j.fuel.2008.09.005.

Vassilev, S. V., Vassileva, C. G. and Vassilev, V. S. (2015) ‘Advantages and Disadvantages of Composition and Properties of Biomass in Comparison with Coal: An Overview’, *Fuel*. Elsevier Ltd, 158, pp. 330–350. doi: 10.1016/j.fuel.2015.05.050.

Viswanathan, R. (1989) *Damage Mechanisms and Life Assessment of High Temperature Components*. Ohio: ASM International.

Viswanathan, R., Henry, J. F., Tanzosh, J., Stanko, G., Shingledecker, J., Vitalis, B. and Purgert, R. (2005) ‘U.S. Program on Materials Technology for Ultra-supercritical Coal Power Plants’, *Journal of Materials Engineering and Performance*, 14(3), pp. 281–292. doi: 10.1007/s11665-013-0717-6.

Watt, J. D. (1969) *The Physical and Chemical Behaviour of the Mineral Matter in Coal Under the Conditions Met in Combustion Plant*.

Weele, S. Van (1991) *Fireside Corrosion Testing of Candidate Superheater Tube Alloys, Coatings, and Claddings*, ORNL/Sub/89-SA 187/02. New Jersey.

Weele, S. Van and Blough, J. L. (1990) *Literature Search Update Fireside Corrosion Testing of Candidate Superheater Tube Alloys, Coatings, and Claddings*.

Wehrens, R. and Mevik, B.-H. (2007) ‘The PLS Package: Principal Component and Partial Least Squares Regression in R’, *Journal of Statistical Software*, 18(2).

Whitehurst, D. D., Mitchell, T. O. and Farcasiu, M. (1980) *Coal Liquefaction: The Chemistry and Technology of Thermal Processes*. New Jersey: Academic Press.

Williams, A., Pourkashanian, M. and Jones, J. M. (2001) ‘Combustion of Pulverised Coal and Biomass’, *Progress in Energy and Combustion Science*, 27(6), pp. 587–610. doi: 10.1016/S0360-1285(01)00004-1.

World Energy Council (2013) *World Energy Resources: Coal*. Available at: http://www.worldenergy.org/wp-content/uploads/2013/10/WER_2013_1_Coal.pdf.

World Energy Council (2018) *Coal in Russia, Energy Resources*. Available at: <https://www.worldenergy.org/data/resources/country/russia/coal/> (Accessed: 10 October 2018).

World Energy Council (2019) *Coal, World Energy Resources*. Available at: <https://www.worldenergy.org/data/resources/resource/coal/> (Accessed: 9 January 2019).

Wright, I. G. and Krause, H. H. (1997a) *Possible Effects of the Chlorine Content of Coal on Fireside Corrosion in Pulverized Coal-Fired Boilers - Volume 1*. Columbus, Ohio.

Wright, I. G. and Krause, H. H. (1997b) 'Survey of the Effects of Coal Chlorine Levels on Fireside Corrosion in Pulverized Coal-Fired Boilers in the U.S.', in *Possible Effects of the Chlorine Content of Coal on Fireside Corrosion in Pulverized Coal-Fired Boilers (Volume 1)*. Nottingham, pp. 1–92.

Wright, I. G. and Kung, S. C. (2018) 'Possible Scenarios for the Causes of Accelerated Fireside Corrosion of Superheater Tubes in Coal-fired Boilers', *Materials at High Temperatures*. Taylor & Francis, 3409(May 2017), p. 0. doi: 10.1080/09603409.2017.1334351.

Wright, I. G., Sethi, V. K. and Markworth, A. J. (1995) 'A Generalized Description of the Simultaneous Processes of Scale Growth by High-temperature Oxidation and Removal by Erosive Impact', *Wear*, 186–187, pp. 230–237. doi: 10.1016/0043-1648(95)07129-6.

Wright, I. G. and Shingledecker, J. P. (2015) 'Rates of Fireside Corrosion of Superheater and Reheater Tubes: Making Sense of Available Data', *Materials at High Temperatures*, 32(4), pp. 426–437.

Yamashita, Y., Iwahashi, S., Kuwahara, T., Kawabata, K. and Yamane, Y. (2017) 'Fouling Monitoring of a Thermosiphon Reboiler', in *Heat Exchanger Fouling and Cleaning*. Occidental Aranjuez.

Yaxley, N. (2007) *British and European Imports of Russian Coal*. Moscow. Available at: www.coalimp.org.uk.

APPENDICES

Appendix A Fuel Data

Appendix A focuses on the UK fuel data used for model building; i.e. coal from the PE-8 corrosion data (Appendix A.1), and co-firing corrosion data (Appendix A.2). Specific fuel elements (Si, Ti) calculated from the oxides (culled from the ashed analysis) is illustrated in Table A-2.

A.1 UK Coal Data (Data subsets 1-4)

This section offers details on the fuel elements used for model building specifically data subsets 1-4. The water-soluble components of Na, K, Mg, Ca in data subsets 1-4 were used for PCA/PLS model building. The water-soluble components are assumed to be the volatile species released during coal combustion (Gibb and Angus, 1983). The source data for data subsets 1-4 reports the percentage metal released in the combustion atmosphere which is taken as the equivalent of the water soluble component of Na, K, Mg and Ca (Wright and Krause, 1997b). The percentage (metal) released also includes Fe and Al in the original report (details in Table A-1 and Table A-2). Table A-2 also illustrates the conversion of SiO_2 and TiO_2 from the ashed composition to their elemental values in the coal (same procedure used to convert elements represented as oxides in the ash to fuel elements in the coal across the other data subsets 5-13).

Table A-1: UK Coal Data

UK Coal	Amount of Metal Released																	
	Na			K			Mg			Al			Ca			Fe		
	Total (wt %)	% release	wt %	Total (wt %)	% release	wt %	Total (wt %)	% release	wt %	Total (wt %)	% release	wt %	Total (wt %)	% release	wt %	Total (wt %)	% release	wt %
Ackton Hall	0.156	17	0.027	0.670	10	0.067	0.150	4	0.006	3.150	2	0.063	0.206	18	0.037	1.900	9	0.171
Askern	0.204	10	0.020	0.983	6	0.059	0.200	2	0.004	4.000	1	0.040	0.240	5	0.012	1.711	9	0.154
Babbington	0.157	22	0.035	0.567	12	0.068	0.129	7	0.009	4.200	1	0.042	0.308	13	0.040	1.633	6	0.098
Bentnck	0.144	20	0.029	0.321	19	0.061	0.113	8	0.009	1.500	3	0.045	0.267	15	0.040	0.817	12	0.098
Bentley	0.224	18	0.040	0.579	14	0.081	0.125	4	0.005	2.750	2	0.055	0.262	13	0.034	1.350	12	0.162
Bilsthorpe	0.198	25	0.050	0.575	16	0.092	0.400	2	0.008	3.133	3	0.094	0.278	18	0.050	1.420	10	0.142
Cotgrave	0.144	8	0.012	0.520	5	0.026	0.150	4	0.006	3.200	1	0.032	0.167	15	0.025	0.700	6	0.042
Creswell	0.105	23	0.024	0.567	9	0.051	0.160	5	0.008	3.100	2	0.062	0.353	19	0.067	1.200	8	0.096
Daw Mill	0.067	37	0.025	0.214	28	0.060	0.124	17	0.021	1.643	7	0.115	0.683	18	0.123	0.664	11	0.073
Florence	0.126	18	0.023	0.391	11	0.043	0.188	8	0.015	4.050	2	0.081	0.638	13	0.083	1.422	9	0.128
Frickley	0.145	17	0.025	0.473	11	0.052	0.140	5	0.007	2.650	2	0.053	0.185	13	0.024	1.440	10	0.144
Glasshoughton	0.170	12	0.020	0.590	10	0.059	0.125	4	0.005	2.600	2	0.052	0.283	12	0.034	1.300	11	0.143
Granville	0.053	30	0.016	0.382	17	0.065	0.150	4	0.006	2.175	4	0.087	0.600	21	0.126	0.467	9	0.042
Goldthorpe	0.161	9	0.014	0.617	6	0.037	0.150	2	0.003	3.400	1	0.034	0.183	6	0.011	1.788	8	0.143
Hatfield Main	0.223	11	0.025	0.650	8	0.052	0.200	4	0.008	2.350	2	0.047	0.329	7	0.023	0.927	15	0.139
Hem Heath	0.103	28	0.029	0.393	15	0.059	0.125	8	0.010	2.067	3	0.062	0.500	14	0.070	1.543	7	0.108
Hickleton	0.134	22	0.029	0.340	15	0.051	0.100	6	0.006	2.300	2	0.046	0.153	17	0.026	1.122	9	0.101
Horse Hay	0.021	29	0.006	0.131	16	0.021	0.036	11	0.004	1.825	4	0.073	0.150	20	0.030	0.600	8	0.048
Hucknall	0.144	18	0.026	0.656	9	0.059	0.200	5	0.010	4.500	1	0.045	0.257	14	0.036	1.757	7	0.123
Kellingley	0.185	17	0.031	0.700	12	0.084	0.022	6	0.001	3.171	4	0.127	0.131	13	0.017	1.564	22	0.344

Kiveton	0.101	22	0.022	0.321	14	0.045	0.100	5	0.005	0.740	5	0.037	0.292	12	0.035	1.650	4	0.066
Lea Hall	0.174	32	0.056	0.338	24	0.081	0.110	10	0.011	1.950	4	0.078	0.578	18	0.104	0.975	8	0.078
Littleton	0.102	23	0.023	0.311	19	0.059	0.100	10	0.010	1.750	4	0.070	0.650	14	0.091	1.429	7	0.100
Lofthouse	0.076	21	0.016	0.725	8	0.058	0.150	4	0.006	2.500	2	0.050	0.205	20	0.041	1.889	9	0.170
Markham Main	0.221	16	0.035	0.538	13	0.070	0.150	4	0.006	2.800	2	0.056	0.363	8	0.029	1.327	11	0.146
Markham - Staveley	0.092	22	0.020	0.544	9	0.049	0.125	4	0.005	3.900	1	0.039	0.209	11	0.023	1.675	4	0.067
Moorgreen	0.116	22	0.026	0.500	13	0.065	0.117	6	0.007	1.950	2	0.039	0.223	13	0.029	1.520	5	0.076
Peckfield	0.046	33	0.015	0.413	15	0.062	0.118	11	0.013	2.100	3	0.063	0.115	46	0.053	1.113	15	0.167
Prince of Wales	0.162	14	0.023	0.786	7	0.055	0.200	3	0.006	4.300	1	0.043	0.175	8	0.014	2.044	9	0.184
Pye Hill	0.114	32	0.036	0.463	16	0.074	0.143	7	0.010	2.550	2	0.051	0.280	15	0.042	1.471	7	0.103
Rossington	0.198	23	0.046	0.512	17	0.087	0.163	8	0.013	2.575	4	0.103	0.341	22	0.075	1.150	14	0.161
Rothwell	0.131	17	0.022	0.410	10	0.041	0.100	4	0.004	2.150	2	0.043	1.267	3	0.038	1.050	12	0.126
Royston Drift	0.081	16	0.013	0.500	10	0.050	0.150	4	0.006	2.850	2	0.057	0.375	8	0.030	2.429	7	0.170
Seymour	0.017	53	0.009	0.194	18	0.035	0.089	9	0.008	1.333	3	0.040	0.240	15	0.036	1.000	6	0.060
Sharlston	0.112	14	0.016	0.738	8	0.059	0.225	4	0.009	2.850	2	0.057	0.233	12	0.028	1.863	8	0.149
Sherwood	0.159	23	0.037	0.529	14	0.074	0.200	4	0.008	2.850	2	0.057	0.286	14	0.040	1.175	8	0.094
Shirebrook	0.144	16	0.023	0.763	8	0.061	0.200	3	0.006	4.500	1	0.045	0.344	9	0.031	1.580	5	0.079
Shireoaks	0.124	6	0.007	0.413	8	0.033	0.129	7	0.009	1.750	2	0.035	0.336	11	0.037	1.029	7	0.072
Silverdale	0.041	39	0.016	0.265	17	0.045	0.140	5	0.007	1.500	4	0.060	0.310	20	0.062	1.814	7	0.127
South Kirkby	0.136	11	0.015	0.650	6	0.039	0.200	2	0.004	3.200	1	0.032	0.171	7	0.012	1.425	8	0.114
Thoresby	0.228	27	0.062	0.500	16	0.080	0.100	9	0.009	2.900	2	0.058	0.592	13	0.077	1.089	9	0.098
Treeton	0.111	14	0.016	0.714	7	0.050	0.200	4	0.008	3.100	1	0.031	0.290	10	0.029	1.867	3	0.056
Whitwell	0.088	8	0.007	0.600	3	0.018	0.200	3	0.006	1.900	1	0.019	0.380	5	0.019	2.250	2	0.045
Yorkshire Main	0.139	18	0.025	0.500	12	0.060	0.114	7	0.008	2.000	3	0.060	0.206	18	0.037	1.063	16	0.170

Table A-2: Fuel elements, Si, Ti, calculated from oxides

Ash (%)	SiO ₂	Mol Weight (g/mol)	g (oxide)	moles cpd	moles element	wt element (g)	wt (%) in coal		TiO ₂	Mol Weight (g/mol)	g (oxide)	moles cpd	moles element	wt element (g)	wt (%) in coal
22.20	48.50	SiO ₂	48.50	0.807	0.807	22.676	5.034		0.90	TiO ₂	0.90	0.011	0.011	0.539	0.120
29.20	52.20	60.08	52.20	0.869	0.869	24.406	7.126		0.90	79.87	0.90	0.011	0.011	0.539	0.158
21.20	49.80	Si	49.80	0.829	0.829	23.284	4.936		1.00	Ti	1.00	0.013	0.013	0.599	0.127
11.90	50.20	28.09	50.20	0.836	0.836	23.471	2.793		1.00	47.87	1.00	0.013	0.013	0.599	0.071
18.20	50.30	-	50.30	0.837	0.837	23.517	4.280		0.90	-	0.90	0.011	0.011	0.539	0.098
19.80	49.80	-	49.80	0.829	0.829	23.284	4.610		1.00	-	1.00	0.013	0.013	0.599	0.119
20.20	52.60	-	52.60	0.875	0.875	24.593	4.968		1.40	-	1.40	0.018	0.018	0.839	0.169
22.40	56.90	-	56.90	0.947	0.947	26.603	5.959		1.00	-	1.00	0.013	0.013	0.599	0.134
12.60	42.90	-	42.90	0.714	0.714	20.058	2.527		1.00	-	1.00	0.013	0.013	0.599	0.076
22.60	47.80	-	47.80	0.796	0.796	22.349	5.051		1.00	-	1.00	0.013	0.013	0.599	0.135
17.00	50.90	-	50.90	0.847	0.847	23.798	4.046		1.00	-	1.00	0.013	0.013	0.599	0.102
18.40	48.40	-	48.40	0.806	0.806	22.629	4.164		0.80	-	0.80	0.010	0.010	0.479	0.088
14.70	48.50	-	48.50	0.807	0.807	22.676	3.333		1.00	-	1.00	0.013	0.013	0.599	0.088
22.20	51.00	-	51.00	0.849	0.849	23.845	5.294		0.90	-	0.90	0.011	0.011	0.539	0.120
21.20	56.20	-	56.20	0.935	0.935	26.276	5.570		0.90	-	0.90	0.011	0.011	0.539	0.114
17.80	47.20	-	47.20	0.786	0.786	22.068	3.928		0.90	-	0.90	0.011	0.011	0.539	0.096
14.80	5.35	-	5.35	0.089	0.089	2.501	0.370		1.00	-	1.00	0.013	0.013	0.599	0.089
11.40	48.90	-	48.90	0.814	0.814	22.863	2.606		1.30	-	1.30	0.016	0.016	0.779	0.089
22.80	52.20	-	52.20	0.869	0.869	24.406	5.565		1.10	-	1.10	0.014	0.014	0.659	0.150
21.10	49.50	-	49.50	0.824	0.824	23.143	4.883		0.90	-	0.90	0.011	0.011	0.539	0.114
15.70	48.80	-	48.80	0.812	0.812	22.816	3.582		0.90	-	0.90	0.011	0.011	0.539	0.085
15.40	48.80	-	48.80	0.812	0.812	22.816	3.514		1.00	-	1.00	0.013	0.013	0.599	0.092
16.70	43.60	-	43.60	0.726	0.726	20.385	3.404		0.90	-	0.90	0.011	0.011	0.539	0.090
23.10	49.50	-	49.50	0.824	0.824	23.143	5.346		0.90	-	0.90	0.011	0.011	0.539	0.125

Ash (%)	SiO ₂	Mol Weight (g/mol)	g (oxide)	moles cpd	moles element	wt element (g)	wt (%) in coal		TiO ₂	Mol Weight (g/mol)	g (oxide)	moles cpd	moles element	wt element (g)	wt (%) in coal
20.20	53.70	-	53.70	0.894	0.894	25.107	5.072		1.00	-	1.00	0.013	0.013	0.599	0.121
18.90	49.60	-	49.60	0.826	0.826	23.190	4.383		1.00	-	1.00	0.013	0.013	0.599	0.113
18.40	50.10	-	50.10	0.834	0.834	23.424	4.310		1.00	-	1.00	0.013	0.013	0.599	0.110
13.30	47.60	-	47.60	0.792	0.792	22.255	2.960		1.10	-	1.10	0.014	0.014	0.659	0.088
26.30	52.50	-	52.50	0.874	0.874	24.546	6.456		0.90	-	0.90	0.011	0.011	0.539	0.142
15.90	47.90	-	47.90	0.797	0.797	22.395	3.561		1.00	-	1.00	0.013	0.013	0.599	0.095
17.10	49.60	-	49.60	0.826	0.826	23.190	3.966		1.00	-	1.00	0.013	0.013	0.599	0.102
17.20	54.80	-	54.80	0.912	0.912	25.621	4.407		0.90	-	0.90	0.011	0.011	0.539	0.093
22.60	46.80	-	46.80	0.779	0.779	21.881	4.945		0.90	-	0.90	0.011	0.011	0.539	0.122
9.40	41.10	-	41.10	0.684	0.684	19.216	1.806		0.90	-	0.90	0.011	0.011	0.539	0.051
23.10	49.30	-	49.30	0.821	0.821	23.050	5.325		0.90	-	0.90	0.011	0.011	0.539	0.125
17.50	50.40	-	50.40	0.839	0.839	23.564	4.124		1.00	-	1.00	0.013	0.013	0.599	0.105
24.70	51.90	-	51.90	0.864	0.864	24.265	5.994		0.90	-	0.90	0.011	0.011	0.539	0.133
19.80	57.40	-	57.40	0.955	0.955	26.837	5.314		0.90	-	0.90	0.011	0.011	0.539	0.107
18.40	43.90	-	43.90	0.731	0.731	20.525	3.777		0.90	-	0.90	0.011	0.011	0.539	0.099
23.40	55.40	-	55.40	0.922	0.922	25.902	6.061		1.00	-	1.00	0.013	0.013	0.599	0.140
19.70	49.10	-	49.10	0.817	0.817	22.956	4.522		0.90	-	0.90	0.011	0.011	0.539	0.106
22.70	50.70	-	50.70	0.844	0.844	23.704	5.381		0.90	-	0.90	0.011	0.011	0.539	0.122
27.50	60.80	-	60.80	1.012	1.012	28.427	7.817		0.90	-	0.90	0.011	0.011	0.539	0.148
17.10	53.50	-	53.50	0.890	0.890	25.014	4.277		1.00	-	1.00	0.013	0.013	0.599	0.102

A.2 Co-Firing Data (Data Subsets 14-16)

This section contains details on how the fuel elements/blends are obtained from the co-fired coal/biomass data. For the co-firing data in this work, the biomass fuels; wood and cereal co-product (CCP) were co-fired with Daw Mill coal.

The straw based cereal co-product was co-milled with the coal and fed to the burner as a single fuel stream. The biomass fuel (wood and CCP) was fired at 20% and 10% on a thermal basis (Table A-3).

Table A-3 shows the fuel blend for the co-firing models 14-16. Table A-4 and Table A-5 in section A.2.1 details how the fuel blend was calculated and the corresponding ash data.

Table A-3: Co-firing Fuel Blend (Coal/Biomass)

FUEL	Na (wt %)	K (wt %)	Al (wt %)	Si (wt %)	P (wt %)	Mg (wt %)	Ca (wt %)	Ti (wt %)	Mn (wt %)	Fe (wt %)	Ba (wt %)	Cl (wt. %)	S (wt %)
Daw Mill Coal	0.070	0.17	1.4	2.2	0.015	0.12	0.30	0.063	0.017	0.62	0.023	0.22	1.5
% released Daw Mill**	0.026	0.047	0.096	2.2	0.015	0.021	0.054	0.063	0.017	0.068	0.023	0.22	1.5
Wood	0.0085	0.015	0.0095	0.096	0.0017	0.014	0.050	0.0073	0.0038	0.032	0.0021	0.035	0.035
Cereal co-product (CCP)	0.056	1.8	0.0086	0.046	1.1	0.45	0.070	0.0007	0.012	0.021	0.0027	0.15	0.23
0.80 Daw Mill + 0.20 CCP	0.066	0.83	0.85	1.40	0.46	0.26	0.22	0.039	0.016	0.39	0.015	0.19	1.1
0.90 Daw Mill + 0.10 CCP	0.068	0.54	1.1	1.8	0.27	0.20	0.25	0.050	0.016	0.49	0.018	0.20	1.3
0.80 Daw Mill + 0.20 Wood	0.074	0.15	0.78	1.6	0.015	0.13	0.38	0.066	0.026	0.47	0.021	0.17	1.1
0.90 Daw Mill + 0.10 Wood	0.074	0.16	1.0	1.9	0.016	0.13	0.36	0.066	0.023	0.54	0.022	0.19	1.3

**Percentage metal released for Daw Mill coal (Wright and Krause, 1997b):

Na - 37% released

K - 28% released

Mg - 17% released

Al - 7% released

Ca - 18% released

Fe - 11% released

A.2.1 Fuel Blend (Coal/Biomass) Calculation

Table A-4: Co-firing fuel blend calculation; biomass was fired at 20% and 10% on a thermal basis (CCP refers to cereal co-product)

	GCV wood (kJ/kg)	GCV Daw mill coal (kJ/kg)
	17610	27840
	Wood	Coal
	w	(100%-w)
80% Daw Mill 20% Wood (weight fuel)	0.283	0.717
90% Daw Mill 10% Wood (weight fuel)	0.149	0.851
	GCV CCP (kJ/kg)	GCV Daw mill coal (kJ/kg)
	16970	27840
	CCP	Coal
	c	(100%-c)
80% Daw Mill 20% CCP (weight fuel)	0.291	0.709
90% Daw Mill 10% CCP (weight fuel)	0.154	0.846

For 20% wood, 80% coal (from thermal basis to weight basis), for example:

$$\therefore \text{weight wood/fuel blend} = \frac{17610 \times w}{(17610 \times w) + (27840 \times (100 - w))} = \frac{20}{100}$$

Given w = 28.33% (or 0.283)

For 20% CCP, 80% coal (from thermal basis to weight basis); for example:

$$\therefore \text{weight CCP/fuel blend} = \frac{16970 \times c}{(16970 \times c) + (27840 \times (100 - c))} = \frac{20}{100}$$

Given c = 29.1% (or 0.291)

A.2.2 Co-firing Data: Ash Percentage of Coal, Biomass (Wood, CCP) and Coal/Biomass Blend

Table A-5: Ash data for coal, wood, CCP, and coal/wood/CCP blend

	Daw Mill	Wood	CCP	Daw Mill/ Wood 20%	Daw Mill / Wood 10%	Daw Mill/ CCP 20%	Daw Mill / CCP 10%
	A_d	A_w	A_c	$(=d1 \cdot A_d + w1 \cdot A_w)^*$	$(=d2 \cdot A_d + w2 \cdot A_w)^*$	$(=d3 \cdot A_d + c3 \cdot A_c)^*$	$(=d4 \cdot A_d + c4 \cdot A_c)^*$
% Ash (As Received)	9.00	0.40	5.30	6.57	7.72	7.92	8.43

Where fuel blend:

	Wood (w)	Coal (d)	*Legend
80% Daw Mill 20% Wood	0.283	0.717	w1, d1
90% Daw Mill 10% Wood	0.149	0.851	w2, d2
	CCP (c)	Coal (d)	
80% Daw Mill 20% CCP	0.291	0.709	c3, d3
90% Daw Mill 10% CCP	0.154	0.846	c4, d4

d1= 80% Daw mill coal (with wood), d2 = 90% Daw mill coal (with wood)

w1 = 20% wood, w2 = 10% wood

d3 = 80% Daw mill coal (with CCP), d4 = 10% Daw mill coal (with CCP)

c3 = 20% CCP, c4 = 10% CCP

Appendix B Correlation Matrix

B.1 Correlation Matrix for data subsets 1-16

The correlation matrix discussed in chapter 4 (section 4.3.1); are presented in this section. The correlation matrices are produced from data subsets 1-16 and the tables presented (i.e. Tables B-1 to B-16) are for the framework model F (section 4.2). The predictor variables are in natural log form.

Table B-1: Correlation matrix UK coal data subset 1, austenitic leading tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 1)																								
	Marked correlations are significant at p < 0.05																								
	Means	Std.Dev.	1000 / Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Manganese %	Phosphorus %	Sulphur %	Silicon %	Chromium %	Nickel %	Molybdenum %	Titanium %	Vanadium %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	LN corr rate (µm/hrs)
1000 / Metal Temp (1000 / K)	1.094	0.019	1.000	-0.456	-0.198	0.163	-0.163	-0.163	-0.186	-0.261	-0.370	-0.245	-0.121	-0.163	0.208	0.139	0.080	0.192	0.159	-0.148	-0.244	0.313	0.059	-0.227	-0.289
Tg-Tm K	5.881	0.157	-0.456	1.000	0.269	0.171	-0.171	-0.171	0.112	0.068	0.087	-0.127	0.299	-0.171	-0.155	-0.044	0.038	-0.153	-0.094	0.185	0.417	-0.119	-0.059	0.351	0.213
Carbon %	-2.326	0.361	-0.198	0.269	1.000	0.026	-0.026	-0.026	0.725	0.765	0.675	-0.507	0.223	-0.026	0.176	0.334	0.264	0.185	0.268	0.253	-0.009	-0.082	0.275	-0.002	-0.418
Manganese %	0.851	0.399	0.163	0.171	0.026	1.000	-1.000	-1.000	-0.644	-0.608	-0.648	-0.361	0.159	-1.000	-0.134	-0.090	-0.050	-0.196	-0.061	0.036	0.078	0.024	-0.197	0.066	0.047
Phosphorus %	-3.136	0.087	-0.163	-0.171	-0.026	-1.000	1.000	1.000	0.644	0.608	0.648	0.361	-0.159	1.000	0.134	0.090	0.050	0.196	0.061	-0.036	-0.078	-0.024	0.197	-0.066	-0.047
Sulphur %	-3.602	0.241	-0.163	-0.171	-0.026	-1.000	1.000	1.000	0.644	0.608	0.648	0.361	-0.159	1.000	0.134	0.090	0.050	0.196	0.061	-0.036	-0.078	-0.024	0.197	-0.066	-0.047
Silicon %	-0.217	0.298	-0.186	0.112	0.725	-0.644	0.644	0.644	1.000	0.958	0.891	-0.218	0.096	0.644	0.214	0.308	0.267	0.294	0.250	0.172	-0.029	-0.087	0.331	-0.031	-0.381
Chromium %	2.925	0.143	-0.261	0.068	0.765	-0.608	0.608	0.608	0.958	1.000	0.922	-0.218	-0.056	0.608	0.223	0.325	0.221	0.255	0.262	0.202	-0.067	-0.085	0.365	-0.052	-0.363
Nickel %	2.606	0.221	-0.370	0.087	0.675	-0.648	0.648	0.648	0.891	0.922	1.000	0.136	0.222	0.648	0.219	0.277	0.178	0.234	0.181	0.084	-0.092	-0.041	0.283	-0.056	-0.237
Molybdenum %	0.376	0.419	-0.245	-0.127	-0.507	-0.361	0.361	0.361	-0.218	-0.218	0.136	1.000	0.361	0.361	-0.024	-0.176	-0.188	-0.069	-0.231	-0.321	-0.092	0.112	-0.184	-0.038	0.394
Titanium %	-0.049	0.124	-0.121	0.299	0.223	0.159	-0.159	-0.159	0.096	-0.056	0.222	0.361	1.000	-0.159	0.018	0.001	0.113	0.063	-0.076	-0.165	0.041	0.052	-0.157	0.051	0.033
Vanadium %	-0.165	0.418	-0.163	-0.171	-0.026	-1.000	1.000	1.000	0.644	0.608	0.648	0.361	-0.159	1.000	0.134	0.090	0.050	0.196	0.061	-0.036	-0.078	-0.024	0.197	-0.066	-0.047
Na %	-4.086	0.496	0.208	-0.155	0.176	-0.134	0.134	0.134	0.214	0.223	0.219	-0.024	0.018	0.134	1.000	0.902	0.466	0.663	0.846	0.462	-0.735	0.554	0.295	-0.688	0.066
K %	-3.153	0.444	0.139	-0.044	0.334	-0.090	0.090	0.090	0.308	0.325	0.277	-0.176	0.001	0.090	0.902	1.000	0.396	0.547	0.884	0.699	-0.620	0.278	0.551	-0.566	-0.118
Mg %	-5.076	0.419	0.080	0.038	0.264	-0.050	0.050	0.050	0.267	0.221	0.178	-0.188	0.113	0.050	0.466	0.396	1.000	0.833	0.673	-0.007	-0.463	0.188	-0.058	-0.417	-0.157
Ca %	-3.630	0.620	0.192	-0.153	0.185	-0.196	0.196	0.196	0.294	0.255	0.234	-0.069	0.063	0.196	0.663	0.547	0.833	1.000	0.749	0.000	-0.672	0.183	0.186	-0.617	-0.281
Al %	-3.209	0.458	0.159	-0.094	0.268	-0.061	0.061	0.061	0.250	0.262	0.181	-0.231	-0.076	0.061	0.846	0.884	0.673	0.749	1.000	0.570	-0.718	0.214	0.342	-0.595	-0.181
Fe %	-2.383	0.478	-0.148	0.185	0.253	0.036	-0.036	-0.036	0.172	0.202	0.084	-0.321	-0.165	-0.036	0.462	0.699	-0.007	0.000	0.570	1.000	-0.139	-0.102	0.535	-0.182	-0.064
Si %	1.649	0.269	-0.244	0.417	-0.009	0.078	-0.078	-0.078	-0.029	-0.067	-0.092	-0.092	0.041	-0.078	-0.735	-0.620	-0.463	-0.672	-0.718	-0.139	1.000	-0.213	-0.245	0.856	0.166
Cl %	-1.227	0.298	0.313	-0.119	-0.082	0.024	-0.024	-0.024	-0.087	-0.085	-0.041	0.112	0.052	-0.024	0.554	0.278	0.188	0.183	0.214	-0.102	-0.213	1.000	-0.360	-0.203	0.589
S %	0.480	0.235	0.059	-0.059	0.275	-0.197	0.197	0.197	0.331	0.365	0.283	-0.184	-0.157	0.197	0.295	0.551	-0.058	0.186	0.342	0.535	-0.245	-0.360	1.000	-0.349	-0.493
Ti %	-2.290	0.207	-0.227	0.351	-0.002	0.066	-0.066	-0.066	-0.031	-0.052	-0.056	-0.038	0.051	-0.066	-0.688	-0.566	-0.417	-0.617	-0.595	-0.182	0.856	-0.203	-0.349	1.000	0.132
LN corr rate (µm/hrs)	3.884	0.654	-0.289	0.213	-0.418	0.047	-0.047	-0.047	-0.381	-0.363	-0.237	0.394	0.033	-0.047	0.066	-0.118	-0.157	-0.281	-0.181	-0.064	0.166	0.589	-0.493	0.132	1.000

Table B-2: Correlation matrix for UK coal data subset 2, austenitic non-leading tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 2)																								
	Marked correlations are significant at p < 0.05																								
	Means	Std.Dev.	1000 / Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Mangan ese %	Phosph orus %	Sulphur %	Silicon %	Chromiu m %	Nickel %	Molybd enum %	Titaniu m %	Vanadiu m %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	LN corr rate (µm/khr)
1000 / Metal Temp (1000 / K)	1.079	0.028	1.000	0.465	-0.239	0.307	-0.307	-0.307	-0.305	-0.387	-0.512	-0.262	-0.156	-0.307	0.509	0.417	0.075	0.299	0.241	0.121	-0.315	0.410	0.180	-0.501	-0.433
Tg-Tm K	5.751	0.223	0.465	1.000	-0.042	0.377	-0.377	-0.377	-0.227	-0.266	-0.360	-0.270	-0.002	-0.377	0.050	0.132	0.006	-0.101	0.060	0.259	0.134	0.066	0.000	-0.086	0.209
Carbon %	-2.348	0.353	-0.239	-0.042	1.000	0.045	-0.045	-0.045	0.748	0.803	0.656	-0.639	0.099	-0.045	-0.043	0.211	0.374	0.088	0.299	0.220	0.204	-0.283	0.110	0.150	-0.405
Manganese %	0.816	0.361	0.307	0.377	0.045	1.000	-1.000	-1.000	-0.601	-0.552	-0.659	-0.431	0.067	-1.000	-0.251	-0.066	-0.348	-0.439	-0.247	0.231	0.442	-0.171	0.029	0.198	0.013
Phosphorus %	-3.128	0.079	-0.307	-0.377	-0.045	-1.000	1.000	1.000	0.601	0.552	0.659	0.431	-0.067	1.000	0.251	0.066	0.348	0.439	0.247	-0.231	-0.442	0.171	-0.029	-0.198	-0.013
Sulphur %	-3.581	0.218	-0.307	-0.377	-0.045	-1.000	1.000	1.000	0.601	0.552	0.659	0.431	-0.067	1.000	0.251	0.066	0.348	0.439	0.247	-0.231	-0.442	0.171	-0.029	-0.198	-0.013
Silicon %	-0.216	0.280	-0.305	-0.227	0.748	-0.601	0.601	0.601	1.000	0.965	0.878	-0.325	0.050	0.601	0.270	0.330	0.627	0.459	0.529	0.072	-0.170	0.034	0.056	-0.064	-0.314
Chromium %	2.920	0.135	-0.387	-0.266	0.803	-0.552	0.552	0.552	0.965	1.000	0.937	-0.276	-0.036	0.552	0.067	0.180	0.462	0.283	0.353	0.054	-0.068	-0.188	0.095	0.023	-0.355
Nickel %	2.630	0.203	-0.512	-0.360	0.656	-0.659	0.659	0.659	0.878	0.937	1.000	0.058	0.140	0.659	-0.051	0.014	0.374	0.241	0.182	-0.115	-0.120	-0.258	0.039	0.045	-0.284
Molybdenum %	0.506	0.414	-0.262	-0.270	-0.639	-0.431	0.431	0.431	-0.325	-0.276	0.058	1.000	0.239	0.431	-0.252	-0.455	-0.310	-0.098	-0.469	-0.467	-0.227	-0.100	-0.135	-0.017	0.264
Titanium %	-0.013	0.067	-0.156	-0.002	0.099	0.067	-0.067	-0.067	0.050	-0.036	0.140	0.239	1.000	-0.067	0.108	0.065	0.344	0.272	0.101	-0.218	-0.116	0.199	-0.222	0.007	0.082
Vanadium %	-0.129	0.379	-0.307	-0.377	-0.045	-1.000	1.000	1.000	0.601	0.552	0.659	0.431	-0.067	1.000	0.251	0.066	0.348	0.439	0.247	-0.231	-0.442	0.171	-0.029	-0.198	-0.013
Na %	-4.015	0.460	0.509	0.050	-0.043	-0.251	0.251	0.251	0.270	0.067	-0.051	-0.252	0.108	0.251	1.000	0.875	0.641	0.810	0.857	0.275	-0.688	0.649	0.347	-0.750	-0.273
K %	-3.177	0.358	0.417	0.132	0.211	-0.066	0.066	0.066	0.330	0.180	0.014	-0.455	0.065	0.066	0.875	1.000	0.561	0.566	0.884	0.642	-0.407	0.327	0.600	-0.718	-0.361
Mg %	-5.151	0.375	0.075	0.006	0.374	-0.348	0.348	0.348	0.627	0.462	0.374	-0.310	0.344	0.348	0.641	0.561	1.000	0.794	0.829	0.028	-0.335	0.584	-0.175	-0.139	-0.169
Ca %	-3.665	0.609	0.299	-0.101	0.088	-0.439	0.439	0.439	0.459	0.283	0.241	-0.098	0.272	0.439	0.810	0.566	0.794	1.000	0.731	-0.238	-0.800	0.601	-0.002	-0.505	-0.300
Al %	-3.214	0.325	0.241	0.060	0.299	-0.247	0.247	0.247	0.529	0.353	0.182	-0.469	0.101	0.247	0.857	0.884	0.829	0.731	1.000	0.442	-0.407	0.489	0.282	-0.459	-0.242
Fe %	-2.495	0.495	0.121	0.259	0.220	0.231	-0.231	-0.231	0.072	0.054	-0.115	-0.467	-0.218	-0.231	0.275	0.642	0.028	-0.238	0.442	1.000	0.295	-0.143	0.642	-0.294	-0.086
Si %	1.546	0.204	-0.315	0.134	0.204	0.442	-0.442	-0.442	-0.170	-0.068	-0.120	-0.227	-0.116	-0.442	-0.688	-0.407	-0.335	-0.800	-0.407	0.295	1.000	-0.315	-0.303	0.755	0.267
Cl %	-1.138	0.205	0.410	0.066	-0.283	-0.171	0.171	0.171	0.034	-0.188	-0.258	-0.100	0.199	0.171	0.649	0.327	0.584	0.601	0.489	-0.143	-0.315	1.000	-0.425	-0.143	0.115
S %	0.365	0.244	0.180	0.000	0.110	0.029	-0.029	-0.029	0.056	0.095	0.039	-0.135	-0.222	-0.029	0.347	0.600	-0.175	-0.002	0.282	0.642	-0.303	-0.425	1.000	-0.729	-0.369
Ti %	-2.294	0.265	-0.501	-0.086	0.150	0.198	-0.198	-0.198	-0.064	0.023	0.045	-0.017	0.007	-0.198	-0.750	-0.718	-0.139	-0.505	-0.459	-0.294	0.755	-0.143	-0.729	1.000	0.393
LN corr rate (µm/khr)	3.570	0.486	-0.433	0.209	-0.405	0.013	-0.013	-0.013	-0.314	-0.355	-0.284	0.264	0.082	-0.013	-0.273	-0.361	-0.169	-0.300	-0.242	-0.086	0.267	0.115	-0.369	0.393	1.000

Table B-3: Correlation matrix for UK coal data subset 3, ferritic leading tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 3) Marked correlations are significant at p < 0.05																							
	Means	Std.Dev.	1000 / Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Mangan ese %	Phosph orus %	Sulphur %	Silicon %	Chromiu m %	Nickel %	Copper %	Molybd enum %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	LN corr rate (µm/khr)
1000 / Metal Temp (1000 / K)	1.179	0.034	1.000	0.363	0.341	0.341	0.341	0.341	0.341	-0.341	0.341	0.341	-0.341	-0.084	-0.193	0.266	-0.094	-0.380	-0.284	0.390	0.190	-0.187	0.374	-0.348
Tg-Tm K	6.022	0.325	0.363	1.000	-0.052	-0.052	-0.052	-0.052	-0.052	0.052	-0.052	-0.052	0.052	-0.038	-0.142	0.228	-0.077	-0.297	-0.332	0.240	0.223	-0.324	0.369	0.270
Carbon %	-2.244	0.168	0.341	-0.052	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	-0.257	-0.302	0.083	-0.208	-0.437	-0.120	0.444	-0.056	0.149	0.112	-0.241
Manganese %	-0.798	0.131	0.341	-0.052	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	-0.257	-0.302	0.083	-0.208	-0.437	-0.120	0.444	-0.056	0.149	0.112	-0.241
Phosphorus %	-4.381	0.366	0.341	-0.052	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	-0.257	-0.302	0.083	-0.208	-0.437	-0.120	0.444	-0.056	0.149	0.112	-0.241
Sulphur %	-4.560	0.429	0.341	-0.052	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	-0.257	-0.302	0.083	-0.208	-0.437	-0.120	0.444	-0.056	0.149	0.112	-0.241
Silicon %	-1.331	0.394	0.341	-0.052	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	-0.257	-0.302	0.083	-0.208	-0.437	-0.120	0.444	-0.056	0.149	0.112	-0.241
Chromium %	0.845	0.156	-0.341	0.052	-1.000	-1.000	-1.000	-1.000	-1.000	1.000	-1.000	-1.000	1.000	0.257	0.302	-0.083	0.208	0.437	0.120	-0.444	0.056	-0.149	-0.112	0.241
Nickel %	-2.797	0.995	0.341	-0.052	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	-0.257	-0.302	0.083	-0.208	-0.437	-0.120	0.444	-0.056	0.149	0.112	-0.241
Copper %	-2.364	0.841	0.341	-0.052	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	-0.257	-0.302	0.083	-0.208	-0.437	-0.120	0.444	-0.056	0.149	0.112	-0.241
Molybdenum %	-0.112	0.142	-0.341	0.052	-1.000	-1.000	-1.000	-1.000	-1.000	1.000	-1.000	-1.000	1.000	0.257	0.302	-0.083	0.208	0.437	0.120	-0.444	0.056	-0.149	-0.112	0.241
Na %	-4.420	0.573	-0.084	-0.038	-0.257	-0.257	-0.257	-0.257	-0.257	0.257	-0.257	-0.257	0.257	1.000	0.969	0.479	0.659	0.320	0.517	-0.252	0.644	0.372	-0.274	0.253
K %	-3.570	0.408	-0.193	-0.142	-0.302	-0.302	-0.302	-0.302	-0.302	0.302	-0.302	-0.302	0.302	0.969	1.000	0.305	0.655	0.481	0.652	-0.417	0.463	0.486	-0.469	0.258
Mg %	-5.200	0.273	0.266	0.228	0.083	0.083	0.083	0.083	0.083	-0.083	0.083	0.083	-0.083	0.479	0.305	1.000	0.608	-0.079	-0.276	0.257	0.655	-0.284	0.293	0.059
Ca %	-3.632	0.450	-0.094	-0.077	-0.208	-0.208	-0.208	-0.208	-0.208	0.208	-0.208	-0.208	0.208	0.659	0.655	0.608	1.000	0.641	0.002	-0.570	0.163	0.046	-0.475	0.034
Al %	-3.348	0.440	-0.380	-0.297	-0.437	-0.437	-0.437	-0.437	-0.437	0.437	-0.437	-0.437	0.437	0.320	0.481	-0.079	0.641	1.000	0.272	-0.925	-0.361	0.036	-0.677	-0.051
Fe %	-2.943	0.343	-0.284	-0.332	-0.120	-0.120	-0.120	-0.120	-0.120	0.120	-0.120	-0.120	0.120	0.517	0.652	-0.276	0.002	0.272	1.000	-0.171	0.113	0.772	-0.495	0.291
Si %	1.540	0.344	0.390	0.240	0.444	0.444	0.444	0.444	0.444	-0.444	0.444	0.444	-0.444	-0.252	-0.417	0.257	-0.570	-0.925	-0.171	1.000	0.464	-0.086	0.742	0.063
Cl %	-1.381	0.483	0.190	0.223	-0.056	-0.056	-0.056	-0.056	-0.056	0.056	-0.056	-0.056	0.056	0.644	0.463	0.655	0.163	-0.361	0.113	0.464	1.000	-0.052	0.498	0.180
S %	0.237	0.222	-0.187	-0.324	0.149	0.149	0.149	0.149	0.149	-0.149	0.149	0.149	-0.149	0.372	0.486	-0.284	0.046	0.036	0.772	-0.086	-0.052	1.000	-0.659	0.275
Ti %	-2.247	0.305	0.374	0.369	0.112	0.112	0.112	0.112	0.112	-0.112	0.112	0.112	-0.112	-0.274	-0.469	0.293	-0.475	-0.677	-0.495	0.742	0.498	-0.659	1.000	-0.111
LN corr rate (µm/khr)	3.206	0.755	-0.348	0.270	-0.241	-0.241	-0.241	-0.241	-0.241	0.241	-0.241	-0.241	0.241	0.253	0.258	0.059	0.034	-0.051	0.291	0.063	0.180	0.275	-0.111	1.000

Table B-4: Correlation matrix for UK coal data subset 4, ferritic non-leading tubes (red text indicates marked correlations are significant at p < 0.05; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 4)																							
	Marked correlations are significant at p < 0.05																							
	Means	Std.Dev.	1000 / Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Manganese %	Phosphorus %	Sulphur %	Silicon %	Chromium %	Nickel %	Copper %	Molybdenum %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	LN corr rate (µm/khr)
1000 / Metal Temp (1000 / K)	1.724	0.066	1.000	0.239	-0.017	-0.017	-0.017	-0.017	-0.017	0.017	-0.017	-0.017	0.017	0.153	0.061	0.003	-0.312	-0.371	0.086	0.260	0.279	0.119	0.174	-0.403
Tg-Tm K	6.100	0.239	0.239	1.000	-0.073	-0.073	-0.073	-0.073	-0.073	0.073	-0.073	-0.073	0.073	0.164	-0.008	0.460	-0.051	-0.290	-0.327	0.302	0.448	-0.470	0.524	0.150
Carbon %	-2.250	0.159	-0.017	-0.073	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	0.255	0.257	0.374	0.295	-0.015	0.163	0.207	0.202	0.177	0.044	0.021
Manganese %	-0.803	0.124	-0.017	-0.073	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	0.255	0.257	0.374	0.295	-0.015	0.163	0.207	0.202	0.177	0.044	0.021
Phosphorus %	-4.395	0.347	-0.017	-0.073	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	0.255	0.257	0.374	0.295	-0.015	0.163	0.207	0.202	0.177	0.044	0.021
Sulphur %	-4.576	0.408	-0.017	-0.073	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	0.255	0.257	0.374	0.295	-0.015	0.163	0.207	0.202	0.177	0.044	0.021
Silicon %	-1.346	0.374	-0.017	-0.073	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	0.255	0.257	0.374	0.295	-0.015	0.163	0.207	0.202	0.177	0.044	0.021
Chromium %	0.851	0.148	0.017	0.073	-1.000	-1.000	-1.000	-1.000	-1.000	1.000	-1.000	-1.000	1.000	-0.255	-0.257	-0.374	-0.295	0.015	-0.163	-0.207	-0.202	-0.177	-0.044	-0.021
Nickel %	-2.835	0.944	-0.017	-0.073	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	0.255	0.257	0.374	0.295	-0.015	0.163	0.207	0.202	0.177	0.044	0.021
Copper %	-2.396	0.798	-0.017	-0.073	1.000	1.000	1.000	1.000	1.000	-1.000	1.000	1.000	-1.000	0.255	0.257	0.374	0.295	-0.015	0.163	0.207	0.202	0.177	0.044	0.021
Molybdenum %	-0.106	0.135	0.017	0.073	-1.000	-1.000	-1.000	-1.000	-1.000	1.000	-1.000	-1.000	1.000	-0.255	-0.257	-0.374	-0.295	0.015	-0.163	-0.207	-0.202	-0.177	-0.044	-0.021
Na %	-4.500	0.463	0.153	0.164	0.255	0.255	0.255	0.255	0.255	-0.255	0.255	0.255	-0.255	1.000	0.940	0.520	0.461	-0.085	0.464	0.127	0.717	0.308	0.077	0.038
K %	-3.624	0.317	0.061	-0.008	0.257	0.257	0.257	0.257	0.257	-0.257	0.257	0.257	-0.257	0.940	1.000	0.277	0.547	0.192	0.660	-0.123	0.467	0.493	-0.221	0.031
Mg %	-5.213	0.220	0.003	0.460	0.374	0.374	0.374	0.374	0.374	-0.374	0.374	0.374	-0.374	0.520	0.277	1.000	0.319	-0.443	-0.254	0.570	0.764	-0.310	0.594	0.131
Ca %	-3.639	0.309	-0.312	-0.051	0.295	0.295	0.295	0.295	0.295	-0.295	0.295	0.295	-0.295	0.461	0.547	0.319	1.000	0.590	0.067	-0.519	-0.041	0.118	-0.442	0.056
Al %	-3.301	0.409	-0.371	-0.290	-0.015	-0.015	-0.015	-0.015	-0.015	0.015	-0.015	-0.015	0.015	-0.085	0.192	-0.443	0.590	1.000	0.235	-0.923	-0.644	0.080	-0.726	0.030
Fe %	-3.017	0.280	0.086	-0.327	0.163	0.163	0.163	0.163	0.163	-0.163	0.163	0.163	-0.163	0.464	0.660	-0.254	0.067	0.235	1.000	-0.107	0.023	0.787	-0.467	-0.038
Si %	1.503	0.328	0.260	0.302	0.207	0.207	0.207	0.207	0.207	-0.207	0.207	0.207	-0.207	0.127	-0.123	0.570	-0.519	-0.923	-0.107	1.000	0.688	-0.086	0.777	0.059
Cl %	-1.386	0.487	0.279	0.448	0.202	0.202	0.202	0.202	0.202	-0.202	0.202	0.202	-0.202	0.717	0.467	0.764	-0.041	-0.644	0.023	0.688	1.000	-0.131	0.709	0.055
S %	0.169	0.203	0.119	-0.470	0.177	0.177	0.177	0.177	0.177	-0.177	0.177	0.177	-0.177	0.308	0.493	-0.310	0.118	0.080	0.787	-0.086	-0.131	1.000	-0.633	-0.143
Ti %	-2.206	0.310	0.174	0.524	0.044	0.044	0.044	0.044	0.044	-0.044	0.044	0.044	-0.044	0.077	-0.221	0.594	-0.442	-0.726	-0.467	0.777	0.709	-0.633	1.000	0.142
LN corr rate (µm/khr)	2.882	0.751	-0.403	0.150	0.021	0.021	0.021	0.021	0.021	-0.021	0.021	0.021	-0.021	0.038	0.031	0.131	0.056	0.030	-0.038	0.059	0.055	-0.143	0.142	1.000

Table B-5: Correlation matrix for US coal data subset 5, austenitic tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 5)																																			
	Marked correlations are significant at p < 0.05																																			
	Means	Std.Dev.	1000 / Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Manganese %	Phosphorus %	Sulphur %	Silicon %	Chromium %	Nickel %	Molybdenum %	Niobium %	Titanium %	Copper %	Vanadium %	Aluminium %	Nitrogen %	Cerium %	Tungsten %	Boron %	Tantalum %	Cobalt %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	P %	Mn %	Ln Corr Rate (µm/hr)
1000 / Metal Temp (1000 / K)	1.099	0.066	1.000	0.730	0.093	-0.128	0.070	0.119	-0.255	-0.121	-0.172	0.100	-0.116	0.062	0.198	-0.080	-0.192	-0.044	0.086	0.135	-0.228	0.075	0.118	0.041	0.266	0.079	0.201	-0.160	0.342	0.156	-0.241	0.433	-0.306	-0.237	0.144	0.405
Tg-Tm K	5.664	0.441	0.730	1.000	0.097	-0.102	0.092	0.196	-0.346	0.096	0.015	0.218	-0.278	0.026	0.203	-0.263	-0.257	-0.165	0.127	0.265	-0.270	0.262	0.271	0.218	0.506	0.248	0.358	-0.010	0.722	0.369	-0.291	0.469	-0.466	-0.694	0.321	0.761
Carbon %	-2.385	0.315	0.093	0.097	1.000	-0.104	-0.386	-0.200	0.174	-0.217	-0.032	-0.299	-0.437	-0.404	-0.183	0.031	0.065	-0.184	-0.040	0.328	-0.263	0.049	-0.364	-0.231	-0.185	-0.255	-0.217	0.060	-0.036	-0.101	0.009	0.197	0.092	-0.113	0.264	0.143
Manganese %	0.300	0.476	-0.128	-0.102	-0.104	1.000	-0.253	-0.288	0.401	0.314	0.068	0.147	-0.035	-0.097	-0.544	-0.141	0.382	-0.076	0.168	-0.108	0.386	0.155	-0.259	0.026	0.016	0.040	0.068	-0.042	0.035	-0.010	-0.032	0.021	-0.028	0.016	-0.005	-0.026
Phosphorus %	-2.288	1.810	0.070	0.092	-0.386	-0.253	1.000	0.897	-0.261	0.204	0.016	-0.016	-0.011	0.312	0.216	0.365	-0.098	-0.156	0.078	-0.006	-0.185	-0.084	0.237	0.293	0.318	0.309	0.344	-0.316	0.056	0.066	0.173	-0.198	-0.112	0.204	-0.276	-0.163
Sulphur %	-2.659	2.219	0.119	0.196	-0.200	-0.288	0.897	1.000	-0.054	0.172	0.000	-0.288	-0.021	0.342	0.056	0.143	-0.226	-0.283	0.058	-0.059	-0.133	-0.072	0.225	0.250	0.310	0.258	0.312	-0.341	0.103	0.055	0.207	-0.114	-0.128	0.124	-0.175	-0.081
Silicon %	-0.267	0.563	-0.255	-0.346	0.174	0.401	-0.261	-0.054	1.000	0.081	0.190	-0.376	0.223	-0.008	-0.717	-0.089	0.168	-0.016	-0.260	-0.085	0.297	0.089	-0.081	-0.182	-0.258	-0.204	-0.212	-0.084	-0.326	-0.206	0.153	-0.078	0.205	0.288	-0.055	-0.289
Chromium %	3.063	0.137	-0.121	0.096	-0.217	0.314	0.204	0.172	0.081	1.000	0.613	0.022	-0.190	-0.130	-0.424	0.034	0.132	-0.310	-0.031	0.137	0.044	0.213	0.213	-0.023	0.093	-0.051	0.041	-0.161	0.192	-0.016	0.014	0.238	-0.093	-0.115	0.255	-0.011
Nickel %	2.956	0.421	-0.172	0.015	-0.032	0.068	0.016	0.000	0.190	0.613	1.000	0.195	-0.166	-0.345	-0.386	-0.214	-0.120	-0.073	0.171	0.302	-0.036	0.018	0.292	-0.010	0.072	-0.012	0.003	0.019	0.114	0.067	-0.113	0.124	-0.067	-0.119	0.093	0.025
Molybdenum %	0.083	0.530	0.100	0.218	-0.299	0.147	-0.016	-0.288	-0.376	0.022	0.195	1.000	-0.345	-0.247	0.402	-0.218	-0.169	-0.093	0.024	0.436	-0.345	-0.029	0.295	0.202	0.222	0.200	0.190	0.158	0.266	0.231	-0.212	0.038	-0.193	-0.261	-0.014	0.325
Niobium %	-0.505	0.731	-0.116	-0.278	-0.437	-0.035	-0.011	-0.021	0.223	-0.190	-0.166	-0.345	1.000	0.510	-0.069	0.297	0.187	0.796	-0.105	-0.634	0.570	0.130	0.038	0.016	-0.102	0.034	-0.031	0.054	-0.163	-0.013	-0.027	-0.182	0.056	0.166	-0.225	-0.173
Titanium %	-0.466	1.007	0.062	0.026	-0.404	-0.097	0.312	0.342	-0.008	-0.130	-0.345	-0.247	0.510	1.000	0.163	0.144	0.009	0.203	-0.071	-0.508	0.329	0.087	0.087	0.223	0.184	0.239	0.200	0.036	0.112	0.157	-0.002	-0.151	-0.139	-0.002	-0.189	0.027
Copper %	0.134	0.487	0.198	0.203	-0.183	-0.544	0.216	0.056	-0.717	-0.424	-0.386	0.402	-0.069	0.163	1.000	0.052	-0.189	0.050	0.042	-0.093	-0.189	-0.052	-0.052	0.220	0.206	0.213	0.158	0.139	0.158	0.207	-0.047	-0.103	-0.146	-0.130	-0.120	0.269
Vanadium %	-0.025	0.137	-0.080	-0.263	-0.031	-0.141	0.365	0.143	-0.089	0.034	-0.214	-0.218	0.297	0.144	0.052	1.000	0.578	0.375	-0.028	0.063	-0.077	0.035	0.035	-0.059	-0.135	-0.057	-0.072	-0.066	-0.245	-0.130	0.103	-0.143	0.142	0.278	-0.142	-0.289
Aluminium %	-0.512	1.106	-0.192	-0.257	0.065	0.382	-0.098	-0.226	0.168	0.132	-0.120	-0.169	0.187	0.009	-0.189	0.578	1.000	0.247	-0.071	-0.081	0.502	0.087	-0.304	-0.138	-0.202	-0.144	-0.158	0.057	-0.179	-0.110	-0.012	-0.010	0.127	0.102	0.000	-0.095
Nitrogen %	-1.412	1.598	-0.044	-0.165	-0.184	-0.076	-0.156	-0.283	-0.016	-0.310	-0.073	-0.093	0.796	0.203	0.050	0.375	0.247	1.000	0.019	-0.363	0.362	0.166	-0.023	-0.026	-0.097	0.002	-0.071	0.175	-0.111	0.038	-0.146	-0.127	0.063	0.047	-0.157	-0.058
Cerium %	-0.057	0.376	0.086	0.127	-0.040	0.168	0.078	0.058	-0.260	-0.031	0.171	0.024	-0.105	-0.071	0.042	-0.028	-0.071	0.019	1.000	0.051	-0.062	0.028	0.028	0.194	0.252	0.253	0.231	0.040	0.209	0.185	-0.055	-0.050	-0.175	-0.110	-0.115	0.132
Tungsten %	0.091	0.274	0.135	0.265	0.328	-0.108	-0.006	-0.059	-0.085	0.137	0.302	0.436	-0.634	-0.508	-0.093	0.063	-0.081	-0.363	0.051	1.000	-0.786	-0.063	0.566	-0.080	0.009	-0.096	-0.043	0.051	0.153	0.021	-0.083	0.231	-0.042	-0.254	0.255	0.232
Boron %	-0.735	1.793	-0.228	-0.270	-0.263	0.386	-0.185	-0.133	0.297	0.044	-0.036	-0.345	0.570	0.329	-0.189	-0.077	0.502	0.362	-0.062	-0.786	1.000	0.077	-0.501	-0.005	-0.080	0.006	-0.038	0.032	-0.124	-0.020	-0.024	-0.111	0.046	0.125	-0.144	-0.118
Tantalum %	0.014	0.074	0.075	0.262	0.049	0.155	-0.084	-0.072	0.089	0.213	0.018	-0.029	0.130	0.087	-0.052	0.035	0.087	0.166	0.028	-0.063	0.077	1.000	-0.035	0.059	0.135	0.057	0.072	0.066	0.245	0.130	-0.103	0.143	-0.142	-0.278	0.142	0.254
Cobalt %	0.037	0.199	0.118	0.271	-0.364	-0.259	0.237	0.225	-0.081	0.213	0.292	0.295	0.038	0.087	-0.052	0.035	-0.304	-0.023	0.028	0.566	-0.501	-0.035	1.000	0.059	0.135	0.057	0.072	0.066	0.245	0.130	-0.103	0.143	-0.142	-0.278	0.142	0.209
Na %	-3.665	1.834	0.041	0.218	-0.231	0.026	0.293	0.250	-0.182	-0.023	-0.010	0.202	0.016	0.223	0.220	-0.059	-0.138	-0.026	0.194	-0.080	-0.005	0.059	0.059	1.000	0.812	0.946	0.836	0.312	0.619	0.777	-0.245	-0.449	-0.639	-0.353	-0.635	0.357
K %	-2.966	1.605	0.266	0.506	-0.185	0.016	0.318	0.310	-0.258	0.093	0.072	0.222	-0.102	0.184	0.206	-0.135	-0.202	-0.097	0.252	0.009	-0.080	0.135	0.135	0.812	1.000	0.797	0.686	0.367	0.780	0.885	-0.298	-0.061	-0.754	-0.376	-0.342	0.499
Mg %	-3.521	1.852	0.079	0.248	-0.255	0.040	0.309	0.258	-0.204	-0.051	-0.012	0.200	0.034	0.239	0.213	-0.057	-0.144	0.002	0.253	-0.096	0.006	0.057	0.057	0.946	0.797	1.000	0.911	0.244	0.599	0.705	-0.318	-0.430	-0.590	-0.388	-0.677	0.326
Ca %	-2.485	2.105	0.201	0.358	-0.217	0.068	0.344	0.312	-0.212	0.041	0.003	0.190	-0.031	0.200	0.158	-0.072	-0.158	-0.071	0.231	-0.043	-0.038	0.072	0.072	0.836	0.686	0.911	1.000	-0.087	0.613	0.464	-0.190	-0.275	-0.498	-0.409	-0.485	0.368
Al %	0.101	0.387	-0.160	-0.010	0.060	-0.042	-0.316	-0.341	-0.084	-0.161	0.019	0.158	0.054	0.036	0.139	-0.066	0.057	0.175	0.040	0.051	0.032	0.066	0.066	0.312	0.367	0.244	-0.087	1.000	0.192	0.648	-0.211	-0.291	-0.166	-0.219	-0.186	0.283
Fe %	-0.730	1.202	0.342	0.722	-0.036	0.035	0.056	0.103	-0.326	0.192	0.114	0.266	-0.163	0.112	0.158	-0.245	-0.179	-0.111	0.209	0.153	-0.124	0.245	0.245	0.619	0.780	0.599	0.613	0.192	1.000	0.711	-0.401	0.303	-0.827	-0.777	0.097	0.779
Si %	0.554	0.455	0.156	0.369	-0.101	-0.010	0.066	0.055	-0.206	-0.016	0.067	0.231	-0.013	0.157	0.207	-0.130	-0.110	0.038	0.185	0.021	-0.020	0.130	0.130	0.777	0.885	0.705	0.464	0.648	0.711	1.000	-0.504	-0.088	-0.797	-0.436	-0.404	0.500
Cl %	-1.939	1.318	-0.241	-0.291	0.009	-0.032	0.173	0.207	0.153	0.014	-0.113	-0.212	-0.027	-0.002	-0.047	0.103	-0.0.																			

Table B-6: Correlation matrix for US coal data subset 6, nickel-based tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 6)																															
	Marked correlations are significant at p < 0.05																															
	Means	Std.Dev.	1000 / Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Manganese %	Phosphorus %	Sulphur %	Silicon %	Chromium %	Molybdenum %	Niobium %	Titanium %	Copper %	Aluminium %	Tungsten %	Boron %	Cobalt %	Iron %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	P %	Mn %	Ln Corr Rate (µm/khr)
1000 / Metal Temp (1000 / K)	1.088	0.090	1.000	0.850	0.069	-0.515	0.088	0.088	-0.211	0.203	0.155	0.218	-0.040	-0.011	-0.321	-0.218	0.449	-0.100	-0.019	-0.102	-0.086	-0.138	-0.232	0.346	-0.138	0.212	-0.332	0.035	-0.027	-0.131	-0.165	-0.191
Tg-Tm K	5.568	0.305	0.850	1.000	-0.034	-0.345	0.214	0.214	-0.052	-0.073	0.192	0.261	0.142	-0.087	-0.194	-0.150	0.316	0.187	-0.208	0.113	0.136	0.123	0.077	0.153	0.134	0.264	-0.361	0.077	-0.122	-0.469	-0.207	0.026
Carbon %	-2.702	0.540	0.069	-0.034	1.000	0.166	0.119	0.119	-0.170	-0.200	0.245	-0.297	-0.392	-0.067	-0.450	0.450	0.195	-0.418	0.121	-0.102	-0.154	-0.116	-0.094	-0.067	-0.191	-0.142	0.083	-0.094	0.102	0.287	0.016	0.064
Manganese %	-0.235	0.569	-0.515	-0.345	0.166	1.000	0.520	0.520	0.516	-0.386	0.387	-0.384	-0.178	-0.229	0.398	0.207	-0.611	0.164	0.082	0.327	0.335	0.410	0.472	-0.533	0.138	-0.047	0.134	-0.064	-0.124	0.328	-0.223	0.063
Phosphorus %	-0.186	0.984	0.088	0.214	0.119	0.520	1.000	1.000	0.338	-0.295	0.710	-0.078	-0.115	-0.105	-0.080	0.158	-0.288	0.218	-0.085	0.452	0.473	0.465	0.417	-0.035	0.297	0.269	-0.008	-0.134	-0.191	-0.036	-0.254	0.083
Sulphur %	-0.218	1.154	0.088	0.214	0.119	0.520	1.000	1.000	0.338	-0.295	0.710	-0.078	-0.115	-0.105	-0.080	0.158	-0.288	0.218	-0.085	0.452	0.473	0.465	0.417	-0.035	0.297	0.269	-0.008	-0.134	-0.191	-0.036	-0.254	0.083
Silicon %	-0.506	0.479	-0.211	-0.052	-0.170	0.516	0.338	0.338	1.000	-0.012	0.572	0.547	0.600	-0.586	0.381	-0.514	-0.074	0.779	-0.685	0.089	0.095	0.165	0.244	-0.336	0.010	-0.104	0.062	-0.030	0.000	0.075	-0.101	-0.202
Chromium %	3.205	0.163	0.203	-0.073	-0.200	-0.386	-0.295	-0.295	-0.012	1.000	-0.364	0.222	-0.024	0.252	-0.011	-0.469	0.483	-0.314	-0.195	-0.721	-0.632	-0.722	-0.684	0.327	-0.476	-0.261	0.028	0.127	0.276	-0.017	0.356	-0.253
Molybdenum %	0.481	0.943	0.155	0.192	0.245	0.387	0.710	0.710	0.572	-0.364	1.000	0.266	0.172	-0.687	-0.038	-0.111	0.070	0.471	-0.286	0.406	0.331	0.417	0.387	-0.093	0.081	0.126	0.066	-0.257	-0.045	0.240	-0.304	-0.147
Niobium %	-0.482	1.193	0.218	0.261	-0.297	-0.384	-0.078	-0.078	0.547	0.222	0.266	1.000	0.915	-0.293	-0.159	-0.523	0.357	0.731	-0.866	-0.128	-0.123	-0.119	-0.104	0.081	-0.067	-0.019	-0.090	0.037	0.055	-0.190	0.031	-0.277
Titanium %	-0.717	1.196	-0.040	0.142	-0.392	-0.178	-0.115	-0.115	0.600	-0.024	0.172	0.915	1.000	-0.251	-0.027	-0.358	0.056	0.860	-0.846	0.033	0.046	0.070	0.107	-0.145	0.089	0.001	-0.096	0.086	-0.048	-0.210	-0.037	-0.183
Copper %	-0.533	0.979	-0.011	-0.087	-0.067	-0.229	-0.105	-0.105	-0.586	0.252	-0.687	-0.293	-0.251	1.000	-0.379	0.454	-0.375	-0.510	0.294	-0.195	-0.099	-0.223	-0.265	0.163	0.002	0.074	-0.124	0.180	-0.081	-0.105	0.114	0.107
Aluminium %	-0.235	0.565	-0.321	-0.194	-0.450	0.398	-0.080	-0.080	0.381	-0.011	-0.038	-0.159	-0.027	-0.379	1.000	-0.447	-0.151	0.229	0.096	0.089	0.089	0.138	0.196	-0.225	0.094	-0.079	0.093	0.013	-0.005	-0.044	0.008	0.039
Tungsten %	0.903	1.103	-0.218	-0.150	0.450	0.207	0.158	0.158	-0.514	-0.469	-0.111	-0.523	-0.358	0.454	-0.447	1.000	-0.429	-0.415	0.370	0.244	0.262	0.254	0.231	-0.195	0.166	0.102	-0.008	0.014	-0.165	0.158	-0.148	0.225
Boron %	-3.865	2.580	0.449	0.316	0.195	-0.611	-0.288	-0.288	-0.074	0.483	0.070	0.357	0.056	-0.375	-0.151	-0.429	1.000	-0.111	-0.317	-0.453	-0.463	-0.483	-0.455	0.385	-0.263	-0.162	0.025	0.007	0.266	-0.288	0.313	-0.056
Cobalt %	1.472	1.301	-0.100	0.187	-0.418	0.164	0.218	0.218	0.779	-0.314	0.471	0.731	0.860	-0.510	0.229	-0.415	-0.111	1.000	-0.715	0.342	0.327	0.387	0.412	-0.242	0.289	0.113	-0.063	-0.006	-0.141	-0.225	-0.174	-0.081
Iron %	1.701	1.139	-0.019	-0.208	0.121	0.082	-0.085	-0.085	-0.685	-0.195	-0.286	-0.866	-0.846	0.294	0.096	0.370	-0.317	-0.715	1.000	0.161	0.101	0.105	0.024	0.101	-0.024	0.092	0.053	-0.124	-0.027	0.348	-0.110	0.111
Na %	-3.197	1.205	-0.102	0.113	-0.102	0.327	0.452	0.452	0.089	-0.721	0.406	-0.128	0.033	-0.195	0.089	0.244	-0.453	0.342	0.161	1.000	0.841	0.968	0.822	0.117	0.500	0.506	0.010	-0.385	-0.213	-0.017	-0.541	0.200
K %	-2.576	1.361	-0.086	0.136	-0.154	0.335	0.473	0.473	0.095	-0.632	0.331	-0.123	0.046	-0.099	0.089	0.262	-0.463	0.327	0.101	0.841	1.000	0.778	0.515	0.193	0.793	0.825	-0.279	0.144	-0.681	-0.108	-0.423	0.138
Mg %	-3.104	1.424	-0.138	0.123	-0.116	0.410	0.465	0.465	0.165	-0.722	0.417	-0.119	0.070	-0.223	0.138	0.254	-0.483	0.387	0.105	0.968	0.778	1.000	0.922	-0.074	0.376	0.386	-0.013	-0.420	-0.122	-0.020	-0.642	0.208
Ca %	-2.134	1.919	-0.232	0.077	-0.094	0.472	0.417	0.417	0.244	-0.684	0.387	-0.104	0.107	-0.265	0.196	0.231	-0.455	0.412	0.024	0.822	0.515	0.922	1.000	-0.331	0.140	0.022	0.157	-0.577	0.176	-0.046	-0.573	0.262
Al %	-0.058	0.316	0.346	0.153	-0.067	-0.533	-0.035	-0.035	-0.336	0.327	-0.093	0.081	-0.145	0.163	-0.225	-0.195	0.385	-0.242	0.101	0.117	0.193	-0.074	-0.331	1.000	0.306	0.469	0.118	-0.038	-0.132	-0.180	0.282	-0.003
Fe %	-0.994	0.779	-0.138	0.134	-0.191	0.138	0.297	0.297	0.010	-0.476	0.081	-0.067	0.089	0.002	0.094	0.166	-0.263	0.289	-0.024	0.500	0.793	0.376	0.140	0.306	1.000	0.728	-0.156	0.433	-0.751	-0.452	0.146	0.266
Si %	0.538	0.385	0.212	0.264	-0.142	-0.047	0.269	0.269	-0.104	-0.261	0.126	-0.019	0.001	0.074	-0.079	0.102	-0.162	0.113	0.092	0.506	0.825	0.386	0.022	0.469	0.728	1.000	-0.597	0.461	-0.856	-0.166	-0.338	-0.013
Cl %	-1.330	1.708	-0.332	-0.361	0.083	0.134	-0.008	-0.008	0.062	0.028	0.066	-0.090	-0.096	-0.124	0.093	-0.008	0.025	-0.063	0.053	0.010	-0.279	-0.013	0.157	0.118	-0.156	-0.597	1.000	-0.629	0.658	0.150	0.559	0.144
S %	0.432	0.608	0.035	0.077	-0.094	-0.064	-0.134	-0.134	-0.030	0.127	-0.257	0.037	0.086	0.180	0.013	0.014	0.007	-0.006	-0.124	-0.385	0.144	-0.420	-0.577	-0.038	0.433	0.461	-0.629	1.000	-0.795	-0.221	0.185	-0.096
Ti %	-1.453	1.462	-0.027	-0.122	0.102	-0.124	-0.191	-0.191	0.000	0.276	-0.045	0.055	-0.048	-0.081	-0.005	-0.165	0.266	-0.141	-0.027	-0.213	-0.681	-0.122	0.176	-0.132	-0.751	-0.856	0.658	-0.795	1.000	0.128	0.142	0.046
P %	-0.121	0.638	-0.131	-0.469	0.287	0.328	-0.036	-0.036	0.075	-0.017	0.240	-0.190	-0.210	-0.105	-0.044	0.158	-0.288	-0.225	0.348	-0.017	-0.108	-0.020	-0.046	-0.180	-0.452	-0.166	0.150	-0.221	0.128	1.000	-0.254	-0.427
Mn %	-2.827	2.143	-0.165	-0.207	0.016	-0.223	-0.254	-0.254	-0.101	0.356	-0.304	0.031	-0.037	0.114	0.008	-0.148	0.313	-0.174	-0.110	-0.541	-0.423	-0.642	-0.573	0.282	0.146	-0.338	0.559	0.185	0.142	-0.254	1.000	0.121
Ln Corr Rate (µm/khr)	2.849	0.864	-0.191	0.026	0.064	0.063	0.083	0.083	-0.202	-0.253	-0.147	-0.277	-0.183	0.107	0.039	0.225	-0.056	-0.081	0.111	0.200	0.138	0.208	0.262	-0.003	0.266	-0.013	0.144	-0.096	0.046	-0.427	0.121	1.000

Table B-7: Correlation matrix for US coal data subset 7, coatings (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (US Data subset 7)																																
	Marked correlations are significant at p < .05000																																
	1000 / Metal Temp (1000 / K)	Carbon %	Manganese (%)	Phosphorus %	Sulphur %	Silicon %	Chromium %	Nickel %	Molybdenum %	Niobium %	Titanium %	Copper %	Vanadium %	Aluminium %	Nitrogen %	Cerium %	Tantalum %	Boron %	Tungsten %	Iron %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	P %	Mn %	Ln Corr Rate (μ _m /khr)
1000 / Metal Temp (1000 / K)	1.000	-0.210	-0.117	-0.224	-0.153	-0.214	-0.155	-0.100	0.080	-0.111	0.231	-0.218	-0.266	-0.163	-0.242	0.086	-0.237	-0.032	0.316	0.029	-0.030	0.032	0.005	0.049	0.058	0.188	0.112	-0.324	0.194	-0.067	-0.411	0.029	0.452
Carbon %	-0.210	1.000	0.205	0.243	0.250	0.513	0.203	0.137	-0.143	0.367	0.083	0.281	0.485	0.427	0.319	-0.088	0.055	-0.234	-0.248	-0.275	-0.112	-0.079	-0.081	-0.035	-0.198	-0.186	-0.118	-0.041	0.030	0.054	0.185	-0.086	-0.168
Manganese %	-0.117	0.205	1.000	0.260	0.187	0.548	-0.145	-0.006	0.268	0.157	0.594	0.490	0.178	0.399	0.358	0.251	-0.090	-0.063	-0.066	0.461	-0.058	-0.072	-0.075	-0.111	-0.014	-0.299	-0.074	0.116	-0.139	0.116	0.387	-0.117	-0.086
Phosphorus %	-0.224	0.243	0.260	1.000	0.901	0.156	0.224	0.388	0.493	0.432	-0.147	0.162	0.309	0.631	0.878	0.117	0.211	-0.076	0.156	-0.343	-0.020	0.140	0.019	0.110	-0.392	-0.136	-0.156	0.238	0.042	-0.004	0.494	-0.063	-0.444
Sulphur %	-0.153	0.250	0.187	0.901	1.000	0.147	0.194	0.333	0.371	0.185	-0.175	0.014	0.199	0.438	0.694	0.130	0.113	-0.079	0.161	-0.348	-0.023	0.173	0.023	0.134	-0.421	-0.078	-0.154	0.241	0.092	-0.027	0.455	-0.022	-0.461
Silicon %	-0.214	0.513	0.548	0.156	0.147	1.000	-0.204	-0.271	-0.256	0.220	0.441	0.602	0.332	0.312	0.240	-0.446	-0.005	-0.094	-0.484	0.477	-0.105	-0.204	-0.141	-0.240	0.193	-0.363	-0.008	-0.063	-0.179	0.158	0.230	-0.156	0.134
Chromium %	-0.155	0.203	-0.145	0.224	0.194	-0.204	1.000	0.882	-0.117	0.147	-0.345	-0.356	0.492	0.049	0.231	0.107	-0.024	0.488	-0.077	-0.747	0.247	0.408	0.307	0.401	-0.304	0.295	0.085	0.035	0.154	-0.244	0.046	-0.092	-0.409
Nickel %	-0.100	0.137	-0.006	0.388	0.333	-0.271	0.882	1.000	0.025	0.154	-0.266	-0.456	0.547	0.328	0.463	0.165	-0.121	0.288	0.175	-0.691	0.185	0.397	0.247	0.367	-0.363	0.286	0.030	0.110	0.194	-0.221	0.101	-0.014	-0.404
Molybdenum %	0.080	-0.143	0.268	0.493	0.371	-0.256	-0.117	0.025	1.000	0.364	0.020	0.362	-0.397	0.166	0.448	0.404	0.069	-0.024	0.604	-0.054	0.011	0.004	0.023	0.048	-0.161	-0.198	-0.118	0.177	-0.126	0.091	0.344	-0.107	-0.209
Niobium %	-0.111	0.367	0.157	0.432	0.185	0.220	0.147	0.154	0.364	1.000	-0.171	0.575	0.333	0.611	0.521	-0.203	0.234	-0.080	0.163	-0.124	-0.042	-0.089	-0.043	-0.047	-0.047	-0.260	-0.100	0.095	-0.152	0.142	0.278	-0.112	-0.106
Titanium %	0.231	0.083	0.594	-0.147	-0.175	0.441	-0.345	-0.266	0.020	-0.171	1.000	0.245	-0.171	-0.007	-0.096	-0.129	-0.072	-0.051	0.104	0.586	-0.050	-0.136	-0.077	-0.133	0.180	-0.105	0.019	-0.063	-0.086	0.082	-0.053	-0.015	0.223
Copper %	-0.218	0.281	0.490	0.162	0.014	0.602	-0.356	-0.456	0.362	0.575	0.245	1.000	-0.162	0.191	0.247	-0.221	0.161	-0.087	-0.058	0.462	-0.053	-0.278	-0.091	-0.210	0.144	-0.555	-0.089	0.028	-0.379	0.248	0.437	-0.309	-0.029
Vanadium %	-0.266	0.485	0.178	0.309	0.199	0.332	0.492	0.547	-0.397	0.333	-0.171	-0.162	1.000	0.676	0.448	-0.126	-0.070	-0.049	-0.484	-0.279	-0.039	0.109	-0.017	0.043	-0.139	0.129	-0.005	0.009	0.184	-0.088	-0.014	0.101	-0.039
Aluminium %	-0.163	0.427	0.399	0.631	0.438	0.312	0.049	0.328	0.166	0.611	-0.007	0.191	0.676	1.000	0.809	-0.064	-0.047	-0.249	0.051	-0.080	-0.139	-0.025	-0.124	-0.061	-0.190	-0.099	-0.136	0.128	0.078	0.055	0.212	0.085	-0.019
Nitrogen %	-0.242	0.319	0.358	0.878	0.694	0.240	0.231	0.463	0.448	0.521	-0.096	0.247	0.448	0.809	1.000	0.029	-0.099	-0.069	0.142	-0.280	-0.023	0.103	0.010	0.081	-0.315	-0.129	-0.126	0.175	0.032	0.002	0.406	-0.066	-0.249
Cerium %	0.086	-0.088	0.251	0.117	0.130	-0.446	0.107	0.165	0.404	-0.203	-0.129	-0.221	-0.126	-0.064	0.029	1.000	-0.053	-0.037	0.077	-0.325	-0.016	0.157	0.019	0.116	-0.240	0.135	-0.051	0.100	0.174	-0.075	0.061	0.106	-0.162
Tantalum %	-0.237	0.055	-0.090	0.211	0.113	-0.005	-0.024	-0.121	0.069	0.234	-0.072	0.161	-0.070	-0.047	-0.099	-0.053	1.000	-0.021	0.043	0.013	0.003	-0.084	-0.008	-0.055	-0.043	-0.317	-0.078	0.089	-0.200	0.100	0.386	-0.206	-0.482
Boron %	-0.032	-0.234	-0.063	-0.076	-0.079	-0.094	0.488	0.288	-0.024	-0.080	-0.051	-0.087	-0.049	-0.249	-0.069	-0.037	-0.021	1.000	0.030	-0.142	0.264	0.269	0.275	0.258	0.031	0.198	0.177	-0.046	-0.019	-0.159	-0.061	-0.144	-0.043
Tungsten %	0.316	-0.248	-0.066	0.156	0.161	-0.484	-0.077	0.175	0.604	0.163	0.104	-0.058	-0.484	0.051	0.142	0.077	0.043	0.030	1.000	-0.089	0.045	0.053	0.061	0.108	-0.129	-0.020	-0.073	0.142	-0.056	0.041	0.124	-0.015	-0.162
Iron %	0.029	-0.275	0.461	-0.343	-0.348	0.477	-0.747	-0.691	-0.054	-0.124	0.586	0.462	-0.279	-0.080	-0.280	-0.325	0.013	-0.142	-0.089	1.000	-0.123	-0.355	-0.203	-0.367	0.430	-0.348	0.008	-0.041	-0.285	0.228	0.044	-0.054	0.341
Na %	-0.030	-0.112	-0.058	-0.020	-0.023	-0.105	0.247	0.185	0.011	-0.042	-0.050	-0.053	-0.039	-0.139	-0.023	-0.016	0.003	0.264	0.045	-0.123	1.000	0.807	0.972	0.774	0.423	0.503	0.700	-0.171	-0.414	-0.394	-0.182	-0.659	0.051
K %	0.032	-0.079	-0.072	0.140	0.173	-0.204	0.408	0.397	0.004	-0.089	-0.136	-0.278	0.109	-0.025	0.103	0.157	-0.084	0.269	0.053	-0.355	0.807	1.000	0.740	0.509	0.389	0.693	0.845	-0.216	0.017	-0.654	-0.061	-0.406	0.031
Mg %	0.005	-0.081	-0.075	0.019	0.023	-0.141	0.307	0.247	0.023	-0.043	-0.077	-0.091	-0.017	-0.124	0.010	0.019	-0.008	0.275	0.061	-0.203	0.972	0.740	1.000	0.892	0.229	0.475	0.572	-0.218	-0.371	-0.365	-0.245	-0.694	-0.007
Ca %	0.049	-0.035	-0.111	0.110	0.134	-0.240	0.401	0.367	0.048	-0.047	-0.133	-0.210	0.043	-0.061	0.081	0.116	-0.055	0.258	0.108	-0.367	0.774	0.509	0.892	1.000	-0.148	0.381	0.189	-0.080	-0.314	-0.149	-0.325	-0.532	-0.110
Al %	0.058	-0.198	-0.014	-0.392	-0.421	0.193	-0.304	-0.363	-0.161	-0.047	0.180	0.144	-0.139	-0.190	-0.315	-0.240	-0.043	0.031	-0.129	0.430	0.423	0.389	0.229	-0.148	1.000	0.220	0.590	-0.049	-0.443	0.628	0.357	0.515	-0.273
Fe %	0.188	-0.186	-0.299	-0.136	-0.078	-0.363	0.295	0.286	-0.198	-0.260	-0.105	-0.555	0.129	-0.099	-0.129	0.135	-0.317	0.198	-0.020	-0.348	0.503	0.693	0.475	0.381	0.220	1.000	0.590	-0.224	0.419	-0.731	-0.641	0.130	0.328
Si %	0.112	-0.118	-0.074	-0.156	-0.154	-0.008	0.085	0.030	-0.118	-0.100	0.019	-0.089	-0.005	-0.136	-0.126	-0.051	-0.078	0.177	-0.073	0.008	0.700	0.845	0.572	0.189	0.705	0.590	1.000	-0.480	0.035	-0.697	-0.142	-0.450	0.318
Cl %	-0.324	-0.041	0.116	0.238	0.241	-0.063	0.035	0.110	0.177	0.095	-0.063	0.028	0.009	0.128	0.175	0.100	0.089	-0.046	0.142	-0.041	-0.171	-0.216	-0.218	-0.080	-0.049	-0.224	-0.480	1.000	-0.443	0.628	0.357	0.515	-0.273
S %	0.194	0.030	-0.139	0.042	0.092	-0.179	0.154	0.194	-0.126	-0.152	-0.086	-0.379	0.184	0.078	0.032	0.174	-0.200	-0.019	-0.056	-0.285	-0.414	0.017	-0.371	-0.314	-0.365	0.419	0.035	-0.443	0.400	-0.621	-0.284	0.402	0.054
Ti %	-0.067	0.054	0.116	-0.004	-0.027	0.158	-0.244	-0.221	0.091	0.142	0.082	0.248	-0.088	0.055	0.002	-0.075	0.100	-0.159	0.041	0.228	-0.394	-0.654	-0.365	-0.149	-0.107	-0.731	-0.697	0.628	-0.621	1.000	0.274	0.216	-0.048
P %	-0.411	0.185	0.387	0.494	0.455	0.230	0.046	0.101	0.344	0.278	-0.053	0.437	-0.014	0.212	0.406	0.061	0.386	-0.061	0.124	0.044	-0.182	-0.061	-0.245	-0.325	-0.086	-0.641	-0.142	0.357	-0.284	0.274	1.000	-0.177	-0.637
Mn %	0.029	-0.086	-0.117	-0.063	-0.022	-0.156	-0.092	-0.014	-0.107	-0.112	-0.015	-0.309	0.101	0.085	-0.066	0.106	-0.206	-0.144	-0.015	-0.054	-0.659	-0.406	-0.694	-0.									

Table B-8: Correlation matrix for world traded coal data subset 8, austenitic tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 8)																					
	Marked correlations are significant at p < 0.05																					
	Means	Std.Dev.	1000/Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Silicon %	Phosphorus %	Sulphur %	Vanadium %	Chromium %	Manganese %	Nickel %	Niobium %	Molybdenum %	Titanium %	Nitrogen %	Tungsten %	Copper %	Boron %	Aluminium %	Cobalt %	Ln Corr Rate (µm/khr)
1000/Metal Temp (1000 / K)	1.029	0.083	1.000	0.971	0.488	-0.183	0.194	-0.024	-0.091	-0.477	0.113	-0.572	0.114	0.091	0.011	-0.063	-0.291	0.135	-0.510	-0.308	-0.291	0.127
Tg-Tm K	5.662	0.231	0.971	1.000	0.567	-0.147	0.226	-0.014	-0.109	-0.567	0.161	-0.631	0.125	0.109	-0.048	0.049	-0.313	0.125	-0.459	-0.248	-0.313	0.157
Carbon %	-2.510	0.231	0.488	0.567	1.000	0.316	0.713	0.363	-0.598	-0.984	0.734	-0.843	0.265	0.598	-0.201	0.536	-0.601	-0.174	-0.201	0.161	-0.601	0.592
Silicon %	-1.216	0.295	-0.183	-0.147	0.316	1.000	0.378	0.264	-0.502	-0.221	0.796	-0.089	0.251	0.502	-0.119	0.719	-0.609	-0.828	0.609	0.925	-0.609	0.179
Phosphorus %	-3.085	1.450	0.194	0.226	0.713	0.378	1.000	0.899	-0.972	-0.710	0.840	-0.273	0.396	0.972	0.075	0.437	-0.190	-0.271	0.093	0.198	-0.190	0.897
Sulphur %	-5.305	2.626	-0.024	-0.014	0.363	0.264	0.899	1.000	-0.923	-0.389	0.648	0.161	0.461	0.923	0.279	0.304	0.192	-0.257	0.279	0.150	0.192	0.833
Vanadium %	-0.252	0.576	-0.091	-0.109	-0.598	-0.502	-0.972	-0.923	1.000	0.571	-0.874	0.127	-0.491	-1.000	-0.200	-0.427	0.200	0.447	-0.200	-0.304	0.200	-0.850
Chromium %	2.963	0.148	-0.477	-0.567	-0.984	-0.221	-0.710	-0.389	0.571	1.000	-0.669	0.804	-0.224	-0.571	0.250	-0.562	0.464	0.061	0.162	-0.119	0.464	-0.607
Manganese %	0.298	0.781	0.113	0.161	0.734	0.796	0.840	0.648	-0.874	-0.669	1.000	-0.374	0.410	0.874	-0.035	0.687	-0.580	-0.641	0.297	0.616	-0.580	0.654
Nickel %	2.607	0.383	-0.572	-0.631	-0.843	-0.089	-0.273	0.161	0.127	0.804	-0.374	1.000	0.031	-0.127	0.347	-0.251	0.734	-0.054	0.512	0.053	0.734	-0.207
Niobium %	-0.671	0.495	0.114	0.125	0.265	0.251	0.396	0.461	-0.491	-0.224	0.410	0.031	1.000	0.491	0.820	0.129	-0.077	-0.688	0.039	0.081	-0.077	0.278
Molybdenum %	0.029	0.066	0.091	0.109	0.598	0.502	0.972	0.923	-1.000	-0.571	0.874	-0.127	0.491	1.000	0.200	0.427	-0.200	-0.447	0.200	0.304	-0.200	0.850
Titanium %	-0.295	0.675	0.011	-0.048	-0.201	-0.119	0.075	0.279	-0.200	0.250	-0.035	0.347	0.820	0.200	1.000	-0.427	0.200	-0.430	-0.200	-0.304	0.200	0.062
Nitrogen %	-0.844	0.902	-0.063	0.049	0.536	0.719	0.437	0.304	-0.427	-0.562	0.687	-0.251	0.129	0.427	-0.427	1.000	-0.317	-0.435	0.690	0.832	-0.317	0.270
Tungsten %	0.213	0.488	-0.291	-0.313	-0.601	-0.609	-0.190	0.192	0.200	0.464	-0.580	0.734	-0.077	-0.200	0.200	-0.317	1.000	0.486	0.200	-0.394	1.000	-0.046
Copper %	0.526	0.538	0.135	0.125	-0.174	-0.828	-0.271	-0.257	0.447	0.061	-0.641	-0.054	-0.688	-0.447	-0.430	-0.435	0.486	1.000	-0.424	-0.681	0.486	-0.078
Boron %	-0.920	2.102	-0.510	-0.459	-0.201	0.609	0.093	0.279	-0.200	0.162	0.297	0.512	0.039	0.200	-0.200	0.690	0.200	-0.424	1.000	0.822	0.200	-0.005
Aluminium %	-1.304	1.960	-0.308	-0.248	0.161	0.925	0.198	0.150	-0.304	-0.119	0.616	0.053	0.081	0.304	-0.304	0.832	-0.394	-0.681	0.822	1.000	-0.394	0.023
Cobalt %	0.068	0.154	-0.291	-0.313	-0.601	-0.609	-0.190	0.192	0.200	0.464	-0.580	0.734	-0.077	-0.200	0.200	-0.317	1.000	0.486	0.200	-0.394	1.000	-0.046
Ln Corr Rate (µm/khr)	1.739	0.767	0.127	0.157	0.592	0.179	0.897	0.833	-0.850	-0.607	0.654	-0.207	0.278	0.850	0.062	0.270	-0.046	-0.078	-0.005	0.023	-0.046	1.000

Table B-9: Correlation matrix for world traded coal data subset 9, coatings (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 9) Marked correlations are significant at $p < .05000$																
	1000/Metal Temp (1000/K)	Aluminium %	Carbon %	Chromium %	Iron %	Molybdenum %	Niobium + Tantalum %	Nickel %	Silicon %	Tungsten %	Yttrium %	Oxygen %	Phosphorus %	Sulphur %	Cobalt %	Copper %	Ln Corr Rate (μ_m /khr)
1000/Metal Temp (1000/K)	1.000	-0.034	0.000	0.176	-0.077	-0.147	0.005	0.021	0.174	-0.217	0.003	0.003	-0.003	-0.003	-0.003	-0.003	-0.882
Aluminium %	-0.034	1.000	-0.135	-0.226	0.380	-0.336	-0.088	-0.372	-0.196	0.044	0.780	-0.564	-0.122	-0.122	-0.122	-0.122	0.068
Carbon %	0.000	-0.135	1.000	0.444	-0.269	-0.470	-0.571	-0.102	-0.104	-0.002	-0.009	0.757	0.733	0.733	0.733	0.733	-0.017
Chromium %	0.176	-0.226	0.444	1.000	-0.314	-0.762	-0.256	-0.023	0.638	-0.790	-0.165	0.252	0.085	0.085	0.085	0.085	-0.063
Iron %	-0.077	0.380	-0.269	-0.314	1.000	0.043	-0.114	-0.877	0.149	0.224	-0.171	-0.351	-0.144	-0.144	-0.144	-0.144	-0.104
Molybdenum %	-0.147	-0.336	-0.470	-0.762	0.043	1.000	0.523	0.316	-0.585	0.718	-0.363	-0.045	-0.351	-0.351	-0.351	-0.351	0.095
Niobium + Tantalum %	0.005	-0.088	-0.571	-0.256	-0.114	0.523	1.000	0.216	-0.284	-0.042	-0.237	-0.091	-0.650	-0.650	-0.650	-0.650	0.153
Nickel %	0.021	-0.372	-0.102	-0.023	-0.877	0.316	0.216	1.000	-0.272	0.055	0.163	0.023	-0.127	-0.127	-0.127	-0.127	0.121
Silicon %	0.174	-0.196	-0.104	0.638	0.149	-0.585	-0.284	-0.272	1.000	-0.791	-0.198	-0.136	0.052	0.052	0.052	0.052	-0.213
Tungsten %	-0.217	0.044	-0.002	-0.790	0.224	0.718	-0.042	0.055	-0.791	1.000	-0.027	0.006	0.027	0.027	0.027	0.027	0.089
Yttrium %	0.003	0.780	-0.009	-0.165	-0.171	-0.363	-0.237	0.163	-0.198	-0.027	1.000	-0.422	0.154	0.154	0.154	0.154	0.066
Oxygen %	0.003	-0.564	0.757	0.252	-0.351	-0.045	-0.091	0.023	-0.136	0.006	-0.422	1.000	0.650	0.650	0.650	0.650	-0.019
Phosphorus %	-0.003	-0.122	0.733	0.085	-0.144	-0.351	-0.650	-0.127	0.052	0.027	0.154	0.650	1.000	1.000	1.000	1.000	-0.126
Sulphur %	-0.003	-0.122	0.733	0.085	-0.144	-0.351	-0.650	-0.127	0.052	0.027	0.154	0.650	1.000	1.000	1.000	1.000	-0.126
Cobalt %	-0.003	-0.122	0.733	0.085	-0.144	-0.351	-0.650	-0.127	0.052	0.027	0.154	0.650	1.000	1.000	1.000	1.000	-0.126
Copper %	-0.003	-0.122	0.733	0.085	-0.144	-0.351	-0.650	-0.127	0.052	0.027	0.154	0.650	1.000	1.000	1.000	1.000	-0.126
Ln Corr Rate (μ_m /khr)	-0.882	0.068	-0.017	-0.063	-0.104	0.095	0.153	0.121	-0.213	0.089	0.066	-0.019	-0.126	-0.126	-0.126	-0.126	1.000

Table B-10: Correlation matrix for biomass data subset 10, austenitic tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 10)																																		
	Marked correlations are significant at p < 0.05																																		
	Means	Std.Dev.	1000 / Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Manganese %	Phosphorus %	Sulphur %	Silicon %	Chromium %	Nickel %	Molybdenum %	Niobium %	Titanium %	Vanadium %	Nitrogen %	Copper %	Tungsten %	Boron %	Aluminium %	Cobalt %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	P %	Ba %	Mn %	Ln Corr Rate (µm/hrs)
1000 / Metal Temp (1000 / K)	1.134	0.088	1.000	0.388	0.367	0.296	0.313	0.288	0.340	-0.063	-0.108	-0.122	-0.041	-0.004	-0.230	0.105	-0.336	-0.330	0.136	0.329	-0.329	0.658	0.758	0.830	0.850	0.690	0.688	0.724	0.707	-0.102	-0.766	0.805	0.816	0.538	0.303
Tg-Tm K	5.725	0.136	0.388	1.000	-0.043	0.097	-0.039	-0.140	0.022	-0.190	-0.278	-0.043	0.331	0.105	-0.064	0.081	-0.036	-0.263	-0.138	0.224	-0.224	0.094	-0.108	0.125	0.025	0.100	0.192	0.142	0.022	0.298	-0.060	0.232	0.106	0.480	-0.234
Carbon %	-2.234	1.040	0.367	-0.043	1.000	0.463	0.825	0.802	0.568	-0.249	-0.238	-0.307	0.128	0.359	-0.245	0.581	-0.205	-0.252	0.136	0.175	-0.175	0.333	0.222	0.333	0.488	0.408	0.342	0.367	0.406	0.059	-0.199	0.149	0.386	0.115	0.556
Manganese %	0.502	0.810	0.296	0.097	0.463	1.000	0.402	0.490	0.873	-0.718	-0.586	0.080	-0.078	0.119	-0.631	0.653	-0.583	-0.440	-0.236	0.463	-0.463	0.105	0.178	0.139	0.214	0.135	0.099	0.127	0.148	-0.102	-0.072	0.076	0.146	-0.002	0.343
Phosphorus %	-3.202	1.227	0.313	-0.039	0.825	0.402	1.000	0.846	0.511	-0.316	-0.251	-0.417	0.104	0.082	-0.301	0.437	-0.123	-0.148	0.076	0.124	-0.124	0.114	0.280	0.195	0.365	0.197	0.141	0.169	0.199	-0.159	-0.044	0.068	0.235	0.146	0.659
Sulphur %	-4.860	2.348	0.288	-0.140	0.802	0.490	0.846	1.000	0.705	-0.252	-0.067	-0.476	-0.098	0.100	-0.562	0.448	-0.194	0.026	0.112	-0.088	0.088	0.122	0.308	0.213	0.391	0.209	0.149	0.184	0.211	-0.184	-0.042	0.086	0.248	0.146	0.675
Silicon %	-0.698	0.737	0.340	0.022	0.568	0.873	0.511	0.705	1.000	-0.417	-0.261	-0.276	-0.244	0.006	-0.698	0.638	-0.677	-0.429	-0.097	0.388	-0.388	0.121	0.313	0.224	0.331	0.178	0.146	0.178	0.181	-0.185	-0.095	0.169	0.230	0.163	0.438
Chromium %	2.991	0.188	-0.063	-0.190	-0.249	-0.718	-0.316	-0.252	-0.417	1.000	0.881	-0.223	-0.363	-0.102	0.459	-0.426	0.021	0.169	0.484	-0.205	0.205	0.160	0.116	0.200	0.132	0.147	0.188	0.174	0.133	0.077	-0.220	0.260	0.183	0.246	-0.298
Nickel %	2.629	0.400	-0.108	-0.278	-0.238	-0.586	-0.251	-0.067	-0.261	0.881	1.000	-0.085	-0.577	-0.292	0.375	-0.240	-0.007	0.400	0.457	-0.466	0.466	0.131	0.096	0.155	0.100	0.115	0.142	0.135	0.111	0.049	-0.183	0.198	0.141	0.151	-0.234
Molybdenum %	-0.216	0.604	-0.122	-0.043	-0.307	0.080	-0.417	-0.476	-0.276	-0.223	-0.085	1.000	-0.175	-0.107	0.407	0.044	0.184	0.133	-0.296	-0.112	0.112	0.204	-0.289	-0.017	-0.133	0.117	0.102	0.094	0.148	0.350	-0.185	-0.062	-0.013	-0.412	-0.381
Niobium %	-0.550	0.372	-0.041	0.331	0.128	-0.078	0.104	-0.098	-0.244	-0.363	-0.577	-0.175	1.000	0.317	-0.174	-0.088	0.312	-0.244	-0.065	0.173	-0.173	-0.252	-0.180	-0.238	-0.198	-0.220	-0.208	-0.227	-0.252	-0.010	0.313	-0.227	-0.225	0.050	0.098
Titanium %	-0.243	0.958	-0.004	0.105	0.359	0.119	0.082	0.100	0.006	-0.102	-0.292	-0.107	0.317	1.000	-0.040	0.248	0.130	0.094	0.308	-0.079	0.079	0.130	-0.132	0.070	0.054	0.136	0.149	0.132	0.105	0.248	-0.038	0.042	0.081	0.082	-0.108
Vanadium %	-0.472	0.725	-0.230	-0.064	-0.245	-0.631	-0.301	-0.562	-0.698	0.459	0.375	0.407	-0.174	-0.040	1.000	-0.126	0.334	0.242	0.073	-0.204	0.204	0.094	-0.250	-0.045	-0.161	0.030	0.050	0.023	0.035	0.292	-0.107	-0.034	-0.044	-0.161	-0.485
Nitrogen %	-1.028	0.861	0.105	0.081	0.581	0.653	0.437	0.448	0.638	-0.426	-0.240	0.044	-0.088	0.248	-0.126	1.000	-0.485	-0.206	0.056	0.161	-0.161	0.059	-0.016	0.028	0.071	0.074	0.049	0.059	0.075	0.040	0.006	-0.031	0.042	-0.067	0.072
Copper %	0.226	0.448	-0.336	-0.036	-0.205	-0.583	-0.123	-0.194	-0.677	0.021	-0.007	0.184	0.312	0.130	0.334	-0.485	1.000	0.559	-0.312	-0.611	0.611	-0.174	-0.360	-0.293	-0.332	-0.204	-0.202	-0.223	-0.209	0.161	0.223	-0.297	-0.283	-0.253	-0.160
Tungsten %	0.138	0.377	-0.330	-0.263	-0.252	-0.440	-0.148	0.026	-0.429	0.169	0.400	0.133	-0.244	0.094	0.242	-0.206	0.559	1.000	0.247	-0.950	0.950	-0.135	-0.196	-0.200	-0.223	-0.158	-0.160	-0.169	-0.152	0.044	0.141	-0.196	-0.196	-0.192	-0.096
Boron %	-1.646	2.483	0.136	-0.138	0.136	-0.236	0.076	0.112	-0.097	0.484	0.457	-0.296	-0.065	0.308	0.073	0.056	-0.312	0.247	1.000	-0.208	0.208	0.259	0.201	0.303	0.327	0.289	0.293	0.291	0.274	0.074	-0.248	0.266	0.316	0.282	0.078
Aluminium %	-0.264	0.856	0.329	0.224	0.175	0.463	0.124	-0.088	0.388	-0.205	-0.466	-0.112	0.173	-0.079	-0.204	0.161	-0.611	-0.950	-0.208	1.000	-1.000	0.104	0.234	0.182	0.207	0.123	0.120	0.135	0.128	-0.113	-0.140	0.185	0.175	0.153	0.107
Cobalt %	0.036	0.116	-0.329	-0.224	-0.175	-0.463	-0.124	0.088	-0.388	0.205	0.466	0.112	-0.173	0.079	0.204	-0.161	0.611	0.950	0.208	-1.000	1.000	-0.104	-0.234	-0.182	-0.207	-0.123	-0.120	-0.135	-0.128	0.113	0.140	-0.185	-0.175	-0.153	-0.107
Na %	-4.393	0.887	0.658	0.094	0.333	0.105	0.114	0.122	0.121	0.160	0.131	0.204	-0.252	0.130	0.094	0.059	-0.174	-0.135	0.259	0.104	-0.104	1.000	0.343	0.910	0.862	0.993	0.983	0.987	0.988	0.529	-0.934	0.764	0.935	0.346	-0.015
K %	-2.385	0.258	0.758	-0.108	0.222	0.178	0.280	0.308	0.313	0.116	0.096	-0.289	-0.180	-0.132	-0.250	-0.016	-0.360	-0.196	0.201	0.234	-0.234	0.343	1.000	0.672	0.728	0.382	0.375	0.437	0.434	-0.592	-0.599	0.733	0.627	0.506	0.366
Mg %	-3.312	0.472	0.830	0.125	0.333	0.139	0.195	0.213	0.224	0.200	0.155	-0.017	-0.238	0.070	-0.045	0.028	-0.293	-0.200	0.303	0.182	-0.182	0.910	0.672	1.000	0.968	0.926	0.938	0.956	0.925	0.199	-0.965	0.945	0.995	0.605	0.086
Ca %	-1.618	0.477	0.850	0.025	0.488	0.214	0.365	0.391	0.331	0.132	0.100	-0.133	-0.198	0.054	-0.161	0.071	-0.332	-0.223	0.327	0.207	-0.207	0.862	0.728	0.968	1.000	0.899	0.881	0.914	0.911	0.086	-0.901	0.868	0.976	0.537	0.308
Al %	-3.464	0.722	0.690	0.100	0.408	0.135	0.197	0.209	0.178	0.147	0.115	0.117	-0.220	0.136	0.030	0.074	-0.204	-0.158	0.289	0.123	-0.123	0.993	0.382	0.926	0.899	1.000	0.987	0.993	0.991	0.496	-0.921	0.775	0.954	0.396	0.067
Fe %	-3.748	0.822	0.688	0.192	0.342	0.099	0.141	0.149	0.146	0.188	0.142	0.102	-0.208	0.149	0.050	0.049	-0.202	-0.160	0.293	0.120	-0.120	0.983	0.375	0.938	0.881	0.987	1.000	0.995	0.964	0.523	-0.924	0.829	0.956	0.508	-0.030
Si %	-1.875	0.775	0.724	0.142	0.367	0.127	0.169	0.184	0.178	0.174	0.135	0.094	-0.227	0.132	0.023	0.059	-0.223	-0.169	0.291	0.135	-0.135	0.987	0.437	0.956	0.914	0.993	0.995	1.000	0.981	0.458	-0.944	0.839	0.974	0.481	0.025
Cl %	-4.231	0.917	0.707	0.022	0.406	0.148	0.199	0.211	0.181	0.133	0.111	0.148	-0.252	0.105	0.035	0.075	-0.209	-0.152	0.274	0.128	-0.128	0.988	0.434	0.925	0.911	0.991	0.964	0.981	1.000	0.423	-0.938	0.762	0.953	0.320	0.110
S %	-3.932	0.698	-0.102	0.298	0.059	-0.102	-0.159	-0.184	-0.185	0.077	0.049	0.350	-0.010	0.248	0.292	0.040	0.161	0.044	0.074	-0.113	0.113	0.529	-0.592	0.199	0.086	0.496	0.523	0.458	0.423	1.000	-0.252	0.065	0.251	0.018	-0.398
Ti %	-6.731	0.537	-0.766	-0.060	-0.199	-0.072	-0.044	-0.042	-0.095	-0.220	-0.183	-0.185	0.313	-0.038	-0.107	0.006	0.223	0.141	-0.248	-0.140	0.140	-0.934	-0.599	-0.965	-0.901	-0.921	-0.924	-0.944	-0.938	-0.252	1.000	-0.900	-0.959	-0.443	0.039
P %	-4.544	0.429	0.805	0.232	0.149	0.076	0.068	0.086	0.169	0.260	0.198	-0.062	-0.227	0.042	-0.034	-0.031	-0.297	-0.196	0.266	0.185	-0.185	0.764	0.733	0.945	0.868	0.775	0.829	0.839	0.762	0.065	-0.900	1.000			

Table B-11: Correlation matrix for biomass data subset 11, nickel-based tubes (red text indicates marked correlations are significant at p < 0.05; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 11)																															
	Marked correlations are significant at p <0.05																															
	Means	Std.Dev.	1000 / Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Manganese %	Phosphorus %	Sulphur %	Silicon %	Chromium %	Molybdenum %	Niobium %	Titanium %	Nitrogen %	Boron %	Aluminium %	Cobalt %	Iron %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	P %	Ba %	Mn %	Ln Corr Rate (µm/khr)
1000 / Metal Temp (1000 / K)	1.081	0.082	1.000	-0.440	0.470	0.376	-0.566	-0.171	-0.199	0.216	0.102	-0.505	-0.384	0.065	0.189	-0.480	-0.864	0.855	0.672	0.910	0.861	0.872	0.664	0.605	0.681	0.750	-0.386	-0.911	0.959	0.824	-0.940	0.888
Tg-Tm K	5.626	0.068	-0.440	1.000	-0.123	-0.191	0.169	0.054	0.068	-0.164	0.053	0.182	0.108	-0.036	-0.098	0.143	0.345	-0.346	-0.667	-0.410	-0.690	-0.689	-0.665	-0.648	-0.669	-0.683	-0.101	0.681	-0.652	-0.691	0.459	-0.526
Carbon %	-2.453	1.288	0.470	-0.123	1.000	-0.246	-0.812	-0.013	-0.043	-0.618	0.667	-0.451	-0.586	0.156	0.096	-0.928	-0.532	0.451	0.158	0.505	0.300	0.309	0.153	0.114	0.164	0.212	-0.376	-0.345	0.402	0.269	-0.500	0.464
Manganese %	-0.873	0.574	0.376	-0.191	-0.246	1.000	-0.141	-0.699	-0.766	0.256	-0.417	-0.718	-0.493	-0.679	-0.537	0.406	-0.590	0.641	-0.066	0.569	0.135	0.150	-0.073	-0.123	-0.058	0.007	-0.610	-0.208	0.307	0.089	-0.540	0.362
Phosphorus %	-3.745	2.471	-0.566	0.169	-0.812	-0.141	1.000	0.540	0.524	0.519	-0.769	0.708	0.833	0.324	0.319	0.585	0.721	-0.700	-0.161	-0.637	-0.346	-0.359	-0.154	-0.104	-0.169	-0.231	0.504	0.407	-0.485	-0.305	0.627	-0.662
Sulphur %	-3.284	2.562	-0.171	0.054	-0.013	-0.699	0.540	1.000	0.985	0.275	-0.268	0.764	0.782	0.955	0.903	-0.337	0.438	-0.495	0.141	-0.325	0.008	-0.002	0.145	0.177	0.136	0.094	0.426	0.042	-0.113	0.040	0.299	-0.329
Silicon %	-1.079	0.325	-0.199	0.068	-0.043	-0.766	0.524	0.985	1.000	0.300	-0.174	0.841	0.827	0.956	0.904	-0.300	0.486	-0.532	0.172	-0.384	0.014	0.002	0.177	0.214	0.165	0.115	0.507	0.046	-0.130	0.051	0.352	-0.327
Chromium %	3.166	0.106	0.216	-0.164	-0.618	0.256	0.519	0.275	0.300	1.000	-0.617	0.383	0.623	0.323	0.485	0.384	-0.053	0.113	0.269	0.135	0.268	0.267	0.269	0.265	0.270	0.272	0.071	-0.261	0.245	0.271	-0.156	0.114
Molybdenum %	0.808	1.293	0.102	0.053	0.667	-0.417	-0.769	-0.268	-0.174	-0.617	1.000	-0.169	-0.452	-0.115	-0.196	-0.485	-0.151	0.136	0.081	0.052	0.085	0.085	0.081	0.079	0.082	0.084	0.011	-0.084	0.081	0.085	-0.058	0.277
Niobium %	-0.257	0.831	-0.505	0.182	-0.451	-0.718	0.708	0.764	0.841	0.383	-0.169	1.000	0.944	0.673	0.622	0.184	0.784	-0.777	0.064	-0.720	-0.188	-0.206	0.073	0.135	0.053	-0.028	0.756	0.278	-0.400	-0.130	0.686	-0.533
Titanium %	-0.764	1.037	-0.384	0.108	-0.586	-0.493	0.833	0.782	0.827	0.623	-0.452	0.944	1.000	0.689	0.691	0.271	0.661	-0.646	0.094	-0.568	-0.112	-0.127	0.101	0.151	0.085	0.019	0.629	0.187	-0.289	-0.065	0.537	-0.469
Nitrogen %	-1.744	1.881	0.065	-0.036	0.156	-0.679	0.324	0.955	0.956	0.323	-0.115	0.673	0.689	1.000	0.979	-0.505	0.210	-0.266	0.280	-0.102	0.198	0.191	0.282	0.298	0.277	0.253	0.312	-0.162	0.107	0.219	0.071	-0.089
Boron %	-2.317	2.767	0.189	-0.098	0.096	-0.537	0.319	0.903	0.904	0.485	-0.196	0.622	0.691	0.979	1.000	-0.456	0.085	-0.127	0.341	0.029	0.292	0.288	0.342	0.348	0.339	0.327	0.229	-0.267	0.223	0.306	-0.061	0.023
Aluminium %	-0.359	0.703	-0.480	0.143	-0.928	0.406	0.585	-0.337	-0.300	0.384	-0.485	0.184	0.271	-0.505	-0.456	1.000	0.439	-0.347	-0.249	-0.460	-0.360	-0.367	-0.244	-0.212	-0.254	-0.293	0.264	0.393	-0.430	-0.337	0.467	-0.403
Cobalt %	1.370	1.427	-0.864	0.345	-0.532	-0.590	0.721	0.438	0.486	-0.053	-0.151	0.784	0.661	0.210	0.085	0.439	1.000	-0.994	-0.267	-0.987	-0.551	-0.570	-0.256	-0.180	-0.279	-0.375	0.768	0.644	-0.762	-0.489	0.974	-0.822
Iron %	1.530	1.588	0.855	-0.346	0.451	0.641	-0.700	-0.495	-0.532	0.113	0.136	-0.777	-0.646	-0.266	-0.127	-0.347	-0.994	1.000	0.270	0.975	0.549	0.568	0.259	0.184	0.282	0.376	-0.754	-0.641	0.756	0.488	-0.963	0.828
Na %	-4.391	0.873	0.672	-0.667	0.158	-0.066	-0.161	0.141	0.172	0.269	0.081	0.064	0.094	0.280	0.341	-0.249	-0.267	0.270	1.000	0.362	0.950	0.943	1.000	0.996	1.000	0.993	0.401	-0.907	0.823	0.971	-0.445	0.618
K %	-2.490	0.251	0.910	-0.410	0.505	0.569	-0.637	-0.325	-0.384	0.135	0.052	-0.720	-0.568	-0.102	0.029	-0.460	-0.987	0.975	0.362	1.000	0.634	0.652	0.351	0.276	0.373	0.466	-0.709	-0.720	0.827	0.575	-0.996	0.834
Mg %	-3.424	0.407	0.861	-0.690	0.300	0.135	-0.346	0.008	0.014	0.268	0.085	-0.188	-0.112	0.198	0.292	-0.360	-0.551	0.549	0.950	0.634	1.000	1.000	0.947	0.918	0.954	0.980	0.095	-0.993	0.959	0.997	-0.702	0.791
Ca %	-1.734	0.495	0.872	-0.689	0.309	0.150	-0.359	-0.002	0.002	0.267	0.085	-0.206	-0.127	0.191	0.288	-0.367	-0.570	0.568	0.943	0.652	1.000	1.000	0.939	0.909	0.947	0.975	0.072	-0.996	0.966	0.995	-0.718	0.801
Al %	-3.495	0.744	0.664	-0.665	0.153	-0.073	-0.154	0.145	0.177	0.269	0.081	0.073	0.101	0.282	0.342	-0.244	-0.256	0.259	1.000	0.351	0.947	0.939	1.000	0.997	1.000	0.992	0.411	-0.902	0.817	0.968	-0.435	0.610
Fe %	-3.828	0.743	0.605	-0.648	0.114	-0.123	-0.104	0.177	0.214	0.265	0.079	0.135	0.151	0.298	0.348	-0.212	-0.180	0.184	0.996	0.276	0.918	0.909	0.997	1.000	0.995	0.979	0.481	-0.866	0.769	0.945	-0.363	0.557
Si %	-1.955	0.737	0.681	-0.669	0.164	-0.058	-0.169	0.136	0.165	0.270	0.082	0.053	0.085	0.277	0.339	-0.254	-0.279	0.282	1.000	0.373	0.954	0.947	1.000	0.995	1.000	0.995	0.389	-0.913	0.831	0.974	-0.456	0.626
Cl %	-4.244	0.987	0.750	-0.683	0.212	0.007	-0.231	0.094	0.115	0.272	0.084	-0.028	0.019	0.253	0.327	-0.293	-0.375	0.376	0.993	0.466	0.980	0.975	0.992	0.979	0.995	1.000	0.293	-0.950	0.883	0.992	-0.545	0.689
S %	-3.739	0.693	-0.386	-0.101	-0.376	-0.610	0.504	0.426	0.507	0.071	0.011	0.756	0.629	0.312	0.229	0.264	0.768	-0.754	0.401	-0.709	0.095	0.072	0.411	0.481	0.389	0.293	1.000	0.022	-0.190	0.168	0.642	-0.352
Ti %	-6.679	0.460	-0.911	0.681	-0.345	-0.208	0.407	0.042	0.046	-0.261	-0.084	0.278	0.187	-0.162	-0.267	0.393	0.644	-0.641	-0.907	-0.720	-0.993	-0.996	-0.902	-0.866	-0.913	-0.950	0.022	1.000	-0.986	-0.982	0.780	-0.836
P %	-4.700	0.235	0.959	-0.652	0.402	0.307	-0.485	-0.113	-0.130	0.245	0.081	-0.400	-0.289	0.107	0.223	-0.430	-0.762	0.756	0.823	0.827	0.959	0.966	0.817	0.769	0.831	0.883	-0.190	-0.986	1.000	0.936	-0.875	0.880
Ba %	-6.232	0.941	0.824	-0.691	0.269	0.089	-0.305	0.040	0.051	0.271	0.085	-0.130	-0.065	0.219	0.306	-0.337	-0.489	0.488	0.971	0.575	0.997	0.995	0.968	0.945	0.974	0.992	0.168	-0.982	0.936	1.000	-0.647	0.757
Mn %	-4.480	0.015	-0.940	0.459	-0.500	-0.540	0.627	0.299	0.352	-0.156	-0.058	0.686	0.537	0.071	-0.061	0.467	0.974	-0.963	-0.445	-0.996	-0.702	-0.718	-0.435	-0.363	-0.456	-0.545	0.642	0.780	-0.875	-0.647	1.000	-0.861
Ln Corr Rate (µm/khr)	2.790	1.262	0.888	-0.526	0.464	0.362	-0.662	-0.329	-0.327	0.114	0.277	-0.533	-0.469	-0.089	0.023	-0.403	-0.822	0.828	0.618	0.834	0.791	0.801	0.610	0.557	0.626	0.689	-0.352	-0.836	0.880	0.757	-0.861	1.000

Table B-12: Correlation matrix for biomass data subset 12, ferritic tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Data subset 12)																											
	Marked correlations are significant at p < 0.05																											
	Means	Std.Dev.	1000 / Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Manganese %	Phosphorus %	Sulphur %	Silicon %	Chromium %	Nickel %	Molybdenum %	Vanadium %	Copper %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	P %	Ba %	Mn %	Ln Corr Rate (µm/khr)
1000 / Metal Temp (1000 / K)	1.306	0.079	1.000	-0.376	0.615	0.187	0.615	0.615	0.125	-0.312	-0.259	-0.344	0.615	-0.205	0.635	0.445	0.696	0.558	0.607	0.671	0.622	0.533	0.615	-0.503	0.642	0.655	0.207	-0.471
Tg-Tm K	5.611	0.340	-0.376	1.000	-0.357	-0.229	-0.357	-0.357	0.291	0.256	-0.236	0.165	-0.357	-0.163	-0.403	-0.905	-0.574	-0.240	-0.340	-0.495	-0.374	-0.193	-0.357	0.138	-0.941	-0.454	-0.742	0.712
Carbon %	-0.485	0.964	0.615	-0.357	1.000	0.497	1.000	1.000	0.158	-0.569	-0.440	-0.569	1.000	-0.267	0.999	0.085	0.965	0.991	1.000	0.987	1.000	0.984	1.000	-0.971	0.482	0.994	-0.280	0.056
Manganese %	-0.583	0.207	0.187	-0.229	0.497	1.000	0.497	0.497	-0.635	-0.335	0.348	-0.408	0.497	0.388	0.493	-0.021	0.464	0.502	0.499	0.481	0.496	0.501	0.497	-0.498	0.184	0.487	-0.200	0.057
Phosphorus %	-0.777	1.545	0.615	-0.357	1.000	0.497	1.000	1.000	0.158	-0.569	-0.440	-0.569	1.000	-0.267	0.999	0.085	0.965	0.991	1.000	0.987	1.000	0.984	1.000	-0.971	0.482	0.994	-0.280	0.056
Sulphur %	-0.777	1.545	0.615	-0.357	1.000	0.497	1.000	1.000	0.158	-0.569	-0.440	-0.569	1.000	-0.267	0.999	0.085	0.965	0.991	1.000	0.987	1.000	0.984	1.000	-0.971	0.482	0.994	-0.280	0.056
Silicon %	-0.543	0.505	0.125	0.291	0.158	-0.635	0.158	0.158	1.000	0.301	-0.942	0.159	0.158	-0.571	0.142	-0.283	0.075	0.195	0.164	0.108	0.152	0.209	0.158	-0.224	-0.184	0.124	-0.329	0.344
Chromium %	-0.519	1.268	-0.312	0.256	-0.569	-0.335	-0.569	-0.569	0.301	1.000	-0.144	0.827	-0.569	0.416	-0.573	-0.124	-0.570	-0.555	-0.568	-0.574	-0.571	-0.546	-0.569	0.535	-0.341	-0.574	0.087	0.137
Nickel %	-0.610	0.735	-0.259	-0.236	-0.440	0.348	-0.440	-0.440	-0.942	-0.144	1.000	0.052	-0.440	0.590	-0.420	0.338	-0.327	-0.486	-0.447	-0.373	-0.433	-0.501	-0.440	0.517	0.118	-0.395	0.485	-0.425
Molybdenum %	-0.572	0.560	-0.344	0.165	-0.569	-0.408	-0.569	-0.569	0.159	0.827	0.052	1.000	-0.569	0.631	-0.565	0.026	-0.530	-0.574	-0.571	-0.550	-0.568	-0.573	-0.569	0.571	-0.209	-0.557	0.231	0.004
Vanadium %	-0.678	1.348	0.615	-0.357	1.000	0.497	1.000	1.000	0.158	-0.569	-0.440	-0.569	1.000	-0.267	0.999	0.085	0.965	0.991	1.000	0.987	1.000	0.984	1.000	-0.971	0.482	0.994	-0.280	0.056
Copper %	-0.361	0.718	-0.205	-0.163	-0.267	0.388	-0.267	-0.267	-0.571	0.416	0.590	0.631	-0.267	1.000	-0.254	0.205	-0.198	-0.294	-0.271	-0.226	-0.262	-0.303	-0.267	0.313	0.071	-0.239	0.294	-0.165
Na %	-2.726	1.158	0.635	-0.403	0.999	0.493	0.999	0.999	0.142	-0.573	-0.420	-0.565	0.999	-0.254	1.000	0.137	0.978	0.983	0.997	0.994	0.999	0.973	0.999	-0.957	0.527	0.998	-0.229	0.009
K %	-2.153	0.098	0.445	-0.905	0.085	-0.021	0.085	0.085	-0.283	-0.124	0.338	0.026	0.085	0.205	0.137	1.000	0.342	-0.046	0.066	0.246	0.103	-0.097	0.085	0.155	0.914	0.197	0.933	-0.897
Mg %	-2.550	0.400	0.696	-0.574	0.965	0.464	0.965	0.965	0.075	-0.570	-0.327	-0.530	0.965	-0.198	0.978	0.342	1.000	0.923	0.960	0.995	0.970	0.902	0.965	-0.875	0.694	0.989	-0.020	-0.182
Ca %	-0.707	0.376	0.558	-0.240	0.991	0.502	0.991	0.991	0.195	-0.555	-0.486	-0.574	0.991	-0.294	0.983	-0.046	0.923	1.000	0.994	0.957	0.989	0.999	0.991	-0.994	0.363	0.970	-0.403	0.174
Al %	-2.047	0.867	0.607	-0.340	1.000	0.499	1.000	1.000	0.164	-0.568	-0.447	-0.571	1.000	-0.271	0.997	0.066	0.960	0.994	1.000	0.983	0.999	0.987	1.000	-0.976	0.465	0.991	-0.299	0.074
Fe %	-2.335	0.872	0.671	-0.495	0.987	0.481	0.987	0.987	0.108	-0.574	-0.373	-0.550	0.987	-0.226	0.994	0.246	0.995	0.957	0.983	1.000	0.990	0.941	0.987	-0.920	0.618	0.999	-0.120	-0.092
Si %	-0.490	0.837	0.622	-0.374	1.000	0.496	1.000	1.000	0.152	-0.571	-0.433	-0.568	1.000	-0.262	0.999	0.103	0.970	0.989	0.999	0.990	1.000	0.980	1.000	-0.967	0.498	0.996	-0.262	0.039
Cl %	-2.396	1.192	0.533	-0.193	0.984	0.501	0.984	0.984	0.209	-0.546	-0.501	-0.573	0.984	-0.303	0.973	-0.097	0.902	0.999	0.987	0.941	0.980	1.000	0.984	-0.998	0.316	0.957	-0.449	0.219
S %	-3.511	0.581	0.615	-0.357	1.000	0.497	1.000	1.000	0.158	-0.569	-0.440	-0.569	1.000	-0.267	0.999	0.085	0.965	0.991	1.000	0.987	1.000	0.984	1.000	-0.971	0.482	0.994	-0.280	0.056
Ti %	-7.469	0.560	-0.503	0.138	-0.971	-0.498	-0.971	-0.971	-0.224	0.535	0.517	0.571	-0.971	0.313	-0.957	0.155	-0.875	-0.994	-0.976	-0.920	-0.967	-0.998	-0.971	1.000	-0.260	-0.938	0.501	-0.270
P %	-4.115	0.389	0.642	-0.941	0.482	0.184	0.482	0.482	-0.184	-0.341	0.118	-0.209	0.482	0.071	0.527	0.914	0.694	0.363	0.465	0.618	0.498	0.316	0.482	-0.260	1.000	0.578	0.706	-0.766
Ba %	-4.249	0.908	0.655	-0.454	0.994	0.487	0.994	0.994	0.124	-0.574	-0.395	-0.557	0.994	-0.239	0.998	0.197	0.989	0.970	0.991	0.999	0.996	0.957	0.994	-0.938	0.578	1.000	-0.170	-0.046
Mn %	-4.378	0.221	0.207	-0.742	-0.200	-0.200	-0.280	-0.329	0.087	0.485	0.231	-0.280	0.294	-0.229	0.933	-0.020	-0.403	-0.299	-0.120	-0.262	-0.449	-0.280	0.501	0.706	-0.170	1.000	-0.885	
Ln Corr Rate (µm/khr)	5.568	0.567	-0.471	0.712	0.056	0.057	0.056	0.056	0.344	0.137	-0.425	0.004	0.056	-0.165	0.009	-0.897	-0.182	0.174	0.074	-0.092	0.039	0.219	0.056	-0.270	-0.766	-0.046	-0.885	1.000

Table B-13: Correlation matrix for biomass data subset 13, coatings (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

	Correlations (Biomass PCA Coatings Spreadsheet DATA 13A (Model F))																																					
	Means	Std.Dev.	1000 / Metal Temp (1000 / K)	Tg-Tm K	Carbon %	Manganese %	Phosphorus %	Sulphur %	Silicon %	Chromium %	Nickel %	Molybdenum %	Niobium %	Titanium %	Vanadium %	Nitrogen %	Copper %	Tungsten %	Aluminium %	Cobalt %	Oxygen %	Yttrium %	Iron %	Na %	K %	Mg %	Ca %	Al %	Fe %	Si %	Cl %	S %	Ti %	P %	Ba %	Mn %	Ln Corr Rate (µm/yr)	
Variable																																						
1000 / Metal Temp (1000 / K)	1.198	0.072	1.000	-0.154	-0.169	-0.230	-0.132	-0.155	-0.216	-0.010	0.110	0.151	0.228	-0.204	0.207	-0.186	0.052	-0.081	-0.271	0.049	0.165	0.086	-0.253	0.789	0.870	0.833	0.783	0.789	0.825	0.807	0.738	0.350	-0.717	0.848	0.827	0.761	-0.068	
Tg-Tm K	5.702	0.260	-0.154	1.000	-0.101	0.060	-0.079	-0.081	0.042	0.106	0.012	-0.111	-0.038	-0.066	0.088	-0.112	-0.229	0.118	0.038	-0.056	-0.198	0.052	0.040	-0.071	-0.250	-0.052	-0.055	-0.067	-0.063	-0.041	-0.019	-0.169	-0.151	-0.109	-0.051	-0.305	-0.068	
Carbon %	-0.069	0.594	-0.169	-0.101	1.000	0.084	0.530	0.523	-0.028	0.102	0.044	-0.074	0.022	0.296	-0.013	0.431	-0.066	-0.136	0.137	-0.078	0.365	0.007	-0.044	-0.183	-0.213	-0.224	-0.178	-0.179	-0.208	-0.202	-0.168	-0.113	0.238	-0.252	-0.207	-0.189	-0.074	
Manganese %	-0.140	0.707	-0.230	0.060	0.084	1.000	0.017	0.013	0.190	-0.398	-0.111	0.184	-0.364	-0.095	0.156	0.053	-0.308	0.393	0.171	-0.201	-0.148	0.012	0.250	-0.189	-0.238	-0.203	-0.172	-0.183	-0.199	-0.188	-0.165	-0.063	0.169	-0.227	-0.196	-0.221	-0.203	
Phosphorus %	-0.038	0.419	-0.132	-0.079	0.530	0.017	1.000	0.991	0.014	0.023	0.180	0.038	0.018	-0.036	-0.010	-0.012	-0.052	-0.005	-0.167	-0.061	0.026	0.005	-0.106	-0.143	-0.167	-0.175	-0.139	-0.139	-0.163	-0.158	-0.131	-0.088	0.186	-0.196	-0.162	-0.148	-0.030	
Sulphur %	-0.053	0.421	-0.155	-0.081	0.523	0.013	0.991	1.000	-0.046	0.023	0.193	0.053	0.024	-0.050	-0.014	-0.016	-0.071	-0.006	-0.165	-0.084	-0.031	0.008	-0.138	-0.205	-0.167	-0.219	-0.203	-0.204	-0.214	-0.215	-0.203	-0.122	0.236	-0.204	-0.215	-0.119	-0.080	
Silicon %	-0.096	0.574	-0.216	0.042	-0.028	0.190	0.014	-0.046	1.000	0.218	-0.167	-0.223	-0.209	0.214	-0.018	0.351	-0.037	-0.083	-0.038	-0.042	0.017	-0.068	0.325	-0.090	-0.355	-0.185	-0.055	-0.058	-0.146	-0.113	-0.019	-0.115	0.132	-0.350	-0.134	-0.419	0.196	
Chromium %	3.161	0.333	-0.010	0.106	0.102	-0.398	0.023	0.023	0.218	1.000	0.135	-0.478	-0.010	0.091	0.276	0.094	-0.128	-0.390	-0.041	0.115	-0.174	-0.025	-0.192	-0.071	-0.053	-0.065	-0.058	-0.067	-0.066	-0.063	-0.062	-0.170	0.042	-0.058	-0.059	-0.041	-0.066	
Nickel %	3.044	1.551	0.110	0.012	0.044	-0.111	0.180	0.193	-0.167	0.135	1.000	0.353	0.150	-0.235	-0.068	-0.091	-0.064	0.181	-0.264	0.048	-0.077	0.041	-0.711	0.095	0.147	0.110	0.093	0.094	0.105	0.099	0.080	0.041	-0.079	0.133	0.105	0.147	0.135	
Molybdenum %	0.602	1.434	0.151	-0.111	-0.074	0.184	0.038	0.053	-0.223	-0.478	0.353	1.000	0.241	-0.457	-0.187	-0.165	0.246	0.325	-0.314	0.060	0.087	-0.025	-0.420	0.206	0.217	0.210	0.181	0.197	0.208	0.198	0.182	0.179	-0.174	0.218	0.200	0.189	0.103	
Niobium %	0.167	0.871	0.228	-0.038	0.022	-0.364	0.018	0.024	-0.209	-0.010	0.150	0.241	1.000	-0.128	-0.280	-0.080	0.052	-0.310	-0.152	0.342	0.193	-0.011	-0.265	0.255	0.231	0.243	0.216	0.243	0.246	0.235	0.234	0.109	-0.216	0.230	0.238	0.183	0.060	
Titanium %	-0.293	0.737	-0.204	-0.066	0.296	-0.095	-0.036	-0.050	0.214	0.091	-0.235	-0.457	-0.128	1.000	-0.292	0.254	0.383	-0.300	0.334	-0.010	0.061	0.024	0.114	-0.067	-0.188	-0.101	-0.057	-0.060	-0.089	-0.076	-0.040	0.122	0.084	-0.166	-0.091	-0.208	0.332	
Vanadium %	-0.023	0.206	0.207	0.088	-0.013	0.156	-0.010	-0.014	-0.018	0.276	-0.068	-0.187	-0.280	-0.292	1.000	-0.014	-0.271	-0.236	0.107	-0.340	0.031	0.007	0.011	0.058	0.074	0.060	0.071	0.063	0.062	0.065	0.064	-0.192	-0.068	0.056	0.073	0.062	-0.377	
Nitrogen %	-0.052	0.407	-0.186	-0.112	0.431	0.053	-0.012	-0.016	0.351	0.094	-0.091	-0.165	-0.080	0.254	-0.014	1.000	0.067	-0.122	0.342	0.082	0.234	0.008	0.235	-0.202	-0.235	-0.246	-0.196	-0.197	-0.229	-0.223	-0.185	-0.124	0.263	-0.277	-0.229	-0.208	-0.004	
Copper %	-0.496	0.879	0.052	-0.229	-0.066	-0.308	-0.052	-0.071	-0.037	-0.128	-0.064	0.246	0.052	0.383	-0.271	0.067	1.000	-0.188	0.119	0.342	0.163	0.034	-0.135	0.305	0.195	0.295	0.284	0.299	0.297	0.296	0.296	0.509	-0.266	0.245	0.283	0.121	0.559	
Tungsten %	-0.037	0.747	-0.081	0.118	-0.136	0.393	-0.005	-0.006	-0.083	-0.390	0.181	0.325	-0.310	-0.300	-0.236	-0.122	-0.188	1.000	-0.098	0.305	-0.041	0.003	0.272	0.079	0.025	0.074	0.046	0.067	0.071	0.066	0.069	0.208	-0.084	0.063	0.059	0.000	0.177	
Aluminium %	0.141	0.895	-0.271	0.038	0.137	0.171	-0.167	-0.165	-0.038	-0.041	-0.264	-0.314	-0.152	0.334	0.107	0.342	0.119	-0.098	1.000	0.141	-0.097	0.136	0.273	-0.227	-0.274	-0.247	-0.223	-0.225	-0.242	-0.235	-0.211	0.024	0.228	-0.264	-0.246	-0.245	0.067	
Cobalt %	-0.653	0.982	0.049	-0.056	-0.078	-0.201	-0.061	-0.084	-0.042	0.115	0.048	0.060	0.342	-0.010	-0.340	0.082	0.342	0.305	0.141	1.000	0.192	0.040	0.160	0.360	0.203	0.337	0.314	0.347	0.342	0.337	0.348	0.548	-0.324	0.271	0.322	0.106	0.577	
Oxygen %	0.293	1.024	0.165	-0.198	0.365	-0.148	0.026	-0.031	0.017	-0.174	-0.077	0.087	0.193	0.061	0.031	0.234	0.163	-0.041	-0.097	0.192	1.000	0.110	0.107	0.322	0.145	0.254	0.306	0.325	0.282	0.288	0.334	0.228	-0.215	0.139	0.278	0.043	0.267	
Yttrium %	0.002	0.032	0.086	0.052	0.007	0.012	0.005	0.008	-0.068	-0.025	0.041	-0.025	-0.011	0.024	0.007	0.008	0.034	0.003	0.136	0.040	0.110	1.000	-0.014	0.094	0.109	0.114	0.091	0.091	0.106	0.103	0.086	0.058	-0.122	0.128	0.106	0.097	0.015	
Iron %	2.344	1.657	-0.253	0.040	-0.044	0.250	-0.106	-0.138	0.325	-0.192	-0.711	-0.420	-0.265	0.114	0.011	0.235	-0.135	0.272	0.273	0.160	0.107	-0.014	1.000	-0.136	-0.311	-0.203	-0.145	-0.134	-0.181	-0.167	-0.101	-0.008	0.165	-0.295	-0.184	-0.336	0.030	
Na %	-4.178	1.133	0.789	-0.071	-0.183	-0.189	-0.143	-0.205	-0.090	-0.071	0.095	0.206	0.255	-0.067	0.058	-0.202	0.305	0.079	-0.227	0.360	0.322	0.094	-0.136	1.000	0.755	0.972	0.962	0.995	0.987	0.985	0.990	0.960	-0.950	0.831	0.982	0.515	0.337	
K %	-2.195	0.100	0.870	-0.250	-0.213	-0.238	-0.167	-0.167	-0.355	-0.053	0.147	0.217	0.231	-0.188	0.074	-0.235	0.195	0.025	-0.274	0.203	0.145	0.109	-0.311	0.755	1.000	0.867	0.776	0.759	0.836	0.810	0.678	0.587	-0.695	0.973	0.834	0.951	0.053	
Mg %	-3.091	0.537	0.833	-0.052	-0.224	-0.203	-0.175	-0.219	-0.185	-0.065	0.110	0.210	0.243	-0.101	0.060	-0.246	0.295	0.074	-0.247	0.337	0.254	0.114	-0.203	0.972	0.867	1.000	0.964	0.973	0.997	0.991	0.946	0.628	-0.945	0.931	0.995	0.674	0.286	
Ca %	-1.387	0.482	0.783	-0.055	-0.178	-0.172	-0.139	-0.203	-0.055	-0.058	0.093	0.181	0.216	-0.057	0.071	-0.196	0.284	0.046	-0.223	0.314	0.306	0.091	-0.145	0.962	0.776	0.964	1.000	0.984	0.976	0.988	0.968	0.679	-0.898	0.830	0.984	0.562	0.378	
Al %	-3.282	0.904	0.789	-0.067	-0.179	-0.183	-0.139	-0.204	-0.068	-0.067	0.094	0.197	0.243	-0.060	0.063	-0.197	0.299	0.067	-0.225	0.347	0.325	0.091	-0.134	0.995	0.759	0.973	0.984	1.000	0.989	0.993	0.993	0.604	-0.937	0.827	0.989	0.523	0.361	
Fe %	-3.544	1.059	0.825	-0.063	-0.208	-0.199	-0.163	-0.214	-0.146	-0.066	0.105	0.208	0.246	-0.089	0.062	-0.229	0.297	0.071	-0.242	0.342	0.282	0.106	-0.181	0.987	0.836	0.997	0.976	0.989	1.000	0.997	0.968	0.620	-0.947	0.900	0.999	0.626	0.311	
Si %	-1.628	0.951	0.807	-0.041	-0.202	-0.188	-0.158	-0.215	-0.113	-0.063	0.099	0.198	0.235	-0.076	0.065	-0.223	0.296	0.066	-0.235	0.337	0.28																	

Table B-14: Correlation matrix for co-firing data subset 14, austenitic tubes (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Co-firing Data subset 14) Marked correlations are significant at p < .05000																					
	1000/Metal Temp (1000/(K))	Carbon %	Silicon %	Chromium %	Nickel %	Niobium %	Nitrogen %	Molybdenum %	Na %	K %	Al %	Si %	P %	Mg %	Ca %	Ti %	Mn %	Fe %	Ba %	Cl %	S %	Ln Corr Rate (μ _m /khr)
1000/Metal Temp (1000/(K))	1.000	0.361	0.361	0.361	0.361	-0.361	-0.361	-0.361	-0.527	0.196	0.059	0.556	0.257	-0.002	-0.371	-0.008	-0.293	-0.286	0.106	0.494	0.641	0.195
Carbon %	0.361	1.000	1.000	1.000	1.000	-1.000	-1.000	-1.000	-0.485	0.195	0.033	0.489	0.250	0.018	-0.350	-0.027	-0.281	-0.275	0.076	0.457	0.577	0.232
Silicon %	0.361	1.000	1.000	1.000	1.000	-1.000	-1.000	-1.000	-0.485	0.195	0.033	0.489	0.250	0.018	-0.350	-0.027	-0.281	-0.275	0.076	0.457	0.577	0.232
Chromium %	0.361	1.000	1.000	1.000	1.000	-1.000	-1.000	-1.000	-0.485	0.195	0.033	0.489	0.250	0.018	-0.350	-0.027	-0.281	-0.275	0.076	0.457	0.577	0.232
Nickel (%)	0.361	1.000	1.000	1.000	1.000	-1.000	-1.000	-1.000	-0.485	0.195	0.033	0.489	0.250	0.018	-0.350	-0.027	-0.281	-0.275	0.076	0.457	0.577	0.232
Niobium %	-0.361	-1.000	-1.000	-1.000	-1.000	1.000	1.000	1.000	0.485	-0.195	-0.033	-0.489	-0.250	-0.018	0.350	0.027	0.281	0.275	-0.076	-0.457	-0.577	-0.232
Nitrogen %	-0.361	-1.000	-1.000	-1.000	-1.000	1.000	1.000	1.000	0.485	-0.195	-0.033	-0.489	-0.250	-0.018	0.350	0.027	0.281	0.275	-0.076	-0.457	-0.577	-0.232
Molybdenum %	-0.361	-1.000	-1.000	-1.000	-1.000	1.000	1.000	1.000	0.485	-0.195	-0.033	-0.489	-0.250	-0.018	0.350	0.027	0.281	0.275	-0.076	-0.457	-0.577	-0.232
Na %	-0.527	-0.485	-0.485	-0.485	-0.485	0.485	0.485	0.485	1.000	-0.794	0.494	-0.424	-0.852	-0.569	0.940	0.582	0.883	0.878	0.428	-0.996	-0.846	-0.788
K %	0.196	0.195	0.195	0.195	0.195	-0.195	-0.195	-0.195	-0.794	1.000	-0.920	-0.213	0.995	0.951	-0.954	-0.956	-0.987	-0.988	-0.889	0.843	0.349	0.944
Al %	0.059	0.033	0.033	0.033	0.033	-0.033	-0.033	-0.033	0.494	-0.920	1.000	0.578	-0.875	-0.996	0.760	0.995	0.844	0.850	0.997	-0.566	0.045	-0.845
Si %	0.556	0.489	0.489	0.489	0.489	-0.489	-0.489	-0.489	-0.424	-0.213	0.578	1.000	-0.112	-0.504	-0.091	0.490	0.051	0.062	0.637	0.345	0.841	-0.141
P %	0.257	0.250	0.250	0.250	0.250	-0.250	-0.250	-0.250	-0.852	0.995	-0.875	-0.112	1.000	0.915	-0.979	-0.921	-0.998	-0.999	-0.837	0.894	0.443	0.946
Mg %	-0.002	0.018	0.018	0.018	0.018	-0.018	-0.018	-0.018	-0.569	0.951	-0.996	-0.504	0.915	1.000	-0.814	-1.000	-0.888	-0.893	-0.987	0.637	0.043	0.879
Ca %	-0.371	-0.350	-0.350	-0.350	-0.350	0.350	0.350	0.350	0.940	-0.954	0.760	-0.091	-0.979	-0.814	1.000	0.824	0.990	0.988	0.710	-0.966	-0.615	-0.919
Ti %	-0.008	-0.027	-0.027	-0.027	-0.027	0.027	0.027	0.027	0.582	-0.956	0.995	0.490	-0.921	-1.000	0.824	1.000	0.896	0.901	0.984	-0.649	-0.059	-0.885
Mn %	-0.293	-0.281	-0.281	-0.281	-0.281	0.281	0.281	0.281	0.883	-0.987	0.844	0.051	-0.998	-0.888	0.990	0.896	1.000	1.000	0.802	-0.920	-0.497	-0.942
Fe %	-0.286	-0.275	-0.275	-0.275	-0.275	0.275	0.275	0.275	0.878	-0.988	0.850	0.062	-0.999	-0.893	0.988	0.901	1.000	1.000	0.809	-0.915	-0.487	-0.943
Ba %	0.106	0.076	0.076	0.076	0.076	-0.076	-0.076	-0.076	0.428	-0.889	0.997	0.637	-0.837	-0.987	0.710	0.984	0.802	0.809	1.000	-0.503	0.119	-0.811
Cl %	0.494	0.457	0.457	0.457	0.457	-0.457	-0.457	-0.457	-0.996	0.843	-0.566	0.345	0.894	0.637	-0.966	-0.649	-0.920	-0.915	-0.503	1.000	0.798	0.830
S %	0.641	0.577	0.577	0.577	0.577	-0.577	-0.577	-0.577	-0.846	0.349	0.045	0.841	0.443	0.043	-0.615	-0.059	-0.497	-0.487	0.119	0.798	1.000	0.388
Ln Corr Rate (μ _m /khr)	0.195	0.232	0.232	0.232	0.232	-0.232	-0.232	-0.232	-0.788	0.944	-0.845	-0.141	0.946	0.879	-0.919	-0.885	-0.942	-0.943	-0.811	0.830	0.388	1.000

Table B-15: Correlation matrix for co-firing data subset 15, TP316 (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Co-firing Data subset 15) Marked correlations are significant at $p < .05000$														
	1000/Metal Temp (1000/(K))	Na %	K %	Al %	Si %	P %	Mg %	Ca %	Ti %	Mn %	Fe %	Ba %	Cl %	S %	Ln Corr Rate (μ_m /khr)
1000/Metal Temp (1000/(K))	1.000	-0.475	0.151	0.056	0.513	0.204	-0.010	-0.308	0.002	-0.235	-0.230	0.093	0.436	0.626	0.219
Na %	-0.475	1.000	-0.816	0.583	-0.245	-0.864	-0.640	0.941	0.650	0.890	0.885	0.533	-0.996	-0.793	-0.807
K %	0.151	-0.816	1.000	-0.945	-0.361	0.996	0.967	-0.963	-0.970	-0.990	-0.991	-0.924	0.864	0.295	0.957
Al %	0.056	0.583	-0.945	1.000	0.645	-0.913	-0.997	0.824	0.996	0.890	0.894	0.998	-0.653	0.032	-0.891
Si %	0.513	-0.245	-0.361	0.645	1.000	-0.277	-0.588	0.098	0.577	0.225	0.235	0.690	0.157	0.785	-0.304
P %	0.204	-0.864	0.996	-0.913	-0.277	1.000	0.940	-0.983	-0.945	-0.999	-0.999	-0.887	0.905	0.378	0.958
Mg %	-0.010	-0.640	0.967	-0.997	-0.588	0.940	1.000	-0.863	-1.000	-0.920	-0.924	-0.991	0.706	0.040	0.914
Ca %	-0.308	0.941	-0.963	0.824	0.098	-0.983	-0.863	1.000	0.869	0.992	0.990	0.788	-0.967	-0.540	-0.934
Ti %	0.002	0.650	-0.970	0.996	0.577	-0.945	-1.000	0.869	1.000	0.926	0.929	0.989	-0.716	-0.053	-0.918
Mn %	-0.235	0.890	-0.990	0.890	0.225	-0.999	-0.920	0.992	0.926	1.000	1.000	0.861	-0.927	-0.427	-0.954
Fe %	-0.230	0.885	-0.991	0.894	0.235	-0.999	-0.924	0.990	0.929	1.000	1.000	0.866	-0.923	-0.418	-0.955
Ba %	0.093	0.533	-0.924	0.998	0.690	-0.887	-0.991	0.788	0.989	0.861	0.866	1.000	-0.606	0.093	-0.868
Cl %	0.436	-0.996	0.864	-0.653	0.157	0.905	0.706	-0.967	-0.716	-0.927	-0.923	-0.606	1.000	0.736	0.850
S %	0.626	-0.793	0.295	0.032	0.785	0.378	0.040	-0.540	-0.053	-0.427	-0.418	0.093	0.736	1.000	0.325
Ln Corr Rate (μ_m /khr)	0.219	-0.807	0.957	-0.891	-0.304	0.958	0.914	-0.934	-0.918	-0.954	-0.955	-0.868	0.850	0.325	1.000

Table B-16: Correlation matrix for co-firing data subset 16, T22 (red text indicates marked correlations are significant at $p < 0.05$; the elements in symbols are the fuel elements and the elements written in full are the alloy elements)

Variable	Correlations (Co-firing Data subset 16) Marked correlations are significant at $p < .05000$														
	1000/Metal Temp (1000/(K))	Na %	K %	Al %	Si %	P %	Mg %	Ca %	Ti %	Mn %	Fe %	Ba %	Cl %	S %	Ln Corr Rate (μ_m /khr)
1000/Metal Temp (1000/(K))	1.000	0.010	0.203	-0.199	-0.259	0.184	0.236	-0.119	-0.184	-0.124	-0.131	-0.208	-0.096	-0.250	-0.788
Na %	0.010	1.000	-0.666	0.496	-0.081	-0.730	-0.499	0.876	0.561	0.824	0.813	0.451	-0.962	-0.513	0.042
K %	0.203	-0.666	1.000	-0.964	-0.685	0.996	0.979	-0.942	-0.974	-0.961	-0.968	-0.953	0.524	-0.299	-0.005
Al %	-0.199	0.496	-0.964	1.000	0.821	-0.943	-0.985	0.850	0.997	0.900	0.909	0.999	-0.386	0.471	0.039
Si %	-0.259	-0.081	-0.685	0.821	1.000	-0.618	-0.819	0.410	0.773	0.494	0.512	0.849	0.209	0.890	-0.007
P %	0.184	-0.730	0.996	-0.943	-0.618	1.000	0.956	-0.969	-0.961	-0.980	-0.985	-0.928	0.597	-0.211	-0.011
Mg %	0.236	-0.499	0.979	-0.985	-0.819	0.956	1.000	-0.854	-0.980	-0.892	-0.902	-0.985	0.348	-0.487	0.003
Ca %	-0.119	0.876	-0.942	0.850	0.410	-0.969	-0.854	1.000	0.886	0.993	0.991	0.823	-0.776	-0.037	0.031
Ti %	-0.184	0.561	-0.974	0.997	0.773	-0.961	-0.980	0.886	1.000	0.931	0.938	0.991	-0.457	0.399	0.046
Mn %	-0.124	0.824	-0.961	0.900	0.494	-0.980	-0.892	0.993	0.931	1.000	1.000	0.877	-0.734	0.049	0.047
Fe %	-0.131	0.813	-0.968	0.909	0.512	-0.985	-0.902	0.991	0.938	1.000	1.000	0.886	-0.718	0.071	0.044
Ba %	-0.208	0.451	-0.953	0.999	0.849	-0.928	-0.985	0.823	0.991	0.877	0.886	1.000	-0.337	0.516	0.035
Cl %	-0.096	-0.962	0.524	-0.386	0.209	0.597	0.348	-0.776	-0.457	-0.734	-0.718	-0.337	1.000	0.632	-0.099
S %	-0.250	-0.513	-0.299	0.471	0.890	-0.211	-0.487	-0.037	0.399	0.049	0.071	0.516	0.632	1.000	-0.052
Ln Corr Rate (μ_m /khr)	-0.788	0.042	-0.005	0.039	-0.007	-0.011	0.003	0.031	0.046	0.047	0.044	0.035	-0.099	-0.052	1.000

Appendix C Variable Selection Criteria (Framework Model F)

This section presents the results from the variables selection procedure for PCA (rotated loadings plot table) and PLS (VIP criterion) explained in chapter 3, section 0 and section 3.2.3.1.3. The number of PCs and PLS components used are also indicated. The results presented are restricted to framework model F (discussed in chapter 4). The first section of Appendix D presents the number of PCs and PLS components for the other framework models A-E.

Table C-1: Description of data subsets

Data subsets	REGION	FUEL	MATERIAL	TUBE POSITION
Data 1A	UK	Coal	Austenitic	Leading
Data 2A	UK	Coal	Austenitic	Non-leading
Data 3A	UK	Coal	Ferritic	Leading
Data 4A	UK	Coal	Ferritic	Non-leading
Data 5A	US	Coal	Austenitic	
Data 6A	US	Coal	Ni based	
Data 7A	US	Coal	Coatings	
Data 8A	UK	Coal (Europe)	Austenitic	
Data 9A	UK	Coal	Coatings	
Data 10A	UK	Biomass	Austenitic	
Data 11A	UK	Biomass	Ni based	
Data 12A	UK	Biomass	Ferritic	
Data 13A	UK	Biomass	Coatings	
Data 14A	UK	Coal/Biomass	Austenitic	
Data 15A	UK	Coal/Biomass	TP316	
Data 16A	UK	Coal/Biomass	Ferritic	

C.1 PCA Variable Selection Criteria: Varimax Rotated Loading Plots

The PCs that correlate with the corrosion rate are determined by the stepwise regression module. The results are presented in this section. Then the predictor variables selected from the varimax rotated loadings table for model building are presented. The variables greater than an absolute value of 0.5 were selected for model building. Not all the PCs (initially selected via eigenvalue criterion) were used for model building (see stepwise regression described in section 3.2.2.1.6). The PCs not highlighted were excluded from

the variable selection process as they were knocked out at the stepwise regression stage (which also excludes variables greater than the 0.5 threshold that loads highly on that PC).

Note on the tables: All the predictor variables except metal temperature are in natural log form. Alloy and fuel variables are in wt %. Highlighted (orange) PC cells are used for corrosion model building. Variables with PC loadings > 0.5 are marked in red and those in yellow cells are selected for model building.

Table C-2: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 1)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model									
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
1	0.79	7	0.27		0.29	0.24	0.41	-0.56	0.25	0.25
2	0.79	8	0.27	-0.051	0.29	0.24	0.41	-0.56	0.25	0.25
3	0.73	6	0.27		0.29		0.41	-0.56	0.25	0.25
4	0.73	6	0.27		0.29	0.24	0.41	-0.56		0.25
5	0.73	6	0.27		0.29	0.24	0.41	-0.56	0.25	
6	0.72	7	0.27	-0.051	0.29		0.41	-0.56	0.25	0.25
7	0.72	7	0.27	-0.051	0.29	0.24	0.41	-0.56		0.25
8	0.72	7	0.27	-0.051	0.29	0.24	0.41	-0.56	0.25	
9	0.71	6			0.29	0.24	0.41	-0.56	0.25	0.25
10	0.71	7		-0.051	0.29	0.24	0.41	-0.56	0.25	0.25

Table C-3: Varimax rotated loadings table for data subset 1 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 1) (Marked loadings are > 0.5)							
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
1000/Metal Temp (1000 / K)	-0.137	0.108	-0.151	0.012	-0.075	0.147	0.215	0.916
T _g -T _m (K)	-0.159	0.052	0.119	0.135	0.213	-0.053	-0.780	-0.336
Carbon (%)	-0.129	0.119	0.962	0.155	0.057	-0.043	-0.089	-0.066
Manganese (%)	-0.991	-0.037	-0.104	-0.012	0.026	0.011	-0.049	0.030
Phosphorus (%)	0.991	0.037	0.104	0.012	-0.026	-0.011	0.049	-0.030
Sulphur (%)	0.991	0.037	0.104	0.012	-0.026	-0.011	0.049	-0.030
Silicon (%)	0.561	0.157	0.782	0.123	0.026	-0.062	-0.112	0.031
Chromium (%)	0.519	0.098	0.823	0.144	-0.092	-0.042	-0.004	-0.093

Variable	PC Loadings (Varimax normalized) (Data subset 1) (Marked loadings are > 0.5)							
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
Nickel (%)	0.578	0.058	0.728	0.088	0.242	0.006	0.056	-0.213
Molybdenum (%)	0.428	-0.144	-0.467	-0.153	0.591	0.120	0.226	-0.300
Titanium (%)	-0.155	0.079	0.155	-0.085	0.930	0.041	-0.147	-0.023
Vanadium (%)	0.991	0.037	0.104	0.012	-0.026	-0.011	0.049	-0.030
Na (%)	0.094	0.478	0.079	0.662	0.079	0.433	0.316	0.061
K (%)	0.045	0.377	0.196	0.848	0.048	0.168	0.186	0.076
Mg (%)	0.004	0.949	0.159	-0.008	-0.003	0.084	-0.035	0.002
Ca (%)	0.152	0.901	0.102	0.142	0.069	0.017	0.225	0.117
Al (%)	0.010	0.684	0.116	0.637	-0.093	0.120	0.174	0.025
Fe (%)	-0.064	-0.045	0.100	0.907	-0.190	-0.083	-0.137	-0.141
Si (%)	-0.020	-0.550	0.045	-0.327	-0.058	-0.079	-0.704	0.011
Cl (%)	-0.009	0.117	-0.052	0.075	0.062	0.943	0.095	0.167
S (%)	0.170	-0.051	0.214	0.662	0.002	-0.541	0.197	0.195
Ti (%)	-0.007	-0.484	0.047	-0.356	-0.056	-0.011	-0.681	-0.008

Table C-4: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 2). Note: eigenvalue criterion reduced to 0.2 to retain metal temperature

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model									
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
1	0.59	8	0.28	-0.25	0.24	-0.18	-0.22	-0.44	-0.20	0.45
2	0.57	7	0.28	-0.25	0.24		-0.22	-0.44	-0.20	0.45
3	0.56	7	0.28	-0.25	0.24	-0.18	-0.22	-0.44		0.45
4	0.55	7	0.28	-0.25	0.24	-0.18		-0.44	-0.20	0.45
5	0.54	6	0.28	-0.25	0.24		-0.22	-0.44		0.45
6	0.53	7	0.28	-0.25		-0.18	-0.22	-0.44	-0.20	0.45
7	0.53	6	0.28	-0.25	0.24			-0.44	-0.20	0.45
8	0.53	7	0.28		0.24	-0.18	-0.22	-0.44	-0.20	0.45
9	0.52	6	0.28	-0.25	0.24	-0.18		-0.44		0.45
10	0.51	6	0.28	-0.25			-0.22	-0.44	-0.20	0.45

Table C-5: Varimax rotated loadings table for data subset 2 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 2) (Marked loadings are > 0.5)							
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
1000/Metal Temp (1000 / K)	-0.301	0.337	-0.258	0.245	0.177	-0.171	-0.295	-0.693
T _g -T _m (K)	-0.282	0.061	-0.093	0.025	0.012	0.085	-0.940	-0.111
Carbon (%)	-0.186	0.062	0.974	0.016	-0.033	0.082	0.011	0.058
Manganese (%)	-0.970	-0.141	-0.137	-0.012	-0.026	0.094	-0.095	-0.032
Phosphorus (%)	0.970	0.141	0.137	0.012	0.026	-0.094	0.095	0.032
Sulphur (%)	0.970	0.141	0.137	0.012	0.026	-0.094	0.095	0.032
Silicon (%)	0.452	0.305	0.831	0.013	0.012	0.024	0.046	0.045
Chromium (%)	0.423	0.079	0.894	0.030	0.055	0.016	0.069	0.068
Nickel (%)	0.571	-0.082	0.777	0.016	-0.173	-0.052	0.108	0.101
Molybdenum (%)	0.562	-0.411	-0.525	-0.021	-0.395	-0.187	0.104	0.060
Titanium (%)	-0.090	0.181	0.048	-0.099	-0.962	-0.094	0.009	0.062
Vanadium (%)	0.970	0.141	0.137	0.012	0.026	-0.094	0.095	0.032
Na (%)	0.135	0.861	-0.063	0.427	-0.009	-0.101	0.000	-0.196
K (%)	-0.041	0.733	0.144	0.621	-0.007	0.189	-0.054	-0.080
Mg (%)	0.196	0.838	0.369	-0.143	-0.193	-0.056	-0.080	0.071
Ca (%)	0.272	0.782	0.138	0.106	-0.122	-0.503	0.025	-0.082
Al (%)	0.099	0.895	0.254	0.288	0.029	0.110	-0.059	0.089
Fe (%)	-0.207	0.194	0.102	0.549	0.159	0.743	-0.137	0.082
Si (%)	-0.342	-0.411	0.120	-0.439	0.063	0.693	-0.042	0.084
Cl (%)	0.119	0.787	-0.300	-0.343	-0.065	-0.020	0.017	-0.340
S (%)	-0.046	-0.040	0.084	0.974	0.126	0.105	0.033	0.055
Ti (%)	-0.157	-0.334	0.128	-0.836	0.031	0.227	0.066	0.249

Table C-6: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 3)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model							
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
1	0.42	5	-0.25		-0.16	-0.31	0.09	-0.51
2	0.42	4	-0.25		-0.16	-0.31		-0.51
3	0.42	6	-0.25	0.07	-0.16	-0.31	0.09	-0.51
4	0.42	5	-0.25	0.07	-0.16	-0.31		-0.51
5	0.40	4	-0.25			-0.31	0.09	-0.51
6	0.40	3	-0.25			-0.31		-0.51
7	0.40	5	-0.25	0.07		-0.31	0.09	-0.51
8	0.40	4	-0.25	0.07		-0.31		-0.51
9	0.36	3			-0.16	-0.31		-0.51
10	0.36	4			-0.16	-0.31	0.09	-0.51

Table C-7: Varimax rotated loadings table for data subset 3 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 3) (Marked loadings are > 0.5)					
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
1000/Metal Temp (1000 / K)	0.271	0.204	0.086	0.163	-0.173	0.906
T _g -T _m (K)	-0.078	0.199	0.081	0.217	-0.932	0.156
Carbon (%)	0.990	0.114	-0.046	0.012	0.008	0.058
Manganese (%)	0.990	0.114	-0.046	0.012	0.008	0.058
Phosphorus (%)	0.990	0.114	-0.046	0.012	0.008	0.058
Sulphur (%)	0.990	0.114	-0.046	0.012	0.008	0.058
Silicon (%)	0.990	0.114	-0.046	0.012	0.008	0.058
Chromium (%)	-0.990	-0.114	0.046	-0.012	-0.008	-0.058
Nickel (%)	0.990	0.114	-0.046	0.012	0.008	0.058
Copper (%)	0.990	0.114	-0.046	0.012	0.008	0.058
Molybdenum (%)	-0.990	-0.114	0.046	-0.012	-0.008	-0.058
Na (%)	-0.201	-0.160	0.823	-0.480	-0.014	0.010
K (%)	-0.233	-0.310	0.688	-0.594	0.029	-0.025
Mg (%)	0.115	0.075	0.875	0.344	-0.074	0.081
Ca (%)	-0.094	-0.677	0.703	0.063	0.007	-0.002
Al (%)	-0.341	-0.861	0.101	-0.070	0.170	-0.086
Fe (%)	-0.103	-0.050	0.073	-0.922	0.162	-0.079
Si (%)	0.348	0.894	0.045	0.089	-0.061	0.092
Cl (%)	-0.089	0.558	0.793	-0.097	-0.056	0.042
S (%)	0.187	-0.121	-0.028	-0.917	0.054	-0.061
Ti (%)	0.005	0.797	0.098	0.527	-0.057	0.120

Table C-8: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 4)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model						
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5
1	0.12	2				-0.23	-0.29
2	0.11	3		0.07		-0.23	-0.29
3	0.11	3	0.03			-0.23	-0.29
4	0.11	3			0.02	-0.23	-0.29
5	0.10	4	0.03	0.07		-0.23	-0.29
6	0.10	4		0.07	0.02	-0.23	-0.29
7	0.10	4	0.03		0.02	-0.23	-0.29
8	0.09	5	0.03	0.07	0.02	-0.23	-0.29
9	0.07	1					-0.29
10	0.07	2		0.07			-0.29

Table C-9: Varimax rotated loadings table for data subset 4 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 4) (Marked loadings are > 0.5)				
	PC 1	PC 2	PC 3	PC 4	PC 5
1000/Metal Temp (1000 / K)	-0.016	0.230	0.043	0.063	-0.917
T _g -T _m (K)	-0.081	0.188	0.290	-0.665	-0.407
Carbon (%)	0.994	0.030	0.099	0.039	0.012
Manganese (%)	0.994	0.030	0.099	0.039	0.012
Phosphorus (%)	0.994	0.030	0.099	0.039	0.012
Sulphur (%)	0.994	0.030	0.099	0.039	0.012
Silicon (%)	0.994	0.030	0.099	0.039	0.012
Chromium (%)	-0.994	-0.030	-0.099	-0.039	-0.012
Nickel (%)	0.994	0.030	0.099	0.039	0.012
Copper (%)	0.994	0.030	0.099	0.039	0.012
Molybdenum (%)	-0.994	-0.030	-0.099	-0.039	-0.012
Na (%)	0.152	0.090	0.953	0.165	-0.081
K (%)	0.158	-0.157	0.890	0.364	-0.058
Mg (%)	0.329	0.422	0.584	-0.495	0.149
Ca (%)	0.268	-0.652	0.564	-0.133	0.259
Al (%)	0.006	-0.946	0.002	0.086	0.150
Fe (%)	0.098	-0.101	0.350	0.832	-0.125
Si (%)	0.180	0.958	0.053	-0.086	-0.054
Cl (%)	0.123	0.662	0.678	-0.200	-0.113
S (%)	0.131	-0.089	0.174	0.905	-0.094
Ti (%)	0.033	0.773	0.075	-0.563	-0.039

Table C-10: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 5)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model																
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14	PC 15
1	0.78	11	-0.63	0.34	0.27	-0.23	0.15				-0.22	-0.12	0.14		0.19	-0.14	-0.06
2	0.78	10	-0.63	0.34	0.27	-0.23	0.15				-0.22	-0.12	0.14		0.19	-0.14	
3	0.77	12	-0.63	0.34	0.27	-0.23	0.15	0.04			-0.22	-0.12	0.14		0.19	-0.14	-0.06
4	0.77	12	-0.63	0.34	0.27	-0.23	0.15				-0.22	-0.12	0.14	0.03	0.19	-0.14	-0.06
5	0.77	11	-0.63	0.34	0.27	-0.23	0.15	0.04			-0.22	-0.12	0.14		0.19	-0.14	
6	0.77	11	-0.63	0.34	0.27	-0.23	0.15				-0.22	-0.12	0.14	0.03	0.19	-0.14	
7	0.77	12	-0.63	0.34	0.27	-0.23	0.15			0.01	-0.22	-0.12	0.14		0.19	-0.14	-0.06
8	0.77	12	-0.63	0.34	0.27	-0.23	0.15		0.00		-0.22	-0.12	0.14		0.19	-0.14	-0.06
9	0.77	13	-0.63	0.34	0.27	-0.23	0.15	0.04			-0.22	-0.12	0.14	0.03	0.19	-0.14	-0.06
10	0.77	11	-0.63	0.34	0.27	-0.23	0.15			0.01	-0.22	-0.12	0.14		0.19	-0.14	

Table C-11: Varimax rotated loadings table for data subset 5 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 5) (Marked loadings are > 0.5)														
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14	PC 15
1000 / Metal Temp (1000 / K)	0.141	0.006	0.073	0.099	-0.164	0.095	0.068	-0.037	0.006	0.033	-0.146	-0.086	0.908	0.120	-0.033
T _g -T _m (K)	0.396	-0.129	0.057	0.167	-0.301	0.153	0.130	-0.042	0.170	0.025	0.048	0.002	0.693	0.015	0.332
Carbon (%)	-0.114	-0.257	-0.233	-0.115	-0.088	0.122	-0.053	-0.865	0.049	-0.010	-0.083	0.041	0.095	-0.005	0.019
Manganese (%)	0.108	-0.267	-0.392	-0.585	-0.011	-0.269	-0.269	0.373	0.131	0.225	0.039	-0.114	0.014	-0.053	-0.067
Phosphorus (%)	0.182	-0.065	0.826	0.213	0.157	0.111	-0.144	0.208	-0.020	0.019	0.094	-0.187	0.038	-0.088	-0.162
Sulphur (%)	0.174	-0.109	0.914	0.003	0.066	0.030	0.068	0.001	-0.038	0.009	0.039	-0.145	0.087	-0.106	-0.023
Silicon (%)	-0.169	0.071	-0.040	-0.874	0.094	-0.083	0.062	-0.105	0.059	-0.208	0.027	0.005	-0.112	-0.028	-0.103
Chromium (%)	0.064	-0.261	0.215	-0.210	-0.255	-0.023	-0.197	0.241	0.198	-0.053	0.714	-0.064	-0.089	-0.035	0.100
Nickel (%)	0.031	0.007	-0.029	-0.173	-0.017	0.152	0.157	0.023	-0.031	0.099	0.911	0.040	-0.069	0.077	0.018
Molybdenum (%)	0.208	-0.217	-0.456	0.365	0.086	0.380	0.058	0.551	0.013	-0.069	0.140	-0.018	0.111	0.041	-0.094
Niobium (%)	-0.038	0.868	0.116	-0.151	0.048	-0.318	-0.057	0.201	0.045	-0.067	-0.141	0.035	-0.090	0.030	0.031
Titanium (%)	0.127	0.271	0.503	-0.045	-0.005	-0.298	0.011	0.328	0.070	-0.059	-0.436	0.160	-0.015	0.046	0.280
Copper (%)	0.129	-0.003	0.026	0.886	0.082	-0.008	0.080	0.104	0.012	-0.058	-0.297	0.063	0.071	0.003	-0.041
Vanadium (%)	-0.107	0.332	0.303	0.113	0.071	0.214	-0.788	-0.085	0.056	0.002	-0.105	-0.054	-0.111	-0.020	-0.158
Aluminium (%)	-0.110	0.042	-0.147	-0.147	-0.015	-0.262	-0.899	-0.004	0.007	-0.028	0.009	0.056	-0.058	0.028	0.057
Nitrogen (%)	-0.034	0.906	-0.203	0.088	0.083	-0.122	-0.192	0.019	0.082	0.046	-0.026	0.048	0.025	0.043	-0.046
Cerium (%)	0.172	-0.006	0.009	0.070	0.043	0.025	0.023	-0.004	0.005	0.972	0.069	0.001	0.035	0.002	0.003
Tungsten (%)	-0.009	-0.327	-0.139	-0.018	-0.072	0.876	-0.118	-0.102	-0.046	0.015	0.184	0.033	0.106	0.034	0.062
Boron (%)	-0.019	0.257	-0.086	-0.219	0.022	-0.870	-0.174	0.154	-0.031	-0.030	0.064	0.053	-0.072	0.031	0.096
Tantalum (%)	0.110	0.103	-0.040	-0.065	-0.086	-0.043	-0.039	-0.028	0.967	0.006	0.045	0.024	0.066	0.018	0.068
Cobalt (%)	0.062	0.209	0.249	-0.071	-0.140	0.738	0.147	0.380	-0.071	-0.011	0.159	0.130	0.044	0.051	0.274
Na (%)	0.891	-0.002	0.102	0.060	0.382	-0.014	0.026	0.068	0.003	0.020	-0.033	0.060	-0.058	-0.004	0.044
K (%)	0.899	-0.065	0.172	0.077	0.015	0.005	0.066	0.073	0.048	0.083	0.058	0.234	0.181	-0.005	-0.100

Variable	PC Loadings (Varimax normalized) (Data subset 5) (Marked loadings are > 0.5)														
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14	PC 15
Mg (%)	0.851	0.018	0.105	0.066	0.455	-0.026	0.028	0.084	0.004	0.087	-0.034	-0.034	0.003	0.071	0.122
Ca (%)	0.787	-0.018	0.119	0.047	0.363	-0.002	0.026	0.080	0.013	0.073	0.000	-0.349	0.120	-0.059	0.218
Al (%)	0.255	0.075	-0.271	0.078	0.148	0.042	-0.027	-0.037	0.025	-0.003	-0.015	0.888	-0.103	0.025	0.042
Fe (%)	0.837	-0.058	-0.038	0.106	-0.345	0.084	0.074	0.018	0.109	0.057	0.077	0.025	0.178	0.040	0.289
Si (%)	0.827	0.023	-0.008	0.070	0.022	0.017	0.038	0.017	0.032	0.033	0.016	0.490	0.057	0.225	-0.078
Cl (%)	-0.325	-0.069	0.186	-0.043	0.035	-0.026	0.021	-0.013	-0.023	0.003	-0.063	-0.060	-0.138	-0.886	-0.109
S (%)	-0.078	-0.076	-0.087	-0.013	-0.841	0.079	0.019	-0.051	0.055	-0.025	0.099	-0.175	0.305	0.301	0.016
Ti (%)	-0.829	0.010	-0.043	-0.034	0.315	-0.019	-0.048	-0.021	-0.019	-0.032	0.012	-0.021	-0.063	-0.409	0.057
P (%)	-0.489	0.049	0.230	-0.143	0.211	-0.149	-0.062	0.068	-0.166	-0.006	-0.091	-0.023	-0.156	-0.204	-0.685
Mn (%)	-0.360	-0.117	-0.146	0.035	-0.762	0.116	0.031	-0.066	0.110	-0.040	0.115	-0.014	0.146	-0.338	0.240

Table C-12: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 6). Forced stepwise regression to include PCs that have high loading(s) with the metal temperature

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model											
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10
1	0.28	10	-0.13	-0.22	0.01	-0.02	-0.24	0.21	-0.20	0.14	-0.38	-0.21

Table C-13: Varimax rotated loadings table for data subset 6 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 6) (Marked loadings are > 0.5)									
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10
1000 / Metal Temp (1000 / K)	-0.153	0.023	0.018	-0.934	0.064	0.139	-0.060	0.064	-0.212	-0.053
T _g -T _m (K)	0.101	-0.124	0.105	-0.903	0.121	0.072	-0.015	0.057	0.009	0.285
Carbon (%)	-0.116	0.314	-0.091	0.046	0.151	0.011	-0.759	0.395	0.116	-0.073
Manganese (%)	0.251	0.140	0.064	0.483	0.566	0.009	0.147	0.132	0.486	-0.162
Phosphorus (%)	0.263	-0.005	0.086	-0.085	0.945	0.009	-0.068	-0.014	0.007	0.033
Sulphur (%)	0.263	-0.005	0.086	-0.085	0.945	0.009	-0.068	-0.014	0.007	0.033
Silicon (%)	0.001	-0.670	-0.027	0.225	0.431	0.047	0.330	0.327	0.220	-0.110
Chromium (%)	-0.804	-0.054	-0.232	0.008	-0.036	0.192	0.236	-0.157	-0.379	0.045
Molybdenum (%)	0.282	-0.286	-0.026	-0.137	0.647	0.005	-0.120	0.534	0.002	-0.264
Niobium (%)	-0.129	-0.946	-0.045	-0.196	-0.068	0.037	0.014	0.072	-0.172	-0.016
Titanium (%)	0.086	-0.976	0.051	-0.022	-0.154	-0.012	0.058	-0.039	0.060	0.018
Copper (%)	-0.188	0.281	0.072	0.031	-0.083	0.043	-0.206	-0.885	-0.090	0.101
Aluminium (%)	0.089	0.108	0.027	0.251	-0.028	-0.031	0.842	0.273	0.230	0.078
Tungsten (%)	0.312	0.393	0.124	0.167	0.030	-0.040	-0.672	-0.330	0.235	0.003
Boron (%)	-0.459	-0.116	-0.194	-0.314	-0.208	0.040	-0.127	0.560	-0.384	0.308
Cobalt (%)	0.347	-0.847	0.114	-0.022	0.131	-0.067	0.262	0.154	0.166	0.032
Iron (%)	0.186	0.904	0.019	-0.020	-0.144	-0.041	0.078	-0.131	-0.019	-0.274
Na (%)	0.948	0.012	0.120	0.025	0.217	0.049	0.038	0.028	-0.165	-0.028
K (%)	0.720	0.000	0.606	0.052	0.263	0.033	0.048	-0.008	-0.163	0.002
Mg (%)	0.952	-0.023	0.021	0.037	0.238	0.159	0.061	0.020	-0.005	0.017
Ca (%)	0.882	-0.067	-0.268	0.074	0.229	0.124	0.073	0.024	0.222	0.110
Al (%)	-0.044	0.111	0.149	-0.162	-0.033	-0.174	-0.002	-0.015	-0.942	0.055
Fe (%)	0.395	-0.038	0.747	0.068	0.143	-0.378	0.051	-0.028	-0.157	0.293
Si (%)	0.328	0.032	0.812	-0.134	0.113	0.205	0.007	-0.038	-0.394	-0.003
Cl (%)	0.070	0.053	-0.631	0.291	0.079	-0.673	0.023	0.064	-0.148	-0.056
S (%)	-0.446	-0.051	0.847	-0.009	-0.104	0.032	0.008	-0.064	0.190	0.112
Ti (%)	-0.077	0.005	-0.989	0.007	-0.089	-0.063	0.007	0.040	0.005	0.028
P (%)	-0.034	0.175	-0.159	0.223	0.037	0.118	-0.111	0.092	0.077	-0.917
Mn (%)	-0.529	0.006	-0.036	0.162	-0.101	-0.780	0.004	0.000	-0.146	0.227

Table C-14: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 7)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model															
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14
1	0.82	11	-0.17	0.51	-0.08	-0.31	0.29	-0.23		-0.45		0.11	-0.18	0.11		-0.26
2	0.82	12	-0.17	0.51	-0.08	-0.31	0.29	-0.23	-0.04	-0.45		0.11	-0.18	0.11		-0.26
3	0.82	12	-0.17	0.51	-0.08	-0.31	0.29	-0.23		-0.45	-0.01	0.11	-0.18	0.11		-0.26
4	0.82	12	-0.17	0.51	-0.08	-0.31	0.29	-0.23		-0.45		0.11	-0.18	0.11	0.00	-0.26
5	0.82	13	-0.17	0.51	-0.08	-0.31	0.29	-0.23	-0.04	-0.45	-0.01	0.11	-0.18	0.11		-0.26
6	0.82	13	-0.17	0.51	-0.08	-0.31	0.29	-0.23	-0.04	-0.45		0.11	-0.18	0.11	0.00	-0.26
7	0.82	10	-0.17	0.51		-0.31	0.29	-0.23		-0.45		0.11	-0.18	0.11		-0.26
8	0.81	13	-0.17	0.51	-0.08	-0.31	0.29	-0.23		-0.45	-0.01	0.11	-0.18	0.11	0.00	-0.26
9	0.81	11	-0.17	0.51		-0.31	0.29	-0.23	-0.04	-0.45		0.11	-0.18	0.11		-0.26
10	0.81	14	-0.17	0.51	-0.08	-0.31	0.29	-0.23	-0.04	-0.45	-0.01	0.11	-0.18	0.11	0.00	-0.26

Table C-15: Varimax rotated loadings table for data subset 7 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 7) (Marked loadings are > 0.5)													
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14
1000 / Metal Temp (1000 / K)	-0.017	-0.128	0.050	0.215	-0.140	0.109	-0.037	-0.050	-0.012	-0.056	0.046	0.123	-0.057	-0.921
Carbon (%)	-0.017	0.159	0.122	-0.255	-0.035	-0.019	0.104	0.067	-0.200	0.246	-0.831	-0.082	0.172	0.060
Manganese (%)	-0.014	0.225	0.840	-0.118	0.053	0.105	0.015	-0.303	-0.004	0.204	0.002	-0.221	-0.034	0.110
Phosphorus (%)	0.038	0.933	-0.005	0.054	0.029	-0.130	0.076	-0.072	-0.012	0.228	-0.032	-0.064	0.131	0.067
Sulphur (%)	0.033	0.955	-0.052	0.046	0.036	-0.064	0.073	-0.046	-0.008	-0.082	-0.129	-0.053	0.088	0.010
Silicon (%)	-0.067	0.209	0.518	-0.518	0.028	0.056	-0.041	0.360	0.052	0.177	-0.323	-0.208	-0.265	0.057
Chromium (%)	0.198	0.090	-0.216	-0.088	-0.050	-0.007	0.002	-0.068	0.387	0.040	-0.187	0.001	0.815	0.072
Nickel (%)	0.145	0.261	-0.079	0.087	-0.034	0.092	0.013	-0.060	0.102	0.069	0.005	0.021	0.919	0.050
Molybdenum (%)	0.058	0.388	0.038	0.629	0.058	0.034	0.054	-0.427	0.101	0.323	0.071	-0.145	-0.225	-0.014
Niobium (%)	-0.017	0.201	-0.072	0.093	0.072	-0.142	0.012	0.096	0.017	0.912	-0.179	-0.100	0.047	0.004
Titanium (%)	-0.033	-0.115	0.899	0.138	0.009	-0.010	-0.010	0.127	-0.006	-0.126	-0.131	0.077	-0.159	-0.157
Copper (%)	0.021	0.074	0.287	0.011	0.063	-0.006	0.029	0.050	0.157	0.543	-0.252	-0.379	-0.557	0.192
Vanadium (%)	-0.049	0.216	0.067	-0.615	-0.033	0.032	-0.006	0.119	-0.180	0.356	-0.056	0.124	0.597	0.077
Aluminium (%)	-0.096	0.525	0.216	-0.130	0.014	0.085	0.047	0.085	-0.347	0.618	0.036	0.075	0.267	0.041
Nitrogen (%)	0.031	0.786	0.088	0.041	0.000	0.208	0.065	0.006	-0.071	0.439	-0.013	-0.097	0.227	0.129
Cerium (%)	0.007	0.068	-0.006	0.079	-0.011	0.017	0.041	-0.966	-0.048	-0.127	0.032	0.028	0.111	-0.038
Tantalum (%)	0.029	0.055	-0.064	0.027	0.052	-0.966	0.044	0.021	0.002	0.077	-0.011	-0.160	-0.072	0.102
Boron (%)	0.170	-0.076	0.013	0.010	-0.030	0.001	-0.063	0.057	0.891	-0.034	0.153	0.012	0.247	0.012
Tungsten (%)	0.042	0.111	0.032	0.938	0.060	-0.027	0.034	0.042	-0.053	0.067	0.110	-0.004	0.093	-0.167
Iron (%)	-0.125	-0.241	0.591	-0.085	0.074	-0.001	-0.062	0.238	-0.074	0.014	0.338	-0.147	-0.581	0.038
Na (%)	0.862	-0.019	-0.016	0.039	-0.011	-0.011	-0.479	0.008	0.078	-0.018	0.024	0.084	0.058	0.065
K (%)	0.501	0.183	-0.078	0.049	-0.211	0.019	-0.713	-0.126	0.086	-0.112	-0.007	0.120	0.289	0.015

Variable	PC Loadings (Varimax normalized) (Data subset 7) (Marked loadings are > 0.5)													
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14
Mg (%)	0.941	0.006	-0.037	0.035	-0.057	0.000	-0.279	-0.010	0.082	-0.023	0.013	0.103	0.100	0.019
Ca (%)	0.926	0.075	-0.091	0.038	0.054	0.042	0.113	-0.066	0.078	-0.052	-0.003	0.204	0.207	-0.060
Al (%)	0.056	-0.320	0.100	-0.094	0.179	0.025	-0.836	0.156	-0.013	0.066	0.095	-0.025	-0.278	-0.043
Fe (%)	0.234	-0.037	-0.135	0.011	-0.302	0.151	-0.444	-0.090	0.065	-0.153	0.042	0.720	0.232	-0.019
Si (%)	0.331	-0.085	0.004	-0.035	-0.375	0.017	-0.856	0.025	0.036	-0.031	0.027	0.011	0.011	-0.038
Cl (%)	-0.209	0.205	0.002	0.124	0.878	-0.040	0.050	-0.094	0.028	-0.024	0.017	0.119	0.091	0.260
S (%)	-0.484	0.114	-0.086	-0.018	-0.721	0.075	0.085	-0.117	0.021	-0.112	-0.026	0.357	0.206	-0.059
Ti (%)	-0.148	-0.070	0.044	-0.036	0.799	0.000	0.421	0.059	-0.076	0.086	0.009	-0.282	-0.139	-0.120
P (%)	-0.218	0.409	0.102	0.130	0.210	-0.236	-0.095	-0.084	0.024	0.054	-0.080	-0.718	0.054	0.294
Mn (%)	-0.761	0.002	-0.062	0.006	0.298	0.115	0.107	-0.078	-0.022	-0.086	0.038	0.526	0.082	0.028

Table C-16: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 8)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model							
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
1	0.81	4	-0.64		-0.51	-0.34	0.23	
2	0.81	5	-0.64		-0.51	-0.34	0.23	-0.04
3	0.80	5	-0.64	0.00	-0.51	-0.34	0.23	
4	0.79	6	-0.64	0.00	-0.51	-0.34	0.23	-0.04
5	0.76	3	-0.64		-0.51	-0.34		
6	0.75	4	-0.64		-0.51	-0.34		-0.04
7	0.75	4	-0.64	0.00	-0.51	-0.34		
8	0.74	5	-0.64	0.00	-0.51	-0.34		-0.04
9	0.69	3	-0.64		-0.51		0.23	
10	0.68	4	-0.64		-0.51		0.23	-0.04

Table C-17: Varimax rotated loadings table for data subset 8 (here the elements in symbols are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 8) (Marked loadings are > 0.5)					
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
1000/Metal Temp (1000 / K)	0.064	-0.144	-0.214	0.021	0.950	-0.135
Tg-Tm (K)	0.062	-0.130	-0.143	0.010	0.940	-0.256
C (%)	0.488	-0.387	0.054	-0.019	0.334	-0.705
Si (%)	0.317	-0.557	0.747	0.106	-0.122	0.074
P (%)	0.953	-0.074	0.082	0.056	0.109	-0.256
S (%)	0.944	0.253	0.113	0.178	-0.030	-0.012
V (%)	-0.957	0.121	-0.166	-0.178	-0.033	0.096
Cr (%)	-0.481	0.227	-0.064	0.070	-0.342	0.769
Mn (%)	0.736	-0.457	0.429	0.112	0.063	-0.222
Ni (%)	-0.041	0.576	0.175	0.170	-0.380	0.680
Nb (%)	0.305	-0.011	0.093	0.934	0.078	-0.140
Mo (%)	0.957	-0.121	0.166	0.178	0.033	-0.096
Ti (%)	0.131	0.111	-0.289	0.906	-0.029	0.255
N (%)	0.261	-0.096	0.844	-0.102	0.030	-0.446
W (%)	-0.038	0.953	-0.135	0.000	-0.160	0.216
Cu (%)	-0.211	0.471	-0.549	-0.636	0.099	-0.136
B (%)	0.118	0.259	0.902	-0.036	-0.278	0.162
Al (%)	0.133	-0.311	0.925	-0.034	-0.168	0.027
Co (%)	-0.038	0.953	-0.135	0.000	-0.160	0.216

Table C-18: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 9)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model								
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7
1	0.78	4	0.13	-0.17			0.88		0.14
2	0.78	3		-0.17			0.88		0.14
3	0.78	3	0.13	-0.17			0.88		
4	0.78	2		-0.17			0.88		
5	0.78	5	0.13	-0.17		-0.10	0.88		0.14
6	0.77	4		-0.17		-0.10	0.88		0.14
7	0.77	4	0.13	-0.17		-0.10	0.88		
8	0.77	3		-0.17		-0.10	0.88		
9	0.77	3	0.13				0.88		0.14
10	0.76	2					0.88		0.14

Table C-19: Varimax rotated loadings table for data subset 9 (here the elements in symbols are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 9) (Marked loadings are > 0.5)						
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7
1000/Metal Temp (1000/K)	-0.006	-0.135	0.004	0.031	-0.990	-0.002	-0.006
Al (%)	-0.136	0.049	-0.922	-0.353	0.013	0.061	-0.011
C (%)	0.678	-0.116	0.063	0.057	0.011	0.703	0.158
Cr (%)	0.018	-0.871	0.169	0.137	-0.056	0.412	0.147
Fe (%)	-0.140	0.139	-0.032	-0.955	0.029	-0.174	0.129
Mo (%)	-0.287	0.806	0.386	0.127	0.048	-0.264	-0.175
Nb + Ta (%)	-0.570	0.161	0.141	0.132	-0.013	-0.083	-0.777
Ni (%)	-0.121	0.148	0.049	0.976	-0.010	-0.093	0.026
Si (%)	0.027	-0.855	0.212	-0.198	-0.065	-0.365	0.214
W (%)	0.040	0.967	0.033	-0.084	0.083	0.075	0.208
Y (%)	0.139	0.009	-0.958	0.220	-0.003	-0.096	0.077
O (%)	0.663	0.004	0.497	0.131	0.000	0.452	-0.303
P (%)	0.993	-0.036	-0.014	0.002	0.001	0.059	0.092
S (%)	0.993	-0.036	-0.014	0.002	0.001	0.059	0.092
Co (%)	0.993	-0.036	-0.014	0.002	0.001	0.059	0.092
Cu (%)	0.993	-0.036	-0.014	0.002	0.001	0.059	0.092

Table C-20: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 10)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model											
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10
1	0.70	9	-0.18	0.48	0.45	-0.07		0.23	0.33	0.07	0.15	-0.28
2	0.70	10	-0.18	0.48	0.45	-0.07	0.06	0.23	0.33	0.07	0.15	-0.28
3	0.70	8	-0.18	0.48	0.45			0.23	0.33	0.07	0.15	-0.28
4	0.70	9	-0.18	0.48	0.45		0.06	0.23	0.33	0.07	0.15	-0.28
5	0.70	8	-0.18	0.48	0.45	-0.07		0.23	0.33		0.15	-0.28
6	0.70	9	-0.18	0.48	0.45	-0.07	0.06	0.23	0.33		0.15	-0.28
7	0.70	7	-0.18	0.48	0.45			0.23	0.33		0.15	-0.28
8	0.70	8	-0.18	0.48	0.45		0.06	0.23	0.33		0.15	-0.28
9	0.68	8	-0.18	0.48	0.45	-0.07		0.23	0.33	0.07		-0.28
10	0.68	7	-0.18	0.48	0.45			0.23	0.33	0.07		-0.28

Table C-21: Varimax rotated loadings table for data subset 10 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 10) (Marked loadings are > 0.5)									
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10
1000/Metal Temp (1000 / K)	0.761	0.160	0.175	-0.374	0.057	-0.175	0.313	-0.105	-0.054	0.040
T _R -T _m (K)	0.088	-0.082	0.147	0.197	0.011	-0.228	0.902	-0.008	0.032	-0.041
Carbon (%)	0.293	0.863	0.132	0.053	0.181	-0.138	-0.072	0.233	0.002	0.036
Manganese (%)	0.106	0.229	0.314	-0.040	0.654	-0.476	-0.042	0.047	-0.384	-0.131
Phosphorus (%)	0.123	0.928	0.052	-0.116	0.079	-0.157	0.016	-0.049	-0.040	0.021
Sulphur (%)	0.141	0.849	-0.161	-0.110	0.239	-0.025	-0.049	-0.015	-0.389	-0.018
Silicon (%)	0.128	0.433	0.290	-0.095	0.637	-0.089	0.006	-0.027	0.517	-0.112
Chromium (%)	0.157	-0.168	-0.066	-0.019	-0.249	0.884	-0.025	0.007	0.183	0.186
Nickel (%)	0.127	-0.111	-0.358	-0.011	0.021	0.835	-0.065	-0.229	0.121	0.174
Molybdenum (%)	0.153	0.515	-0.165	0.258	0.249	-0.395	-0.255	-0.154	0.421	-0.200
Niobium (%)	-0.242	0.143	0.205	0.047	-0.552	0.542	0.282	0.255	0.017	0.235
Titanium (%)	0.081	0.107	-0.091	0.130	0.026	-0.158	0.046	0.943	0.000	0.141
Vanadium (%)	0.024	-0.216	-0.117	0.154	-0.112	0.283	-0.056	0.011	0.891	-0.030
Nitrogen (%)	-0.022	0.423	0.101	0.079	0.789	-0.222	0.059	0.159	0.155	0.117
Copper (%)	-0.174	-0.010	0.563	0.137	0.627	-0.151	-0.022	0.124	0.248	-0.364
Tungsten (%)	-0.123	-0.086	0.951	-0.005	-0.059	0.099	-0.111	0.037	0.061	0.077
Boron (%)	0.250	0.067	-0.174	-0.041	0.032	0.336	-0.013	0.206	-0.011	0.853
Aluminium (%)	0.106	0.003	0.970	-0.078	0.087	-0.133	0.053	-0.018	-0.040	-0.038
Cobalt (%)	-0.106	-0.003	0.970	0.078	-0.087	0.133	-0.053	0.018	0.040	0.038
Na (%)	0.972	0.026	0.023	0.210	0.046	0.015	-0.040	0.024	0.053	0.021
K (%)	0.527	0.130	0.122	0.812	0.035	0.077	0.023	-0.070	-0.120	0.044
Mg (%)	0.969	0.066	0.073	-0.156	0.041	0.089	0.108	0.022	-0.040	0.034
Ca (%)	0.927	0.246	0.098	-0.212	0.021	0.045	0.009	-0.016	-0.109	0.088

Variable	PC Loadings (Varimax normalized) (Data subset 10) (Marked loadings are > 0.5)									
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10
Al (%)	0.972	0.112	0.039	0.188	0.030	0.020	-0.016	0.022	0.003	0.049
Fe (%)	0.968	0.051	0.037	0.189	0.029	0.067	0.106	0.052	0.001	0.034
Si (%)	0.983	0.072	0.045	0.126	0.038	0.051	0.053	0.038	-0.007	0.035
Cl (%)	0.976	0.105	0.039	0.120	0.041	-0.007	-0.107	-0.005	0.026	0.045
S (%)	0.351	-0.102	-0.082	0.901	-0.015	0.006	0.116	0.116	0.121	-0.012
Ti (%)	-0.976	0.092	-0.036	0.118	-0.060	-0.055	0.009	0.004	-0.092	0.006
P (%)	0.865	-0.077	0.075	-0.314	0.053	0.168	0.296	0.059	-0.043	-0.013
Ba (%)	0.979	0.115	0.071	-0.090	0.028	0.069	0.069	0.012	-0.039	0.055
Mn (%)	0.450	0.064	0.091	-0.241	-0.054	0.279	0.691	0.123	-0.197	0.060

Table C-22: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 11)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model						
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5
1	0.83	3	-0.89	0.21			-0.14
2	0.82	2	-0.89	0.21			
3	0.81	4	-0.89	0.21		0.03	-0.14
4	0.81	4	-0.89	0.21	-0.02		-0.14
5	0.80	3	-0.89	0.21		0.03	
6	0.80	3	-0.89	0.21	-0.02		
7	0.80	5	-0.89	0.21	-0.02	0.03	-0.14
8	0.79	2	-0.89				-0.14
9	0.79	4	-0.89	0.21	-0.02	0.03	
10	0.79	1	-0.89				

Table C-23: Varimax rotated loadings table for data subset 11 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 11) (Marked loadings are > 0.5)				
	PC 1	PC 2	PC 3	PC 4	PC 5
1000/Metal Temp (1000 / K)	0.669	-0.003	0.100	-0.717	0.107
T _g -T _m (K)	-0.706	0.084	0.046	0.119	0.538
Carbon (%)	0.125	0.141	0.877	-0.425	-0.109
Manganese (%)	0.014	-0.640	-0.481	-0.582	-0.125
Phosphorus (%)	-0.194	0.353	-0.736	0.505	-0.151
Sulphur (%)	0.031	0.953	-0.071	0.250	-0.125
Silicon (%)	0.066	0.941	-0.052	0.327	-0.003
Chromium (%)	0.259	0.317	-0.832	-0.174	0.261
Molybdenum (%)	0.094	-0.168	0.870	0.075	0.365
Niobium (%)	-0.001	0.646	-0.257	0.674	0.215
Titanium (%)	0.029	0.677	-0.520	0.493	0.141
Nitrogen (%)	0.170	0.983	0.028	0.065	0.000
Boron (%)	0.237	0.961	-0.099	-0.064	0.051
Aluminium (%)	-0.179	-0.489	-0.736	0.410	0.124
Cobalt (%)	-0.293	0.209	-0.159	0.917	-0.012
Iron (%)	0.305	-0.268	0.092	-0.901	0.068
Na (%)	0.992	0.114	0.019	0.001	0.007
K (%)	0.377	-0.112	0.092	-0.914	-0.047
Mg (%)	0.949	0.057	0.047	-0.305	-0.010
Ca (%)	0.942	0.052	0.048	-0.326	-0.011
Al (%)	0.992	0.116	0.018	0.012	0.008
Fe (%)	0.987	0.128	0.011	0.089	0.012
Si (%)	0.992	0.112	0.020	-0.012	0.007
Cl (%)	0.988	0.094	0.029	-0.112	0.001
S (%)	0.380	0.196	-0.076	0.898	0.051
Ti (%)	-0.908	-0.034	-0.056	0.412	0.016
P (%)	0.828	0.000	0.068	-0.556	-0.024
Ba (%)	0.968	0.071	0.040	-0.235	-0.006
Mn (%)	-0.459	0.096	-0.090	0.877	0.044

Table C-24: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 12)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model						
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5
1	0.86	4		0.85	0.29	-0.18	0.22
2	0.85	5	0.00	0.85	0.29	-0.18	0.22
3	0.83	3		0.85	0.29		0.22
4	0.82	4	0.00	0.85	0.29		0.22
5	0.81	3		0.85	0.29	-0.18	
6	0.80	4	0.00	0.85	0.29	-0.18	
7	0.79	2		0.85	0.29		
8	0.77	3		0.85		-0.18	0.22
9	0.77	3	0.00	0.85	0.29		
10	0.76	4	0.00	0.85		-0.18	0.22

Table C-25: Varimax rotated loadings table for data subset 12 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 12) (Marked loadings are > 0.5)				
	PC 1	PC 2	PC 3	PC 4	PC 5
1000/Metal Temp (1000 / K)	0.526	0.357	0.106	0.099	0.758
T _g -T _m (K)	-0.318	-0.912	0.156	-0.021	0.129
Carbon (%)	0.981	0.065	0.034	0.160	0.073
Manganese (%)	0.544	-0.112	-0.790	-0.010	0.044
Phosphorus (%)	0.981	0.065	0.034	0.160	0.073
Sulphur (%)	0.981	0.065	0.034	0.160	0.073
Silicon (%)	0.162	-0.206	0.954	-0.142	0.036
Chromium (%)	-0.450	-0.112	0.243	-0.794	0.035
Nickel (%)	-0.451	0.281	-0.832	0.097	-0.062
Molybdenum (%)	-0.446	0.046	0.133	-0.849	-0.083
Vanadium (%)	0.981	0.065	0.034	0.160	0.073
Copper (%)	-0.138	0.147	-0.646	-0.721	-0.065
Na (%)	0.977	0.116	0.029	0.159	0.080
K (%)	0.018	0.987	-0.093	-0.015	0.125
Mg (%)	0.930	0.320	0.008	0.147	0.102
Ca (%)	0.982	-0.065	0.047	0.163	0.057
Al (%)	0.983	0.046	0.036	0.161	0.071
Fe (%)	0.958	0.224	0.018	0.154	0.092
Si (%)	0.980	0.083	0.033	0.160	0.076
Cl (%)	0.977	-0.114	0.051	0.163	0.051
S (%)	0.981	0.065	0.034	0.160	0.073
Ti (%)	-0.969	0.172	-0.056	-0.163	-0.043
P (%)	0.415	0.895	-0.068	0.052	0.140
Ba (%)	0.968	0.175	0.023	0.156	0.086
Mn (%)	-0.338	0.928	-0.102	-0.072	0.094

Table C-26: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 13)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model																
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14	PC 15
1	0.74	14	-0.30	0.33	0.30	0.41	0.23	-0.33	0.14	0.10	-0.15	0.12		0.14	-0.18	-0.15	0.09
2	0.74	15	-0.30	0.33	0.30	0.41	0.23	-0.33	0.14	0.10	-0.15	0.12	-0.01	0.14	-0.18	-0.15	0.09
3	0.73	13	-0.30	0.33	0.30	0.41	0.23	-0.33	0.14	0.10	-0.15	0.12		0.14	-0.18	-0.15	
4	0.73	13	-0.30	0.33	0.30	0.41	0.23	-0.33	0.14		-0.15	0.12		0.14	-0.18	-0.15	0.09
5	0.73	14	-0.30	0.33	0.30	0.41	0.23	-0.33	0.14	0.10	-0.15	0.12	-0.01	0.14	-0.18	-0.15	
6	0.73	14	-0.30	0.33	0.30	0.41	0.23	-0.33	0.14		-0.15	0.12	-0.01	0.14	-0.18	-0.15	0.09
7	0.73	13	-0.30	0.33	0.30	0.41	0.23	-0.33	0.14	0.10	-0.15			0.14	-0.18	-0.15	0.09
8	0.73	14	-0.30	0.33	0.30	0.41	0.23	-0.33	0.14	0.10	-0.15		-0.01	0.14	-0.18	-0.15	0.09
9	0.73	12	-0.30	0.33	0.30	0.41	0.23	-0.33	0.14		-0.15	0.12		0.14	-0.18	-0.15	
10	0.72	13	-0.30	0.33	0.30	0.41	0.23	-0.33	0.14		-0.15	0.12	-0.01	0.14	-0.18	-0.15	

Table C-27: Varimax rotated loadings table for data subset 13 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 13) (Marked loadings are > 0.5)														
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14	PC 15
1000/Metal Temp (1000 / K)	0.841	-0.068	0.036	0.084	-0.139	0.130	0.122	0.152	0.040	0.102	0.022	-0.076	-0.069	-0.211	-0.229
T _g -T _m (K)	-0.033	0.047	0.064	-0.022	-0.103	-0.007	0.016	-0.971	-0.011	0.004	0.038	-0.035	-0.100	-0.013	0.102
Carbon %	-0.171	-0.407	-0.565	0.070	-0.111	0.101	-0.352	-0.021	0.119	-0.094	-0.048	-0.048	0.458	-0.030	-0.030
Manganese (%)	-0.159	-0.019	-0.012	-0.188	-0.190	-0.164	0.015	-0.037	-0.066	-0.884	0.013	-0.130	-0.071	-0.013	0.001
Phosphorus (%)	-0.111	0.033	-0.983	0.000	0.004	-0.033	0.032	0.035	0.060	0.005	0.010	0.002	0.017	-0.004	0.047
Sulphur (%)	-0.167	0.028	-0.974	0.009	-0.001	0.024	0.050	0.035	0.081	0.014	0.015	0.010	-0.022	-0.018	-0.002
Silicon (%)	-0.089	-0.171	0.023	-0.061	-0.009	-0.921	-0.090	-0.003	-0.154	-0.040	-0.022	0.001	-0.023	-0.017	0.135
Chromium (%)	-0.068	-0.041	-0.027	0.037	-0.206	-0.315	-0.219	-0.102	0.232	0.648	-0.029	-0.415	-0.122	0.186	-0.095
Nickel (%)	0.079	0.000	-0.115	-0.070	-0.115	0.033	0.143	0.014	0.913	0.044	0.032	0.077	-0.030	0.108	0.049
Molybdenum (%)	0.152	0.019	-0.029	0.116	0.358	0.099	0.593	0.033	0.397	-0.422	-0.055	0.226	0.100	-0.044	-0.021
Niobium (%)	0.199	0.019	-0.029	0.885	-0.057	0.104	0.133	0.002	0.112	0.124	-0.023	0.222	0.096	0.167	0.007
Titanium (%)	-0.061	-0.109	0.015	-0.037	0.241	-0.105	-0.889	0.022	-0.096	0.061	0.006	0.212	0.057	-0.061	0.046
Vanadium (%)	0.097	-0.013	-0.002	-0.134	-0.137	0.023	0.142	-0.036	-0.059	-0.004	-0.003	-0.913	0.033	-0.206	0.017
Nitrogen (%)	-0.193	-0.912	0.013	-0.016	0.043	-0.207	-0.100	0.056	-0.075	0.025	0.010	-0.005	0.162	0.053	0.006
Copper (%)	0.236	-0.050	0.022	-0.002	0.906	0.015	-0.159	0.116	0.011	0.110	0.007	0.131	0.033	0.141	0.007
Tungsten (%)	0.064	0.049	0.000	-0.583	-0.227	0.112	0.339	-0.097	0.016	-0.370	-0.018	0.375	0.006	0.392	0.057
Aluminium (%)	-0.224	-0.377	0.169	0.043	0.139	0.308	-0.421	0.019	-0.209	-0.226	0.167	-0.305	-0.212	0.304	0.241
Cobalt (%)	0.273	-0.091	0.023	0.108	0.113	0.004	0.057	0.008	-0.056	0.137	0.010	0.190	0.039	0.881	0.040
Oxygen (%)	0.250	-0.135	-0.023	0.073	0.059	0.006	0.015	0.115	-0.103	0.025	0.066	-0.008	0.910	0.053	0.053
Yttrium (%)	0.088	-0.013	-0.015	-0.014	0.002	0.025	-0.026	-0.036	0.020	-0.015	0.989	0.000	0.049	0.008	-0.022
Iron (%)	-0.137	-0.098	0.073	-0.218	-0.162	-0.147	-0.020	0.001	-0.856	-0.111	0.007	0.055	0.077	0.224	0.146
Na (%)	0.984	0.032	0.042	0.032	0.055	-0.009	0.031	0.033	0.023	0.016	0.005	0.018	0.076	0.075	0.077

Variable	PC Loadings (Varimax normalized) (Data subset 13) (Marked loadings are > 0.5)														
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11	PC 12	PC 13	PC 14	PC 15
K (%)	0.795	0.013	0.068	0.030	-0.009	0.219	0.105	0.196	0.091	0.071	0.041	0.003	-0.062	-0.013	-0.488
Mg (%)	0.979	0.052	0.065	0.022	0.060	0.062	0.038	0.001	0.045	0.023	0.024	0.012	0.019	0.067	-0.121
Ca (%)	0.967	0.059	0.039	0.027	0.071	-0.066	-0.016	0.008	0.029	-0.027	0.000	-0.024	0.083	0.089	-0.065
Al (%)	0.985	0.040	0.039	0.031	0.061	-0.038	0.012	0.027	0.024	-0.001	0.001	0.002	0.085	0.082	0.041
Fe (%)	0.987	0.047	0.056	0.026	0.059	0.028	0.031	0.016	0.038	0.016	0.016	0.009	0.043	0.071	-0.063
Si (%)	0.987	0.054	0.052	0.025	0.066	-0.005	0.014	-0.006	0.034	0.002	0.012	-0.001	0.055	0.078	-0.050
Cl (%)	0.972	0.043	0.035	0.031	0.064	-0.077	0.001	-0.015	0.012	-0.008	-0.003	0.001	0.101	0.082	0.141
S (%)	0.546	0.119	0.018	-0.063	0.348	0.011	-0.152	0.075	-0.016	-0.181	-0.009	0.084	0.097	0.509	-0.394
Ti (%)	-0.947	-0.070	-0.079	-0.014	-0.052	-0.033	-0.035	0.189	-0.028	-0.038	-0.034	-0.018	-0.001	-0.030	-0.098
P (%)	0.863	0.045	0.087	0.014	0.031	0.214	0.089	0.050	0.079	0.065	0.051	0.022	-0.073	0.023	-0.386
Ba (%)	0.987	0.050	0.055	0.027	0.053	0.013	0.025	0.004	0.040	0.012	0.016	-0.003	0.043	0.059	-0.076
Mn (%)	0.573	0.003	0.067	0.022	-0.029	0.289	0.118	0.250	0.106	0.081	0.049	-0.001	-0.112	-0.039	-0.679

Table C-28: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 14). Forced stepwise regression to include PC that have high loading(s) with metal temperature

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model					
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3	PC 4
1	0.84	4	-0.84	0.44	0.02	0.05

Table C-29: Varimax rotated loadings table for data subset 14 (elements in symbols are the fuel elements, and the elements in full are from the metal/alloy)

Variable	PC Loadings (Varimax normalized) (Data subset 14) (Marked loadings are > 0.5)			
	PC 1	PC 2	PC 3	PC 4
1000/Metal Temp (1000/(K))	0.092	0.239	0.373	0.891
Carbon (%)	0.075	0.982	0.158	0.068
Silicon (%)	0.075	0.982	0.158	0.068
Chromium (%)	0.075	0.982	0.158	0.068
Nickel (%)	0.075	0.982	0.158	0.068
Niobium (%)	-0.075	-0.982	-0.158	-0.068
Nitrogen (%)	-0.075	-0.982	-0.158	-0.068
Molybdenum (%)	-0.075	-0.982	-0.158	-0.068
Na (%)	-0.694	-0.330	-0.617	-0.172
K (%)	0.988	0.102	0.110	0.044
Al (%)	-0.967	0.066	0.239	0.048
Si (%)	-0.357	0.378	0.828	0.212
P (%)	0.967	0.144	0.199	0.067
Mg (%)	0.986	-0.029	-0.164	-0.028
Ca (%)	-0.897	-0.221	-0.367	-0.110
Ti (%)	-0.988	0.022	0.150	0.025
Mn (%)	-0.950	-0.168	-0.251	-0.080
Fe (%)	-0.953	-0.163	-0.241	-0.078
Ba (%)	-0.946	0.097	0.301	0.065
Cl (%)	0.753	0.306	0.561	0.159
S (%)	0.205	0.419	0.855	0.228

Table C-30: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 15). Forced stepwise regression to include PC that have high loading(s) with metal temperature

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model				
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3
1	0.88	3	-0.96	0.01	-0.05

Table C-31: Varimax rotated loadings table for data subset 15 (elements in symbols are the fuel elements)

Variable	PC Loadings (Varimax normalized) (Data subset 15) (Marked loadings are > 0.5)		
	PC 1	PC 2	PC 3
1000/Metal Temp (1000/(K))	-0.052	0.411	0.910
Na (%)	0.728	-0.661	-0.182
K (%)	-0.990	0.129	0.051
Al (%)	0.981	0.191	0.031
Si (%)	0.486	0.849	0.208
P (%)	-0.974	0.213	0.072
Mg (%)	-0.993	-0.121	-0.013
Ca (%)	0.917	-0.382	-0.114
Ti (%)	0.994	0.109	0.010
Mn (%)	0.961	-0.264	-0.085
Fe (%)	0.964	-0.255	-0.082
Ba (%)	0.968	0.248	0.046
Cl (%)	-0.787	0.595	0.166
S (%)	-0.161	0.956	0.247

Table C-32: Stepwise regression module highlighting (orange cells) the number of PCs retained for model building (data subset 16)

Subset No.	Summary of best subsets Adjusted R square and standardized regression coefficients for each sub model				
	Adjusted R ²	No. of Effects	PC 1	PC 2	PC 3
1	0.65	1			0.82
2	0.63	2	-0.05		0.82
3	0.63	2		0.02	0.82
4	0.62	3	-0.05	0.02	0.82
5	-0.05	1	-0.05		
6	-0.05	1		0.02	
7	-0.10	2	-0.05	0.02	

Table C-33: Varimax rotated loadings table for data subset 16 (elements in symbols are the fuel elements)

Variable	PC Loadings (Varimax normalized) (Data subset 16) (Marked loadings are > 0.5)		
	PC 1	PC 2	PC 3
1000/Metal Temp (1000/K)	-0.124	0.102	-0.987
Na (%)	0.561	0.824	0.006
K (%)	-0.982	-0.129	-0.097
Al (%)	0.992	-0.066	0.068
Si (%)	0.775	-0.622	0.100
P (%)	-0.967	-0.218	-0.089
Mg (%)	-0.988	0.076	-0.109
Ca (%)	0.888	0.451	0.057
Ti (%)	0.994	0.013	0.061
Mn (%)	0.928	0.370	0.047
Fe (%)	0.935	0.350	0.051
Ba (%)	0.987	-0.117	0.073
Cl (%)	-0.439	-0.884	0.064
S (%)	0.409	-0.905	0.109

C.2 PLS Variable Selection Criteria: Variable Importance in Projection (VIP)

To recap, the VIP selection criteria for PLS models is given by equation C-1 ((Farres *et al.*, 2015); i.e.:

$$VIP_j = \sqrt{J \cdot \left(\frac{\sum_{f=1}^F w^2 \cdot SSY_f}{SSY_{total}} \right)} \quad \text{C-1}$$

Where;

J = total number of predictor (X) variables

w^2 = the importance of the j_{th} variable in each extracted f^{th} (PLS) component

SSY_f = sum of squares of explained variance for each f^{th} component

SSY_{total} = total sum of explained variance of the f^{th} component (Farres *et al.*, 2015).

The criterion for variable selection to build the PLS model is for the predictor variables to have a VIP score ≥ 0.8 (except for rare instances where the metal temperature input parameter was excluded for model building). The VIP scores presented in the following tables are for the framework model F (results discussed in chapter 4).

Table C-34: VIP scores calculated for the predictor variables for data subsets 1B-16B (B indicates PLS models; shaded cells indicate the variables not present in the data subset; red text indicate variables with VIP score > 0.8 threshold)

VAR	1B	2B	3B	4B	5B	6B	7B	8B*	9B	10B	11B	12B	13B	14B**	15B***	16B
1000/T _m	1.42	2.41	2.01	3.47	1.04	1.04	1.54	0.29	3.44	1.03	1.44	1.39	1.31	0.37	0.27	3.56
(T _g -T _m)	0.96	1.42	2.06	1.30	2.03	0.43		0.35		1.08	0.85	1.87	0.20			
ALLOY ELEMENTS																
C	1.24	1.23	0.62	0.34	0.66	0.57	0.57	1.11	0.43	1.60	0.75	0.15	0.51	0.41	-	-
Mn	0.49	0.55	0.62	0.34	0.096	0.50	0.51	1.23		1.02	0.59	0.45	0.74	-	-	-
P	0.49	0.55	0.62	0.34	0.79	0.49	1.34	1.77	0.52	1.89	1.07	0.15	0.19			
S	0.49	0.55	0.62	0.34	0.56	0.49	1.33	1.70	0.52	1.90	0.54	0.15	0.22			
Si	1.06	0.77	0.62	0.34	0.77	1.04	0.67	0.68	0.86	1.24	0.53	0.96	1.04	0.41	-	-
Cr	1.01	0.97	0.62	0.34	0.36	1.17	1.26	1.15	0.65	0.86	0.19	0.38	0.25	0.41	-	-
Ni	0.68	0.92	0.62	0.34	0.30	Base	1.21	0.45	0.19	0.74	Base	1.14	1.01	0.41	-	
Mo	1.37	0.88	0.62	0.34	0.84	1.00	0.75	1.65	0.27	1.12	0.45	0.19	0.32	0.41	-	-
Nb	-	-			0.58	1.30	0.83	0.58		0.54	0.86		0.41	0.41	-	
Ti	0.48	0.40			0.35	0.89	0.76	0.12		0.93	0.76		1.45			
V	0.49	0.55			0.77	ND	0.65	1.65		1.38		0.15	1.54			
Cu			0.62	0.34	0.78	0.57	0.26	0.71	0.52	0.78		0.67	1.98			
N					0.34	ND	1.14	0.65		1.51	0.14		0.72	0.41	-	
Ce					0.37	ND	0.58	ND								
Ta					0.73	ND	1.78	ND								
Al					0.65	0.27	1.16	0.64	0.30	0.57	0.65		0.57			
W					0.65	1.08	0.59	0.63	0.53	0.60			0.70			
B					0.63	0.85	0.58	0.29		0.79	0.04		-			
Co					0.56	0.50		0.63	0.52	0.57	1.34		2.02			

VAR	1B	2B	3B	4B	5B	6B	7B	8B*	9B	10B	11B	12B	13B	14B**	15B***	16B
Fe	Base	Base	Base	Base	Base	0.77	1.05	Base	0.52	Base	1.34	Base	0.60	Base	NA	NA
(Nb + Ta)									0.58							
O									0.35				0.84			
Y									0.28				0.14			
FUEL ELEMENTS																
Na	0.95	0.75	0.94	0.26	0.99	0.95	0.27	-	-	0.45	1.00	0.02	0.84	1.17	0.99	0.23
K	0.65	0.91	0.90	0.38	1.28	0.76	0.20	-	-	1.03	1.35	2.36	0.93	1.41	1.17	0.36
Mg	0.48	0.69	0.57	1.05	0.94	0.97	0.25	-	-	0.47	1.28	0.48	0.76	1.32	1.12	0.37
Ca	0.86	0.78	0.61	0.80	0.99	1.26	0.40	-	-	0.93	1.30	0.46	0.96	1.37	1.14	0.30
Al	0.60	0.88	1.04	0.54	0.79	0.39	1.74	-	-	0.46	0.99	0.19	0.89	1.27	1.09	0.28
Fe	0.63	0.91	1.17	0.95	1.99	1.30	1.04	-	-	0.49	0.90	0.24	0.79	1.41	1.17	0.30
Si	0.52	1.00	1.06	0.63	1.27	0.63	0.95	-	-	0.43	1.02	0.10	0.84	0.28	0.37	0.26
Cl	2.42	0.90	0.98	0.63	1.08	0.95	0.83	-	-	0.54	1.12	0.57	0.96	1.24	1.04	0.41
S	1.54	1.09	1.42	1.10	0.94	0.50	0.37	-	-	1.25	0.57	0.15	2.18	0.59	0.40	0.32
Ti	0.51	1.05	0.58	1.04	1.37	0.64	0.78	-	-	0.59	1.36	0.71	0.73	1.32	1.12	0.29
P					2.13	2.92	2.08	-	-	0.99	1.43	2.01	0.84	1.41	1.17	0.35
Mn					1.32	1.12	0.76	-	-	0.99	1.40	2.32	1.13	1.40	1.17	0.30
Ba										0.48	1.23	0.12	0.79	1.22	1.06	0.28

VAR – Predictor variables (except metal temperature) in natural log

1000/T_m - Metal temperature in 1000/K

(T_a-T_m) – The temperature difference in natural log (K)

(-) – Not analysed

* VIP Criteria was reduced to 0.2 in order to include metal temperature for model building

** VIP Criteria was reduced to 0.3 in order to include metal temperature for model building

*** VIP Criteria was reduced to 0.2 in order to include metal temperature for model building

Appendix D Framework Model A-E Results

This section presents the results for the other framework models A-E defined in chapter 4, section 4.2.1 (i.e. equations 4-2 to 4-6), including the number of PCs and PLS components used to build the corrosion models. Framework model A includes all data subsets and was built without any transformation of the predictor variables. Framework model B was also built without transforming the predictor variables although the temperature difference variable replaces the gas temperature input variable which is present in framework model A. Framework models B, C, and D, however, were mainly attempted for data subsets where the model performances were poor.

D.1 Number of PCs and PLS Components used for Model Building (Framework Models A-F)

The number of principal components (PCs) and PLS components selected and used for model building across all data subsets are presented in Table D-1 and Table D-2.

Table D-1: Number of principal components used for model building (i.e. PCA corrosion framework models A-F; shaded cells were not analysed)

PCA MODELS					Model A	Model B	Model C	Model D	Model E	Model F
	REGION	FUEL	MATERIAL	TUBE POSITION	Number of Principal Components					
Data 1A	UK	Coal	Austenitic	Leading	8	8	7	7	7	7
Data 2A	UK	Coal	Austenitic	Non-leading	7	6				8
Data 3A	UK	Coal	Ferritic	Leading	6		5	5		5
Data 4A	UK	Coal	Ferritic	Non-leading	4					2
Data 5A	US	Coal	Austenitic		11	10			10	11
Data 6A	US	Coal	Ni based		9		9	8		10
Data 7A	US	Coal	Coatings		12					11
Data 8A	UK	Coal (Europe)	Austenitic		5					4
Data 9A	UK	Coal	Coatings		4					4
Data 10A	UK	Biomass	Austenitic		9	10			8	9
Data 11A	UK	Biomass	Ni based		3					3
Data 12A	UK	Biomass	Ferritic		3					4
Data 13A	UK	Biomass	Coatings		11					14
Data 14A	UK	Coal/Biomass	Austenitic		4					2
Data 15A	UK	Coal/Biomass	TP316		3					2
Data 16A	UK	Coal/Biomass	Ferritic		1					1

Table D-2: Number of PLS components used for model building (i.e. PLS corrosion framework models A-F; shaded cells were not analysed)

PLS MODELS					Model A	Model B	Model C	Model D	Model E	Model F
	REGION	FUEL	MATERIAL	TUBE POSITION	Number of PLS Components					
Data 1B	UK	Coal	Austenitic	Leading	3	3	4	6	4	6
Data 2B	UK	Coal	Austenitic	Non-leading	4	3				6
Data 3B	UK	Coal	Ferritic	Leading	4		2	4		4
Data 4B	UK	Coal	Ferritic	Non-leading	3		3	3		5
Data 5B	US	Coal	Austenitic		1	1		4	4	4
Data 6B	US	Coal	Ni based		1		1	1		6
Data 7B	US	Coal	Coatings		4					5
Data 8B	UK	Coal (Europe)	Austenitic		2					2
Data 9B	UK	Coal	Coatings		2					4
Data 10B	UK	Biomass	Austenitic		6	6			8	8
Data 11B	UK	Biomass	Ni based		1					1
Data 12B	UK	Biomass	Ferritic		1					2
Data 13B	UK	Biomass	Coatings		6					3
Data 14B	UK	Coal/Biomass	Austenitic		4					4
Data 15B	UK	Coal/Biomass	TP316		3					1
Data 16B	UK	Coal/Biomass	Ferritic		4					2

D.2 Variables Selected across Framework Models A-E

The variables selected for model building for framework models A-E are presented for PCA and PLS corrosion models.

D.2.1 Framework Model A (PCA, PLS)

The framework model A is presented in equation D-1 and the variables for model building in Table D-3 and Table D-4.

Framework model A

$$\ln \text{corr rate} = \ln A + B.1000/T_m + c.T_g + d.M_{(\text{alloy})} + e.N_{(\text{fuel})} \quad \text{D-1}$$

Where;

$\ln \text{corr rate}$ = fireside corrosion rate (microns/1000 hrs or μ_m/khr)

$1000/T_m$ = 1000 / metal temperature (1000/K)

T_g = gas temperature (K)

$M_{(\text{alloy})}$ = alloy elements selected for model building

$N_{(\text{fuel})}$ = fuel elements selected for model building

Table D-3: PCA framework model A: Estimated standardised regression coefficients for the predictor variables in PCA models 1A-16A for framework A. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant.

VAR	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A
1000/T _m	-0.12	-0.34	-0.29	-0.34	0.14	-0.11	0.30	0.035	-0.10	0.065	0.084	-0.049	-0.13	0.015	0.097	-0.80
T _{gas}	0.14	NS	0.35	0.17	0.38	0.18	ND	NA	ND	-0.20	-0.083	0.078	-0.024	ND	ND	ND
C	-0.078	-0.12	-0.0072	NS	0.073	0.029	0.15	0.10	0.084	-0.29	-0.021	NS	-0.25	0.013	NA	NA
Mn	-0.0015	NS	-0.0072	NS	-0.026	0.038	NS	0.19	-0.014	0.059	0.033	0.038	-0.16	NA	NA	NA
P	0.0015	NS	-0.0072	NS	0.073	-0.0003	0.081	-0.099	-0.014	-0.046	NS	NS	0.040	ND	ND	ND
S	0.0015	NS	-0.0072	NS	0.20	-0.0003	0.22	0.025	-0.014	0.080	NS	NS	0.11	ND	ND	ND
Si	-0.093	-0.032	-0.0072	NS	-0.13	-0.052	0.055	-0.018	NS	0.022	-0.050	-0.046	0.25	0.013	NA	NA
Cr	-0.060	-0.082	0.0072	NS	-0.053	-0.032	-0.088	-0.077	NS	-0.16	NS	0.044	NS	0.013	NA	NA
Ni	-0.045	-0.12	0.0072	NS	NS	Base	-0.098	0.0039	NS	-0.10	Base	0.034	0.11	0.013	NA	ND
Mo	0.093	-0.069	0.0072	NS	NS	-0.039	-0.042	0.23	NS	0.17	0.034	0.017	0.11	-0.013	NA	NA
Nb	-0.10	0.16	ND	ND	0.026	0.0026	-0.093	-0.092	ND	-0.11	-0.064	ND	NS	0.013	NA	ND
Ti	0.066	-0.0073	ND	ND	NS	-0.0085	-0.040	0.037	ND	0.33	-0.084	ND	-0.14	ND	ND	ND
V	-0.0015	NS	ND	ND	0.19	ND	-0.076	0.23	ND	0.10	NS	NS	0.017	ND	ND	ND
Cu	ND	ND	0.0072	NS	0.14	-0.098	-0.097	0.12	-0.014	-0.0079	ND	-0.020	-0.33	ND	ND	ND
N	ND	ND	ND	ND	0.17	ND	-0.052	0.017	ND	-0.11	NS	ND	-0.055	0.013		ND
Ce	ND	ND	ND	ND	NS	ND	-0.028	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ta	ND	ND	ND	ND	NS	ND	0.24		ND	ND	ND	ND	ND	ND	ND	ND
Al	ND	ND	ND	ND	NS	-0.041	0.33	0.055	NS	0.023	-0.081	ND	0.066	ND	ND	ND
W	ND	ND	ND	ND	NS	0.0089	-0.026	0.042	-0.12	0.042	ND	ND	0.16	ND	ND	ND
B	ND	ND	ND	ND	NS	-0.048	-0.11	0.080	ND	NS	-0.017	ND		ND	ND	ND
Co	ND	ND	ND	ND	0.025	-0.022	ND	0.042	-0.014	0.023	-0.096	ND	-0.15	ND	ND	ND

VAR	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A
Fe	Base	Base	Base	Base	Base	0.084	0.063	Base	NS	Base	0.074	Base	-0.14	Base	Base	Base
(Nb + Ta)	ND	ND	ND	ND	ND	ND	ND	ND	0.033	ND	ND	ND	ND	ND	ND	ND
O	ND	ND	ND	ND	ND	ND	ND	ND	0.066	ND	ND	ND	0.051	ND	ND	ND
Y	ND	ND	ND	ND	ND	ND	ND	ND	NS	ND	ND	ND	-0.034	ND	ND	ND
FUEL ELEMENTS																
Na	0.12	-0.0026	NS	NS	-0.024	-0.0033	0.040	NA	NA	0.049	0.042	NS	0.041	-0.080	-0.010	NS
K	0.040	-0.042	NS	0.013	0.047	-0.036	0.044	NA	NA	0.053	0.090	-0.12	-0.050	0.10	0.11	NS
Mg	-0.059	-0.049	NS	NS	-0.052	0.030	-0.038	NA	NA	-0.082	0.053	-0.036	-0.0038	0.097	0.11	NS
Ca	-0.080	-0.019	NS	NS	0.12	0.083	0.015	NA	NA	0.11	0.052	NS	0.040	-0.097	-0.11	NS
Al	-0.013	0.016	NS	0.013	0.10	0.021	0.11	NA	NA	0.077	0.042	NS	0.049	-0.10	-0.11	NS
Fe	0.057	-0.0080	0.092	0.095	0.36	0.14	0.22	NA	NA	-0.081	0.040	NS	0.0033	-0.10	-0.11	NS
Si	0.039	-0.039	NS	0.040	0.10	-0.019	0.040	NA	NA	-0.026	0.042	NS	0.019	-0.029	-0.036	NS
Cl	0.27	0.0070	NS	0.024	0.16	-0.020	0.11	NA	NA	0.15	0.044	NS	0.075	0.081	0.10	NS
S	-0.18	-0.043	0.11	-0.015	0.044	-0.040	-0.029	NA	NA	-0.11	-0.062	NS	0.088	0.027	0.036	NS
Ti	0.056	0.033	-0.027	0.035	0.10	-0.0075	0.074	NA	NA	0.044	-0.077	NS	-0.0067	-0.10	-0.11	NS
P	ND	ND	ND	ND	0.13	0.17	0.061	NA	NA	-0.23	0.070	-0.11	-0.049	0.10	0.11	NS
Mn	ND	ND	ND	ND	0.11	0.060	0.067	NA	NA	-0.13	-0.090	-0.12	-0.072	-0.10	-0.12	NS
Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND	-0.063	0.046	NS	0.0035	-0.099	-0.11	NS

VAR – Predictor variables

1000/T_m – 1000/Metal temperature, 1000/K

T_{gas} – Gas temperature in K

Yellow cells – most influential variable (highest standardised regression coefficient)

Orange cells – positively correlated with the corrosion rate

Blue cells – negatively correlated with the corrosion rate

NS – Not selected for model building (grey cells)

NA – Not analysed but present in the data subset (grey cells)

ND – Not present in data subset (white cells)

Base – Base metal

Table D-4: PLS framework model A: Estimated standardised regression coefficients for the predictor variables in PLS models 1B-16B for framework A. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant.

VAR	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13B	14B	15B	16B
1000/T _m	-0.16	-0.28	-0.31	-0.33	0.12	-0.057	0.24	0.0065	-0.92	0.16	0.076	-0.056	-0.40	NS		-0.89
T _{gas}	0.15	0.20	0.38	0.13	0.24	0.14	ND	NA	ND	-0.20	-0.077	0.077	NS	ND	ND	ND
ALLOY ELEMENTS																
C	-0.082	-0.10	NS	NS	NS	NS	0.16	0.11	NS	-0.35	NS	NS	-0.26	NS	NA	NA
Mn	NS	NS	NS	NS	NS	NS	NS	0.16	NA	0.17	NS	NS	0.0041	NA	NA	NA
P	NS	NS	NS	NS	NS	NS	0.062	-0.083	NS	NS	NS	NS	NS	ND	ND	ND
S	NS	NS	NS	NS	0.096	NS	0.27	0.051	NS	0.17	NS	NS	-0.21	ND	ND	ND
Si	-0.086	-0.050	NS	NS	NS	NS	0.072	-0.018		NS	NS	-0.054	0.19	NS	NA	NA
Cr	-0.068	-0.074	NS	NS	NS	-0.073	-0.081	-0.10	NS	-0.013	NS	NS	NS	NS	NA	NA
Ni	NS	-0.084	NS	NS	NS	Base	-0.080	-0.0007	NS	NS	Base	0.050	0.21	NS	NA	ND
Mo	0.088	0.011	NS	NS	0.12	NS	NS	0.18	NS	0.0015	NS	NS	NS	NS	NA	NA
Nb	NA	NA	ND	ND	NS	NS	NS	0.020	ND	-0.23	-0.050	ND	-0.31	NS	NA	ND
Ti	NS	NS	ND	ND	NS	NS	NS	NS	ND	0.32	-0.063	ND	-0.092	ND	ND	ND
V	NS	NS	ND	ND	0.089	ND	NS	0.18	ND	0.15	ND	NS	NS	ND	ND	ND
Cu	ND	ND	NS	NS	NS	-0.075	-0.11	0.061	NS	NS	ND	NS	-0.30	ND	ND	ND
N	ND	ND	ND	ND	0.083	ND	NS	-0.040	ND	-0.16	NS	ND	NS	NS	NA	ND
Ce	ND	ND	ND	ND	NS	ND	NS	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ta	ND	ND	ND	ND	NS	ND	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND
Al	ND	ND	ND	ND	-0.091	NS	0.31	0.070	NS	NS	-0.065	ND	NS	ND	ND	ND
W	ND	ND	ND	ND	NS	0.047	NS	0.065	NS	NS	ND	ND	-0.022	ND	ND	ND
B	ND	ND	ND	ND	NS	NS	NS	0.023	ND	NS	NS	ND	NA	ND	ND	ND
Co	ND	ND	ND	ND	NS	NS	NS	0.065	NS	NS	-0.072	ND	-0.085	ND	ND	ND
Fe	Base	Base	Base	Base	Base	0.071	0.048	Base	NS	Base	0.067	Base	-0.20	Base	NA	NA

VAR	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13B	14B	15B	16B
(Nb + Ta)	ND	ND	ND	ND	ND	ND	ND	ND	NS	ND	ND	ND	ND	ND	ND	ND
O	ND	ND	ND	ND	ND	ND	ND	ND	NS	ND	ND	ND	0.050	ND	ND	ND
Y	ND	ND	ND	ND	ND	ND	ND	ND	NS	ND	ND	ND	NS	ND	ND	ND
FUEL ELEMENTS																
Na	0.089	NS	NS	NS	NS	NS	0.046	NA	NA	NS	0.058	NS	NS	-0.087	-0.010	-1.9
K	NS	-0.024	0.054	NS	0.10	NS	NS	NA	NA	0.055	0.073	-0.11	NS	0.095	0.11	NS
Mg	NS	NS	NS	0.022	NS	NS	NS	NA	NA	NS	0.064	-0.040	NS	0.086	0.11	NS
Ca	-0.11	NS	NS	NS	NS	0.062	NS	NA	NA	0.14	0.064	NS	0.32	-0.099	-0.11	NS
Al	NS	0.044	-0.094	NS	0.11	NS	0.12	NA	NA	NS	0.058	NS	0.15	-0.093	-0.11	NS
Fe	NS	NS	0.065	0.052	0.26	0.10	0.27	NA	NA	NS	0.056	-0.039	NS	-0.10	-0.11	NS
Si	NS	NS	0.16	NS	0.14	NS	NS	NA	NA	NS	0.058	NS	NS	NS	NS	NS
Cl	0.30	NS	-0.057	NS	NS	-0.053	0.13	NA	NA	0.17	0.059	0.048	0.29	0.088	0.10	-1.9
S	-0.17	-0.034	0.16	-0.033	0.11	NS	NS	NA	NA	-0.11	NS	NS	0.60	0.041	NS	NS
Ti	NS	0.080	NS	0.057	0.17	NS	0.085	NA	NA	NS	-0.076	NS	0.39	-0.097	-0.11	NS
P	ND	ND	ND	ND	0.15	0.13	0.079	NA	NA	-0.30	0.074	-0.10	-0.23	0.096	0.11	NS
Mn	ND	ND	ND	ND	-0.081	0.046	0.083	NA	NA	NS	-0.074	-0.11	0.0079	-0.10	-0.12	NS
Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND	NS	0.061	NS	NS	-0.089	-0.11	NS

VAR – Predictor variables

$1000/T_m$ – 1000/Metal temperature, 1000/K

T_{gas} – Gas temperature in K

Yellow cells – most influential variable (highest standardised regression coefficient)

Orange cells – positively correlated with the corrosion rate

Blue cells – negatively correlated with the corrosion rate

NS – Not selected for model building (grey cells)

NA – Not analysed but present in the data subset (grey cells)

ND – Not present in data subset (white cells)

Base – Base metal

D.2.2 Framework Model B (PCA, PLS)

The framework model *B* is presented in equation D-2 and the variables selected after analysis in Table D-5 and Table D-6. Only data subsets analysed using this framework are presented.

Framework model B

$$\ln \text{corr rate} = \ln A + \frac{B}{T_m} + c. (T_g - T_m) + d. M_{(\text{alloy})} + e. N_{(\text{fuel})} \quad \text{D-2}$$

Where;

$\ln \text{corr rate}$ = fireside corrosion rate (microns/1000 hrs or μ_m/KHR)

T_m = 1000 / metal temperature (1000/K)

$T_g - T_m$ = Temperature difference (K)

$M_{(\text{alloy})}$ = alloy elements selected for model building

$N_{(\text{fuel})}$ = fuel elements selected for model building

Table D-5: PCA framework model B: Estimated standardised regression coefficients for the predictor variables in PCA models 1A, 5A and 10A for framework B. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant

VAR	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A
1000/T _m	-0.13				0.070					0.077						
(T _g -T _m)	0.13				0.32					-0.17						
ALLOY EL ELEMENTS																
C	-0.075				0.088					-0.29						
Mn	-0.0001				0.0009					0.077						
P	0.0001				0.078					-0.058						
S	0.0001				0.20					0.053						
Si	-0.095				-0.11					0.020						
Cr	-0.058				0.029					-0.18						
Ni	-0.040				0.025					-0.12						
Mo	0.010				NS					0.18						
Nb	-0.12				0.026					-0.13						
Ti	0.069				-0.035					0.35						
V	-0.0001				0.19					0.12						
Cu	ND				0.17					-0.0019						
N	ND				NS					-0.11						
Ce	ND				-0.083					ND						
Ta	ND				NS					ND						
Al	ND				-0.083					0.020						
W	ND				NS					0.039						
B	ND				NS					-0.16						

VAR	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A
Co	ND				NS					0.020						
Fe	Base				Base					Base						
(Nb + Ta)	ND				ND					ND						
O	ND				ND					ND						
Y	ND				ND					ND						
FUEL ELEMENTS																
Na	0.12				-0.0059					0.050						
K	0.038				0.044					0.087						
Mg	-0.057				-0.031					-0.058						
Ca	-0.081				0.10					0.12						
Al	-0.011				0.11					0.077						
Fe	0.058				0.35					-0.063						
Si	0.038				0.092					-0.014						
Cl	0.27				0.15					0.14						
S	-0.18				0.028					-0.12						
Ti	0.057				0.12					0.036						
P	ND				0.16					-0.19						
Mn	ND				0.067					-0.072						
Ba	ND				ND					-0.045						

VAR – Predictor variables

1000/T_m - Metal temperature, 1000/K

(T_g-T_m) – The temperature difference in K

Yellow cells – most influential variable (highest standardised regression coefficient)

Orange cells – positively correlated with the corrosion rate

Blue cells – negatively correlated with the corrosion rate

Blank cells – data subsets not analysed with this framework

NS – Not selected for model building (grey cells)

NA – Not analysed but present in the data subset (grey cells)

ND – Not present in data subset (white cells)

Base – Base metal

Table D-6: PLS framework model B: Estimated standardised regression coefficients for the predictor variables in PLS models 1B, 2B, 5B and 10B for framework B. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant

VAR	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13B	14B	15B	16B
1000/T _m	-0.17	-0.24			0.12					0.25						
(T _g -T _m)	0.14	0.14			0.24					-0.0074						
ALLOY ELEMENTS																
C	-0.080	-0.10			NS					-0.37						
Mn	NS	NS			NS					0.16						
P	NS	NS			NS					NS						
S	NS	NS			0.095					0.19						
Si	-0.085	-0.049			NS					-0.0054						
Cr	-0.066	-0.076			NS					-0.0074						
Ni	NS	-0.085			NS					-0.027						
Mo	0.091	0.010			0.12					0.0013						
Nb	NA	NA			NS					-0.22						
Ti	NS	NS			NS					0.31						
V	NS	NS			0.088					0.15						
Cu	ND	ND			NS					NS						
N	ND	ND			0.083					-0.17						
Ce	ND	ND			NS					ND						
Ta	ND	ND			NS					ND						
Al	ND	ND			-0.091					NS						
W	ND	ND			NS					NS						
B	ND	ND			NS					NS						

VAR	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13B	14B	15B	16B
Co	ND	ND	ND	ND	NS					NS						
Fe	Base	Base	Base	Base	Base					Base						
(Nb + Ta)	ND	ND	ND	ND	ND					ND						
O	ND	ND	ND	ND	ND					ND						
Y	ND	ND	ND	ND	ND					ND						
FUEL ELEMENTS																
Na	0.088	NS			NS					NS						
K	NS	-0.020			0.10					0.096						
Mg	NS	NS			NS					NS						
Ca	-0.11	-0.055			NS					0.16						
Al	NS	0.054			0.11					NS						
Fe	NS	0.082			0.26					NS						
Si	NS	NS			0.14					NS						
Cl	0.30	NS			NS					0.19						
S	-0.18	-0.073			0.11					-0.16						
Ti	NS	0.098			0.17					NS						
P	ND	ND			0.15					-0.32						
Mn	ND	ND			-0.081					NS						
Ba	ND	ND			ND					NS						

VAR – Predictor variables

1000/T_m – Metal temperature, 1000/K

(T_g-T_m) – The temperature difference in K

Yellow cells – most influential variable (highest standardised regression coefficient)

Orange cells – positively correlated with the corrosion rate

Blue cells – negatively correlated with the corrosion rate

Blank cells – data subsets not analysed with this framework

NS – Not selected for model building (grey cells)

NA – Not analysed but present in the data subset (grey cells)

ND – Not present in data subset (white cells)

Base – Base metal

D.2.3 Framework Models C and D (PCA, PLS)

The framework models *C* and *D* are presented in equations D-3 and D-4. The variables selected after analysis are presented in Table D-7 and Table D-8. Only data subsets analysed using this framework are presented. These models were only used for the data subsets where the PCA/PLS model performances were poor.

Framework model C

$$\ln \text{corr rate} = \ln A + b. \ln T_m + c. \ln T_g + d. \ln M_{(\text{alloy})} + e. \ln N_{(\text{fuel})} \quad \text{D-3}$$

Framework model D

$$\begin{aligned} \ln \text{corr rate} = \ln A + b. \ln T_m + c. \ln (T_g - T_m) + d. \ln M_{(\text{alloy})} \\ + e. \ln N_{(\text{fuel})} \end{aligned} \quad \text{D-4}$$

Where;

$\ln \text{corr rate}$ = fireside corrosion rate (microns/1000 hrs or μ_m/hr)

$\ln. T_m$ = metal temperature in natural log form

$\ln. T_g$ = gas temperature in natural log form

$\ln. (T_g - T_m)$ = temperature difference in natural log form

$\ln. M_{(\text{alloy})}$ = alloy elements in natural log form selected for model building

$\ln. N_{(\text{fuel})}$ = fuel elements in natural log form selected for model building

Table D-7: PCA framework models C (LHS) and D (RHS): Estimated standardised regression coefficients for the predictor variables in PCA models 1A, 3A and 6A. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant

VAR	1A		3A		6A				1A		3A		6A
1000/T _m	0.18		0.28		0.095				0.20		0.37		NS
T _{gas}	0.13		0.36		0.20			(T _g -T _m)	0.095		0.38		NS
ALLOY EL ELEMENTS													
C	-0.087		-0.0079		0.081				-0.087		-0.0098		0.067
Mn	-0.0085		-0.0079		0.026				-0.0088		-0.0098		0.013
P	0.0085		-0.0079		0.0050				0.0088		-0.0098		0.022
S	-0.0085		-0.0079		0.0050				-0.0088		-0.0098		0.022
Si	-0.092		-0.0079		-0.045				-0.093		-0.0098		-0.063
Cr	-0.047		0.0079		-0.025				-0.048		0.0098		-0.044
Ni	-0.020		-0.0079		Base				-0.017		-0.0098		Base
Mo	0.11		0.0079		-0.066				0.12		0.0098		-0.088
Nb	NA		ND		-0.088				NA		ND		-0.098
Ti	-0.077		ND		-0.067				-0.068		ND		-0.067
V	0.0085		ND		ND				0.0088		ND		ND
Cu	ND		-0.0079		0.0071				ND		-0.0098		0.011
N	ND		ND		ND				ND		ND		ND
Ce	ND		ND		ND				ND		ND		ND
Ta	ND		ND		ND				ND		ND		ND
Al	ND		ND		0.024				ND		ND		0.039
W	ND		ND		0.068				ND		ND		0.084
B	ND		ND		0.076				ND		ND		0.11

VAR	1A		3A		6A			1A		3A		6A
Co	ND		ND		-0.051			ND		ND		-0.040
Fe	Base		Base		-0.031			Base		Base		-0.059
(Nb + Ta)	ND		ND		ND			ND		ND		ND
O	ND		ND		ND			ND		ND		ND
Y	ND		ND		ND			ND		ND		ND
FUEL ELEMENTS												
Na	0.13		0.057		0.030			0.12		0.057		0.034
K	0.037		0.054		-0.0003			0.041		0.051		0.0070
Mg	-0.055		-0.023		0.049			NS		-0.016		0.064
Ca	-0.099		-0.049		0.088			NS		-0.046		0.12
Al	0.0090		-0.079		-0.0080			0.022		NS		-0.029
Fe	0.066		0.071		NS			0.084		0.057		NS
Si	NS		0.041		NS			0.021		NS		NS
Cl	0.30		0.072		0.041			0.29		0.073		0.024
S	-0.22		0.087		NS			-0.23		0.10		NS
Ti	NS		NS		NS			0.044		-0.031		NS
P	ND		ND		-0.21			ND		ND		-0.33
Mn	ND		ND		0.039			ND		ND		0.056
Ba	ND		ND		ND			ND		ND		ND

VAR – Predictor variables in natural log

T_{metal} – Metal temperature in natural log

T_g – Gas temperature in natural log; (T_g-T_m) – The temperature difference in natural log

Yellow cells – most influential variable (highest standardised regression coefficient)

Orange cells – positively correlated with the corrosion rate

Blue cells – negatively correlated with the corrosion rate

Blank cells – data subsets not analysed with this framework

NS – Not selected for model building (grey cells)

NA – Not analysed but present in the data subset (grey cells)

ND – Not present in data subset (white cells)

Base – Base metal

Table D-8: PLS framework models C (LHS) and D (RHS): Estimated standardised regression coefficients for the predictor variables in PLS models 1B, 3B and 6B. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant

VAR	1B		3B	4B	6B				1B		3B	5B	6B
1000/T _m	0.20		0.15	0.31	0.046				0.30		0.15	-0.085	0.049
T _{gas}	0.16		0.20	0.13	0.12			(T _g -T _m)	0.12		0.16	0.37	NS
ALLOY EL ELEMENTS													
C	-0.10		NS	NS	NS				-0.099		NS	NS	NS
Mn	NS		NS	NS	NS				NS		NS	NS	NS
P	NS		NS	NS	NS				NS		NS	NS	NS
S	NS		NS	NS	NS				NS		NS	NS	NS
Si	-0.079		NS	NS	-0.049				-0.075		NS	NS	-0.052
Cr	-0.057		NS	NS	-0.061				-0.059		NS	NS	-0.066
Ni	NS		NS	NS	Base				NS		NS	NS	Base
Mo	0.092		NS	NS	NS				0.062		NS	0.13	-0.038
Nb	NA		ND	ND	-0.067				NA		ND	NS	-0.072
Ti	NS		ND	ND	-0.044				NS		ND	NS	-0.047
V	NS		ND	ND	ND				NS		ND	NS	ND
Cu	ND		NS	NS	NS				ND		NS	NS	NS
N	ND		ND	ND	ND				ND		ND	NS	ND
Ce	ND		ND	ND	ND				ND		ND	NS	ND
Ta	ND		ND	ND	ND				ND		ND	NS	ND
Al	ND		ND	ND	NS				ND		ND	NS	NS
W	ND		ND	ND	0.054				ND		ND	NS	0.058
B	ND		ND	ND	NS				ND		ND	NS	NS

VAR	1B		3B	4B	6B			1B		3B	5B	6B
Co	ND		ND		NS			ND		ND	NS	NS
Fe	Base		Base		NS			Base		Base	Base	NS
(Nb + Ta)	ND		ND		ND			ND		ND	ND	ND
O	ND		ND		ND			ND		ND	ND	ND
Y	ND		ND		ND			ND		ND	ND	ND
FUEL ELEMENTS												
Na	0.10		0.074	NS	0.049			0.065		0.075	0.11	0.052
K	NS		0.070	NS	NS			NS		0.070	0.072	0.036
Mg	NS		NS	0.019	0.050			NS		NS	0.025	0.054
Ca	-0.12		NS	NS	0.063			-0.13		NS	0.13	0.068
Al	NS		-0.095	NS	NS			NS		-0.097	NS	NS
Fe	NS		0.12	0.041	0.064			NS		0.12	0.30	0.069
Si	NS		0.10	NS	NS			NS		0.10	0.070	NS
Cl	0.35		0.075	NS	NS			0.42		0.077	0.20	0.037
S	-0.15		0.15	-0.038	NS			-0.11		0.15	-0.0079	NS
Ti	NS		NS	0.058	NS			NS		NS	0.062	NS
P	ND		ND	ND	-0.10			ND		ND	-0.40	-0.11
Mn	ND		ND	ND	NS			ND		ND	0.34	NS
Ba	ND		ND	ND	ND			ND		ND		ND

VAR – Predictor variables in natural log

T_{metal} - Metal temperature in natural log

T_g – Gas temperature in natural log; (T_g-T_m) – The temperature difference in natural log

Yellow cells – most influential variable (highest standardised regression coefficient)

Orange cells – positively correlated with the corrosion rate

Blue cells – negatively correlated with the corrosion rate

Blank cells – data subsets not analysed with this framework

NS – Not selected for model building (grey cells)

NA – Not analysed but present in the data subset (grey cells)

ND – Not present in data subset (white cells)

Base – Base metal

D.2.4 Framework Model E (PCA, PLS)

The framework model *E* is presented in equation D-5. The variables selected after analysis are presented in Table D-9 and Table D-10. Only data subsets analysed using this framework are presented; i.e. UK coal data (austenitic tubes leading position, data subset 1), US coal data subset 5 (austenitic tubes), and woody biomass data subset 10 (austenitic tubes).

Framework Model E

$$\ln \text{corr rate} = \ln A + \frac{B}{T_m} + c. \ln T_g + d. \ln M_{(\text{alloy})} + e. \ln N_{(\text{fuel})} \quad \text{D-5}$$

Where;

$\ln \text{corr rate}$ = fireside corrosion rate (microns/1000 hrs or $\mu\text{m}/\text{khr}$)

$1000/T_m$ = 1000 / metal temperature (1000/K)

$\ln T_g$ = gas temperature in natural log form

$\ln M_{(\text{alloy})}$ = alloy elements in natural log form selected for model building

$\ln N_{(\text{fuel})}$ = fuel elements in natural log form selected for model building

Table D-9: PCA framework model E: Estimated standardised regression coefficients for the predictor variables in PCA models 1A, 5A, and 10A. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant

VAR	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A
1000/T _m	-0.18				0.11					0.036						
T _{gas}	0.13				0.32					-0.25						
ALLOY EL ELEMENTS																
C	-0.086				NS					0.14						
Mn	-0.0083				-0.017					-0.016						
P	0.0083				-0.16					0.21						
S	0.0083				-0.11					0.19						
Si	-0.092				-0.086					-0.0074						
Cr	-0.047				-0.044					-0.084						
Ni	-0.020				-0.093					-0.051						
Mo	0.11				NS					-0.088						
Nb	NA				0.015					0.15						
Ti	-0.077				0.019					-0.19						
V	0.0083				NS					-0.19						
Cu	ND				0.060					0.0026						
N	ND				0.076					-0.13						
Ce	ND				NS					ND						
Ta	ND				0.0004					ND						
Al	ND				NS					-0.010						
W	ND				0.047					0.019						
B	ND				0.022					0.16						
Co	ND				0.047					0.010						

VAR	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A
Fe	Base				Base					Base						
(Nb + Ta)	ND				ND					ND						
O	ND				ND					ND						
Y	ND				ND					ND						
FUEL ELEMENTS																
Na	0.13				0.095					0.017						
K	0.037				0.11					0.048						
Mg	-0.054				0.071					-0.032						
Ca	-0.098				0.15					0.095						
Al	0.0093				NS					0.044						
Fe	0.066				0.30					-0.039						
Si	NS				0.061					-0.0078						
Cl	0.30				0.16					0.085						
S	-0.22				0.056					NS						
Ti	NS				-0.031					0.041						
P	ND				-0.33					-0.18						
Mn	ND				0.29					NS						
Ba	ND				ND					0.011						

VAR – Predictor variables in natural log (except metal temperature)

1000/T_m - Metal temperature, 1000/K

T_g – Gas temperature in natural log

Yellow cells – most influential variable (highest standardised regression coefficient)

Orange cells – positively correlated with the corrosion rate

Blue cells – negatively correlated with the corrosion rate

Blank cells – data subsets not analysed with this framework

NS – Not selected for model building (grey cells)

NA – Not analysed but present in the data subset (grey cells)

ND – Not present in data subset (white cells)

Base – Base metal

Table D-10: PLS framework model E: Estimated standardised regression coefficients for the predictor variables in PCA models 1B, 5B, and 10B. The coloured cells (see footnote) have significant correlations with the corrosion rate; the yellow cells are the most significant

VAR	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13B	14B	15B	16B
1000/T _m	-0.26				0.20					0.18						
T _{gas}	0.14				0.38					0.14						
ALLOY ELEMENTS																
C	-0.10				NS					0.48						
Mn	NS				NS					0.13						
P	NS				NS					0.13						
S	NS				NS					0.16						
Si	-0.072				NS					0.14						
Cr	-0.061				NS					-0.18						
Ni	NS				NS					NS						
Mo	0.056				0.13					0.056						
Nb	NA				NS					NS						
Ti	NS				NS					-0.23						
V	NS				NS					0.11						
Cu	ND				NS					NS						
N	ND				NS					-0.70						
Ce	ND				NS					ND						
Ta	ND				NS					ND						
Al	ND				NS					NS						
W	ND				NS					NS						
B	ND				NS					0.29						
Co	ND				NS					NS						
Fe	Base				Base					Base						

VAR	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13B	14B	15B	16B
(Nb + Ta)	ND				ND					ND						
O	ND				ND					ND						
Y	ND				ND					ND						
FUEL ELEMENTS																
Na	0.060				0.10					NS						
K	NS				0.075					0.072						
Mg	NS				0.027					NS						
Ca	-0.14				0.15					0.26						
Al	NS				NS					NS						
Fe	NS				0.28					NS						
Si	NS				0.058					NS						
Cl	0.42				0.19					NS						
S	-0.093				0.0090					-0.15						
Ti	NS				0.066					NS						
P	ND				-0.36					-0.40						
Mn	ND				0.31					-0.081						
Ba	ND				ND					NS						

VAR – Predictor variables in natural log (except metal temperature)

1000/T_m - Metal temperature, 1000/K

T_g – Gas temperature in natural log

Yellow cells – most influential variable (highest standardised regression coefficient)

Orange cells – positively correlated with the corrosion rate

Blue cells – negatively correlated with the corrosion rate

Blank cells – data subsets not analysed with this framework

NS – Not selected for model building (grey cells)

NA – Not analysed but present in the data subset (grey cells)

ND – Not present in data subset (white cells)

Base – Base metal

Appendix E Model Performance Summary (Frameworks A-F)

A summary of the model performances for the framework models A-F are presented in this section.

E.1 Coefficient of Determination (R^2) for PCA and PLS Fireside Corrosion Models A-F

The R^2 values are presented in Table E-1 and Table E-2.

E.2 Root Mean Squared Error (RMSE) Values for PCA and PLS Fireside Corrosion Models A-F

The RMSE values are presented in Table E-3 and Table E-4.

Table E-1: R² values for PCA fireside corrosion models 1A-16A (framework models A-F; shaded cells not analysed)

PCA MODELS					Model A	Model B	Model C	Model D	Model E	Model F
R ² =	REGION	FUEL	MATERIAL	TUBE POSITION						
Data 1A	UK	Coal	Austenitic	Leading	0.79	0.78	0.82	0.76	0.82	0.77
Data 2A	UK	Coal	Austenitic	Non-leading	0.59	0.52				0.71
Data 3A	UK	Coal	Ferritic	Leading	0.41		0.44	0.42		0.42
Data 4A	UK	Coal	Ferritic	Non-leading	0.24					0.12
Data 5A	US	Coal	Austenitic		0.79	0.79			0.77	0.77
Data 6A	US	Coal	Ni based		0.41		0.40	0.38		0.41
Data 7A	US	Coal	Coatings		0.90					0.64
Data 8A	UK	Coal (Europe)	Austenitic		0.83					0.83
Data 9A	UK	Coal	Coatings		0.79					0.83
Data 10A	UK	Biomass	Austenitic		0.79	0.78			0.71	0.71
Data 11A	UK	Biomass	Ni based		0.86					0.74
Data 12A	UK	Biomass	Ferritic		0.79					0.77
Data 13A	UK	Biomass	Coatings		0.68					0.81
Data 14A	UK	Coal/Biomass	Austenitic		0.90					0.89
Data15A	UK	Coal/Biomass	TP316		0.92					0.89
Data 16A	UK	Coal/Biomass	Ferritics		0.62					0.62

Table E-2: R² values for PLS fireside corrosion models 1B-16B (framework models A-F; shaded cells not analysed)

PLS MODELS					Model A	Model B	Model C	Model D	Model E	Model F
R ² =	REGION	FUEL	MATERIAL	TUBE POSITION						
Data 1B	UK	Coal	Austenitic	Leading	0.77	0.77	0.85	0.85	0.85	0.85
Data 2B	UK	Coal	Austenitic	Non-leading	0.75	0.67				0.82
Data 3B	UK	Coal	Ferritic	Leading	0.42		0.36	0.31		0.44
Data 4B	UK	Coal	Ferritic	Non-leading	0.23					0.25
Data 5B	US	Coal	Fe based		0.72	0.72		0.75	0.74	0.75
Data 6B	US	Coal	Ni based		0.36		0.30	0.26		0.37
Data 7B	US	Coal	Coatings		0.88					0.79
Data 8B	UK	Coal (Europe)	Austenitic		0.79					0.82
Data 9B	UK	Coal	Coatings		0.78					0.78
Data 10B	UK	Biomass	Austenitic		0.70	0.71			0.75	0.73
Data 11B	UK	Biomass	Ni based		0.83					0.80
Data 12B	UK	Biomass	Ferritic		0.81					0.80
Data 13B	UK	Biomass	Coatings		0.76					0.75
Data 14B	UK	Coal/Biomass	Austenitic		0.89*					0.90
Data 15B	UK	Coal/Biomass	TP316		0.92					0.92
Data 16B	UK	Coal/Biomass	Ferritic		0.83					0.62

*inverse of metal temperature and all alloy elements excluded in this model

Table E-3: RMSE values for PCA fireside corrosion models 1A-16A (framework models A-F; shaded cells not analysed)

PCA MODELS					Model A	Model B	Model C	Model D	Model E	Model F
RMSE =	REGION	FUEL	MATERIAL	TUBE POSITION						
Data 1A	UK	Coal	Austenitic	Leading	0.30	0.30	0.27	0.31	0.27	0.31
Data 2A	UK	Coal	Austenitic	Non-leading	0.31	0.43				0.26
Data 3A	UK	Coal	Ferritic	Leading	0.58		0.56	0.57		0.57
Data 4A	UK	Coal	Ferritic	Non-leading	0.73					0.78
Data 5A	US	Coal	Fe based		0.70	0.72			0.72	0.73
Data 6A	US	Coal	Ni based		0.66		0.66	0.68		0.66
Data 7A	US	Coal	Coatings		0.37					0.69
Data 8A	UK	Coal (Europe)	Austenitic		0.31					0.33
Data 9A	UK	Coal	Coatings		0.49					0.44
Data 10A	UK	Biomass	Austenitic		0.49	0.74			0.57	0.56
Data 11A	UK	Biomass	Ni based		0.46					0.71
Data 12A	UK	Biomass	Ferritic		0.25					0.27
Data 13A	UK	Biomass	Coatings		0.68					0.56
Data 14A	UK	Coal/Biomass	Austenitic		0.34					0.35
Data 15A	UK	Coal/Biomass	TP316		0.32					0.35
Data 16A	UK	Coal/Biomass	Ferritic		0.57					0.57

Table E-4: RMSE values for PLS fireside corrosion models 1B-16B (framework models A-F; shaded cells not analysed)

PLS MODELS					Model A	Model B	Model C	Model D	Model E	Model F
RMSE =	REGION	FUEL	MATERIAL	TUBE POSITION						
Data 1B	UK	Coal	Austenitic	Leading	0.31	0.31	0.25	0.25	0.25	0.25
Data 2B	UK	Coal	Austenitic	Non-leading	0.24	0.28				0.67
Data 3B	UK	Coal	Ferritic	Leading	0.81		0.67	0.69		0.56
Data 4B	UK	Coal	Ferritic	Non-leading	0.73					0.72
Data 5B	US	Coal	Austenitic		0.80	0.80		0.76	0.77	0.76
Data 6B	US	Coal	Ni based		0.69		0.72	0.74		0.68
Data 7B	US	Coal	Coatings		0.40					0.54
Data 8B	UK	Coal (Europe)	Austenitic		0.35			0.63		0.31
Data 9B	UK	Coal	Coatings		0.50					0.50
Data 10B	UK	Biomass	Austenitic		0.59	0.58		0.55	0.52	0.55
Data 11B	UK	Biomass	Ni based		0.52					0.55
Data 12B	UK	Biomass	Ferritic		0.24					0.25
Data 13B	UK	Biomass	Coatings		0.57					0.58
Data 14B	UK	Coal/Biomass	Austenitic		0.36*					0.34
Data 15B	UK	Coal/Biomass	TP316		0.34					0.33
Data 16B	UK	Coal/Biomass	Ferritic		0.38					0.57

*inverse of metal temperature and all alloy elements excluded in this model

Appendix F Corrosion Data Sensitivity (PCA Model)

A data sensitivity analysis was performed using PCA (and PLS, section 5.4.1) and a scatterplot showing the original and modified version is presented. The Cr content was altered to its minimum/nominal value to ascertain if small changes modify the results significantly. Eight PCA components were used for model building and as observed (Figure F-1); the revised version did not alter the model performance.

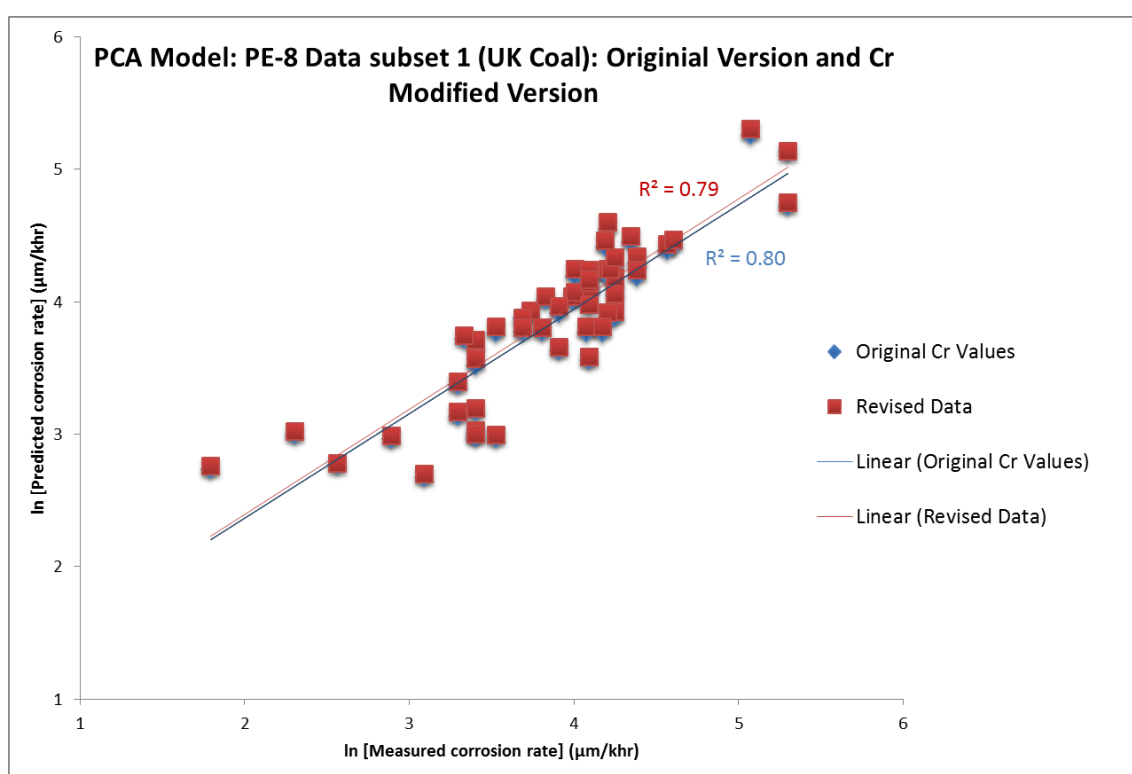


Figure F-1: Comparison of measured corrosion rates and predicted (PCA) corrosion rates using original Cr values and modified Cr values for data subset 1

Appendix G Notes on the PCA/PLS Modelling Approach

PCA and PLS can be implemented using other software platforms such as STATISTICA, SPSS, R, etc. This research has employed the multivariate and exploratory PCA, PLS module from the platform, STATISTICA, to implement some of the crucial steps in the algorithms, such as the calculation of the eigenvalues and eigenvectors (PCA), and the latent variables or scores in PLS. However, the author has taken liberties in the execution of the methodologies and performed part of it using a spreadsheet (MS Excel) were appropriate for both techniques (discussed in section 3.2.2 and 3.2.3). Hence a simplified, hands-on procedure has been devised to build the fireside corrosion model using only relevant variables. The methodology and utilisation of these data analysis techniques are continually evolving, and numerous literature on the subject have proposed variations on the procedure for prediction or as a confirmatory tool depending on the researcher's objectives.

The following sub-sections review the variations in developing the fireside corrosion models, what has worked, and what can be improved if the methodology is to be adapted.

G.1 Data Pre-processing

Data pre-processing is essential for these techniques (PCA/PLS) to work optimally. This section summarises various elements to consider before and during the PCA/PLS analyses.

As a recap on the methodology (chapter 3):

- The data is gathered in Excel, and gaps filled as described in section 3.1 (also section 4.1).
- The data is then exported to STATISTICA.
- At the start of the PCA/PLS module, STATISTICA centres (covariance basis) or scales (correlation basis) the dataset.
- STATISTICA then computes the orthogonal set of vectors by diagonalizing the original matrix (X); i.e. $X^T X$ is the correlation matrix if the values are standardised for PCA; $X^T X$ is the covariance matrix if the values are centred

about their means (PCA); $X^T Y$ is the correlation matrix for PLS (where X is the input data, Y is the output data, and X^T is the transposed input data matrix).

- The outputs from the PCA/PLS analyses (described in sections 3.2.2 and 3.2.3) are transferred to Excel for model building.

For this research, the transformation to latent variables is based on a correlation matrix (standardised), which eliminates scale dependence. The analysis can also be done using a covariance basis, which was attempted for PCA but was not effective primarily due to scaling issues (In STATISTICA, the PCA module presents both options; PLS automatically employs the correlation basis). The correlation basis is generally recommended, so variables do not add superficial variability as a result of their scale (Jolliffe, 2002). If the correlation basis is chosen, it is not necessary to standardise the variables before proceeding as this forms part of the procedure when processed in STATISTICA. However, if a transformation of the variables (e.g. converting to natural log etc.) is required, it is recommended to do the conversion before exporting the data from Excel to STATISTICA.

Very importantly, there must be enough variation (differences in values) in the input data for the analysis to proceed; otherwise, it will stall. Hence if all the observations of an input variable have a constant value, this variable would have to be excluded. This exclusion may lead to the loss of information on the contribution of the affected variable(s). Hence a decision must be made on how this missing input may impact the interpretation of the result. One way to deal with this is to add some variation in the data before analysing - e.g. use maximum and minimum values for the same alloy element.

G.2 Featured Model Structure, Arrhenius Construct (Retaining Metal Temperature)

On a few occasions, adjustments were made on the selection criteria to ensure the inverse of metal temperature (1000/K) was retained in the model, so it conforms to the Arrhenius construct (e.g. changed eigenvalue criterion to 0.2 as was done for PCA Model 2A). It may be worth relaxing this restriction in cases where the variable selection criteria exclude the metal temperature so that the corrosion model can be built without the (metal) temperature-dependent relationship. This would imply that the corrosion rate in this instance may not be particularly sensitive to changes in

temperature. The model structure would have to be re-defined to accommodate this. An attempt was made to build the corrosion model for cases where the variable selection phase excluded metal temperature (e.g. model 2A, model 14A, 14B etc.; not discussed in this thesis) with mixed results as the model performance (judged by R^2 value) was improved in most cases. In other instances (particularly for PLS), there was no significant change either way, although the R^2 value was always slightly better than the version which included the inverse of metal temperature.

G.3 Notes on Principal Component Analysis

The key steps in PCA are summarised in chapter 3, section 3.2.2.1 and Figure 3-2.

G.3.1 Supplementary Variables

In the PCA module, STATISTICA includes the option for projecting non-active variables on to the vector sub-space generated by PCA termed *supplementary variables*. The author elected to input the base metal (i.e. Fe or Ni) and the dependent variable (corrosion rate) as supplementary variables to determine their association with the other variables in the PC space (as visualised by the loadings plot). The loadings are usually only calculated for the input data (equation 3-6, chapter 3), hence to obtain a loadings value for the output variable (or any other input variable not included for analysis), it must be entered as a supplementary variable on the PCA module before running the analysis. The loadings for the supplementary variables are calculated (in STATISTICA) using the formula below:

$$\frac{\sum_{i=1}^n Y_{ti} \cdot (\sum_{j=1}^p X_{ij} U_{\alpha j})}{(\lambda_{\alpha})^{1/2}}$$

Where;

Y_{ti} is the (t, i)th element of the transpose of the matrix Y for n supplementary variables and p in the summation sign is the number of active (input) variables.

α is the factor axis in consideration (i.e. PC 1, PC 2, or PC 3 etc.)

λ is the eigenvalue for α PC.

And U is the corresponding eigenvector for the j th variable

G.3.2 PC Selection

A crucial aspect of this technique is to decide on a suitable criterion for the number of PCs to use for model building without any loss of information. Section 3.2.2.1.3 reviews other selection criteria proposed in the literature. This research uses a threshold of *eigenvalue* > 0.5 as a compromise between the popular Kaiser's selection criterion, i.e. retaining only PCs with *eigenvalues* > 1 , and other tests of significance. As Joliffe (2002) surmised, previous studies have contended that the choice of PCs should not be based solely on the size of their variance, particularly if low-variance PCs (identified by low eigenvalues) have predictive value. However, there has been no consensus on which of the other criteria proposed gives an overall 'best' trade-off between predictive accuracy and bias (systematic errors – i.e. variation in Y due to PCs not included in the model). Thus, this selection is subjective. An extensive review of the various selection criteria proposed is documented in Joliffe (2002).

G.3.3 Stepwise Regression Module for the Selection of PCs

The methodology employed in this research includes a 'best subset stepwise regression' module to retain only PCs that have a significant correlation with the corrosion rate (i.e. the response or output variable, Y). It is important to note that as the rotation and transformation of the original data to the reduced dimensional (PC) space is only carried out on the input data (X), there is no guarantee that the variation in the input data (X) optimally explains the variation in the response data (Y). The idea is thus to establish this association by incorporating a stepwise regression stage in the PCA module to exclude uncorrelated or uninfluential PCs. The *best subset* option was chosen for this work. Other staged regression modules that can be employed include forward and backward regression stepwise regression step. The goal is to obtain a good fit of the data at a relatively low model complexity.

G.3.4 Variable Selection

Just as the selection of PCs is subjective, the criteria for the selection of relevant input variables that will be used to build the corrosion model is entirely up to the researcher. For this research, the author has elected to use varimax *rotated* plots (rotation of the

PCs) to achieve this. There are various rotation strategies available in STATISTICA. The rotation methods are either orthogonal or oblique. Orthogonal rotation methods assume that the factors in the analysis are uncorrelated. In contrast, oblique rotation methods assume that the factors are correlated.

The varimax normalized rotation strategy (orthogonal) chosen for this research involves rotating the axes (PCs) within the reduced PC (k -dimensional) space in a way that simplifies the interpretation of the axes as much as possible (Joliffe, 2002). By so doing, it produces a clear pattern of variable loadings for the selected PCs (i.e. PCs selected via the ≥ 0.5 eigenvalue criterion) and is not solely concentrated on the first few PCs. From the varimax normalised table produced (e.g. Table 3-22); a cut-off value of 0.5 is applied to select the input variables for corrosion model building. The default selection threshold in STATISTICA is 0.7, which can be changed. The author chooses 0.5 as a safe bet and to minimise loss of contribution of variables. Researchers from various disciplines have tended to stick to a 0.5 threshold as well (Liu *et al.*, 2003; Tan *et al.*, 2016). However, as PCA tends to nominate more variables than necessary for prediction in many instances, this 0.5 marker is subject to review. Other researchers may opt to increase or retain the default value (0.7) and/or use the initial raw (unrotated) loadings plot to select variables. Ultimately, the flexibility in the modelling approach allows for different standards on PC and variable selection.

G.3.5 Classification/Combining of Variables Using Loadings Plot

Although the PCA loadings plot is a powerful visualisation tool, a preliminary inspection of the plot with the aim to classify or combine variables would only work optimally if only one group of variables is being analysed (e.g. only the fuel composition or alloy composition, but not both). However, this is subject to various interpretations as researchers may choose to make a connection on, as an example, the chemical potential for a group of fuel species that form clusters in the plot (for instance, the potential for the fuel species in question to form sulphates, chlorides etc.). The approach in this research was to combine only chemically similar (fuel) elements (e.g. alkali or alkaline earth etc.), or alloy elements that have the same characteristics (e.g. formation of a non-porous oxide scale that prevents further corrosion damage).

G.3.6 Combining PCA and PLS

There have been proposals on the possibility of combining procedures from PCA and PLS drawing from the strengths of both techniques. A good case for adopting this strategy is to identify patterns from the loadings plot from PCA and perhaps classify the variables based on those patterns, and then use PLS for prediction. However, following the methodology proposed in this research, and given the unique nature of the dataset employed, it is the author's opinion that a combined analysis may not be necessary, nor does it improve the prediction as such (also see section 5.2.1.2). Both techniques have served well enough as stand-alone PCA/PLS corrosion models.

G.4 Notes on Partial Least Squares

The key steps in PLS are summarised in chapter 3, section 3.2.3 and Figure 3-4.

Running the PLS application in STATISTICA produces the weight vectors (section 3.2.3, equations 3-20 and 3-21), the scores (equation 3-15), and the PLS components (Table 3-23) which summarise the level of model complexity. The PLS algorithm automatically predicts Y (the corrosion rate) using the extracted X and Y -scores (i.e. T and U , respectively, see section 3.2.3.1). However, Maitra and Yan (2008) suggested that the X -scores are sufficient to use independently. Following this recommendation, the PLS methodology entailed extraction of the X -scores (t , see equation 3-15) from the PLS decomposition derived using STATISTICA, and then utilised separately. First, a regression on the scores was done via the General Linear Module (GLM) in STATISTICA, and the results from GLM and the weight vectors were used to build the PLS corrosion model (this latter process was computed/completed on MS Excel). This approach provides the flexibility to use PLS orthogonal factors derived from the input data, X , and not be restricted to the original model constructed by the PLS module in STATISTICA (Maitra and Yan, 2008). Part of the rationale for doing this is that the original PLS model includes *all* input variables in the model, and hence, the only requirement for the user would be selecting an appropriate number of PLS components to improve predictive accuracy. The core objective of this research is to highlight crucial variables for model building. Hence, as the default process in STATISTICA does not provide the flexibility to integrate a variable selection process in the same workbook without some form of coding, the 'variable importance in projection' (VIP)

calculation (equation 3-24) and the rest of the model-building procedure using the coefficients from regressing the X -scores were completed using a spreadsheet.

The final regression estimates obtained were very similar to the original PLS model from STATISTICA, but the main difference was that only nominated variables determined from the VIP selection procedure were present in the reconstructed PLS corrosion model that was done. Thus, the exclusion of irrelevant variables did not affect the final regression outcome, which is the core advantage of the PLS (and PCA) technique. The success of this reconstructed model supports Maitra and Yan's (2008) assertion that a significant statistic resulting from PLS is, in fact, the X -scores (t).

G.4.1 Variable Selection in PLS

There is also no consensus in the literature on the appropriate threshold to adapt using the VIP method. This research has opted for a $VIP \geq 0.8$ variable selection criterion following the lower end of Mehmood *et al.* (2012) recommendation.