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I do hereby declare that

**"A SYSTEMATIC APPROACH TO FIRESIDE BOILER TUBE
INVESTIGATIONS"**

here submitted complies fully with the requirements for the

MASTERS OF SCIENCE

issued by the

DEPARTMENT OF CHEMISTRY

of the

UNIVERSITY OF THE WITWATERSRAND.

I further declare that the dissertation is entirely my own work and that all sources, used or referred to, have, by means of complete references, been listed and acknowledged.


.....

G.J. Broodryk

1995-09-05

**A SYSTEMATIC APPROACH TO FIRESIDE
BOILER TUBE INVESTIGATIONS**

by

GIDEON JACOBUS BROODRYK

Submitted for the

MASTERS OF SCIENCE

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in the

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1.2. FIRESIDE CORROSION:

The main categories of fireside corrosion are coal ash corrosion, oil ash corrosion, waterwall fireside corrosion, and cold-end corrosion (Southwest Research Institute 1985: 4-1).

High temperature fireside corrosion is related to the sulphur, chlorine, sodium, potassium, and ash content of the coal (Crossley 1963: 228). For common coals used in the United States, the elements which have been found to have the most influence on the high temperature corrosivity of the coal are aluminium, potassium, sodium, sulphur, iron and chlorine (Electric Power Research Institute 1993: 3-110). According to Flatley, Betham and Morris (1988: 84-89), the corrosion process is relatively slow but can also increase dramatically with changes in coal quality and boiler operating conditions.

1.2.1. High temperature coal ash corrosion:

High temperature coal ash corrosion results when a molten ash of complex alkali-iron-trisulphates, $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ and $\text{K}_3\text{Fe}(\text{SO}_4)_3$, forms on boiler tube surfaces. The elements involved in coal ash corrosion (sulphur, sodium, potassium, and iron) are derived from the mineral matter commonly found in all coals (Port and Herro 1991: 130; Babcock & Wilcox 1978: 15-20; and Southwest Research Institute 1985: 4-16).

CHAPTER 1

FIRESIDE BOILER TUBE FAILURES

1.1. INTRODUCTION TO BOILER TUBE FAILURES:

According to the Southwest Research Institute (1985), boiler tube failures due to fireside corrosion and fireside erosion are the prime causes of forced outages in fossil-fired utilities.

Boiler tube failures and the subsequent forced outages cost ESKOM millions of rands per year in terms of repairs and loss of revenue. A survey of boiler tube failures on various power stations over a five year period (Botha 1991) revealed that fly ash erosion, wallblower erosion and internal pitting corrosion during off-load conditions were the main causes of boiler tube failures. Creep exhaustion was becoming a major factor at two power stations while sulphide containing deposits were frequently observed at virtually all utilities investigated.

Fireside corrosion is a phenomenon which has received increasingly interest and attention in ESKOM over the past few years. Although this type of corrosion has not been responsible for unplanned unit shut-downs, there is some concern that this corrosion type may contribute to future tube failures.

The available data and investigation results were combined and analysed to suggest a root cause analysis technique for general fireside boiler tube failures. Because of the complexity of these failure mechanisms, the root cause analysis technique was compiled to suit the general needs of an investigator and will only provide guidelines for a systematic approach to the problem.

SUMMARY

The extent and causes of fireside boiler tube failures/deterioration were investigated. The approach was based on research at three Eskom power stations located in the South Eastern Transvaal. The main contributing factors to these failures were identified as deposit-buildup, overheating, thermal fatigue and tube defects.

Although no tube failures due to fireside corrosion had been recorded to date, there is a concern that this corrosion phenomenon may cause future problems in ESKOM. Fireside corrosion is considered to be a major problem at those units burning coal that is rated as very aggressive (mainly high sulphur, iron and calcium content).

Various analyses techniques were applied to study the feed coals and tube structures while X-ray diffraction and combined Scanning Electron Microscopic-Energy Dispersive Spectroscopic techniques were applied to analyse slag deposit samples removed from selected superheater, waterwall and economiser tube sections. A general trend in the distribution of the main elements present in the different deposit layers was observed. Various case studies and overseas publications were also used to investigate the tube failures and the deposit buildup on the fireside surface of the tubes.

Pulverised fuel ash: Ash from the combustion of pulverised fuel and is divided into fly ash and bottom ash.

Scanning Electron Microscopy (SEM): An electron microscopic technique which reveals specimen surface topography.

Slagging: Phenomenon where molten coe' ash impingement on the furnace walls freezes and stick to the walls.

Stress rupture (creep rupture): Stress rupture, a form of long term overheating damage, is the rupture of metal due to sustained load at high temperature. Superheater and reheater tubes that exhibit scaling and/or thick walled ruptures are suspect.

Superheaters: Devices which superheat dry steam and consist of a large number of small bore multi-loop tubes connected to inlet and outlet headers, located in the hot gas path, just after the combustion chamber.

X-ray Diffraction Spectroscopy (XRD): A technique in which an X-ray beam is diffracted by the sample and used to identify the phases or compounds present in a solid by classifying the size and type of their crystal structure.

X-ray Fluorescence Spectroscopy (XRF): A technique which uses the wavelengths or energies of X-rays emitted by a sample to identify the elements present in a solid.

Hematite: A magnetic form of iron oxide, Fe_2O_3 . Hematite is gray to bright red. The reddish forms are non-protective, and their occurrence indicates the presence of high levels of oxygen.

Induced draught fans: Fans provided to remove the products of combustion from the boiler and discharge it to the chimney.

Long-term overheating: Condition in which metal temperatures exceed design limits for days, weeks, months, or longer. Long-term overheating depends on temperature, length of time at temperature, and tube metallurgy.

Magnetite: A magnetic form of iron oxide, Fe_3O_4 . Magnetite is dark grey to black, and forms a protective film on iron surfaces.

Microstructure: The structure of a metal as revealed by microscopic examination of the etched surface of a polished specimen.

Overheating: Heating of a metal or alloy to such a high temperature that its properties are impaired.

Pitting: The formation of small, sharp cavities in a metal surface by corrosion.

Precipitators: Devices provided to extract fly ash particles from the furnace.

Economiser: A heat-exchange device for increasing feedwater temperature by recovery of heat from gases leaving the boiler. An economiser is usually located in the gas path immediately after the superheaters.

Electrostatic precipitators: Located between the air-heater and induced-draught fan, they are provided to extract fly ash particles from the boiler.

Exfoliation: Corrosion that proceeds laterally from the sites of initiation along planes parallel to the surface, generally at grain boundaries, forming corrosion products that force metal away from the body of the material, giving rise to a layered appearance.

Failure: Term used to imply that a part in service has deteriorated seriously, to the point that it has become unreliable or unsafe for continued use.

Flue gas: Combustion gas released during the combustion of coal which is released through the smoke stack.

Fly ash: Fine powder which is carried from the furnace by the flue gases and is mainly collected by the precipitators.

Fouling: The buildup of bonded and sintered deposits on superheater and reheater tubes of a boiler.

Furnace: Heat from the furnace heats up the water in the riser tubes inside the boiler furnace.

Glossary of terms

Air heater: The air heater in a steam generating unit reclaims some heat (which would otherwise be lost) from the flue gas and adds that heat to the air required for the combustion of the fuel.

Austenitic stainless steel: A nonmagnetic stainless steel possessing a microstructure of austenite. In addition to chromium, these steels commonly contain at least 8% nickel.

Bottom ash: Remaining proportion of pulverised fuel ash which is collected from the bottom of the furnace combustion chamber.

Carburization: Carburization conditions are caused by incomplete combustion and too little oxygen in the furnace. this may involve insufficient mixing of the flue gas within the furnace to assure an oxidizing atmosphere across the unit.

Combustion: The rapid reaction of the basic elements in coal (carbon, hydrogen, nitrogen and sulphur) with oxygen with the subsequent release of heat and the formation of combustion gases.

Energy Dispersive X-ray Spectroscopy (EDS): A microscopic chemical analysis technique which measures the characteristic energies of X-rays emitted by atoms of an element.

MW	:	Megawatt
μm	:	Micrometer
mg	:	Milligram
mm	:	Millimetre
ND	:	Not detected
PA fan	:	Primary air fan
ppm	:	Parts per million
Rev	:	Revision
S/H	:	Superheater
Sec	:	Secondary

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Abbreviations

$^{\circ}\text{C.min}^{-1}$	: Degree celcius per minute
Elm	: Element
FD fan	: Forced draft fan
g	: Gram
Hv	: Hardness value
ID fan	: Induced draft fan
MJ/Kg	: Megajoules per kilogram
MPa	: Megapascal

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1.4. LONG- AND SHORT-TERM OVERHEATING:

Overheating is the heating of a metal or alloy to such a high temperature that its properties are impaired. Boiler tube failures can be caused by long-term overheating or by short-term overheating, as described by Port and Herro (1991: 29 to 55):

1.4.1. Long term overheating:

Long term overheating predominantly occurs in superheaters, reheaters, and wall tubes when tube metal temperatures exceed the design limits for periods of days, weeks, or longer. Overheating is caused by internal deposits, overfiring, incorrect flame pattern, restricted coolant flow, or inadequate attemperation. Failed tubes are either ruptured or bulged and often contain internal deposits. Bulging usually precedes rupture and causes deposits to spall at the bulge site, thus reducing the metal temperatures locally.

1.4.2. Short term overheating:

Short-term overheating occurs when tube metal temperatures exceed their design limits for short term periods only. These temperatures often exceed 730°C but are at least 454°C. Failures caused by short-term overheating are more commonly found in high temperature components such as superheaters and reheaters.

This type of erosion can be experienced in the primary superheater and economiser where non-uniform gas flow distribution may occur. Since ash particles are more abrasive when particle temperatures are lower, fly ash erosion is believed to be more significant in the economiser sections. As temperatures increase, erosive metal loss decreases because particles become softer.

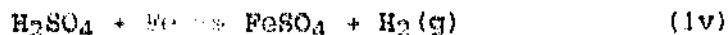
Also, as the angle of impingement between gas flow and the metal surface increases, the erosive loss tends to increase. Particles containing high levels of silicon and aluminium compounds are more abrasive because of their large particle kinetic energy and high particle hardness (Southwest Research Institute 1985; 5-4 to 5-11; and Port and Herro 1991; 192-202).

1.3.3. Sootblower erosion:

Sootblower erosion is caused by the malfunction of a sootblower or sootblowing system, or operation of a blowing system which entrains a large amount of fly ash at a velocity high enough to cause significant wear.

Superheater tubes and furnace corners opposite wall blowers are usually attacked. Sootblower erosion normally produces flat spots on the fireside surface on the tube (Southwest Research Institute 1985; 5-16 to 5-20; and Port and Herro 1991; 192-202).

(5) Corrosion of the metal by the acid then takes place according to the following reaction:



Corrosion failures are due to stress rupture from loss of load-carrying material on the fireside of the tube (Southwest Research Institute 1985: 4-6).

1.3. FIRESIDE EROSION:

1.3.1. Introduction:

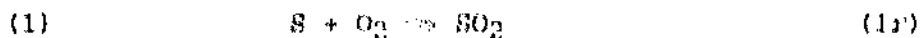
Apart from fireside corrosion, boiler tube failures can also be caused by fireside erosion problems. Two of the main contributors of fireside erosion are fly ash erosion and sootblower erosion.

1.3.2. Fly ash erosion:

Fly ash erosion is related to the impaction by fly ash particles at high velocities against the boiler tube steel. This normally results in smooth, polished, flat spots on the fireside surface, leading to excessive reduction in wall thickness and final tube rupture. In other cases, grooving and irregular flow marks are caused by eddies around slag encrustations.

1.3.4.2. Corrosion mechanism:

In general, corrosion problems are associated with the combustion of fuels that contain sulphur or sulphur compounds. Sulphur in the fuel is oxidized to sulphur trioxide (SO_3) in the following sequence (Port and Herro 1991: 144; Hedley 1963: 45 to 54; Needham and Jones 1984: 36; and Levv and Merryman 1965: 116 to 123):



- (2) A small portion of the SO_2 formed in reaction (1r) is oxidized to SO_3 by reaction with atomic oxygen in the high temperature flame:



- (3) In the presence of vanadium pentoxide (V_2O_5), SO_2 can also be converted to SO_3 :



- (4) In the presence of water, SO_3 condenses to form sulphuric acid (H_2SO_4) at temperatures below the dew point:



The sulphidation mechanism occurs beneath a previously existing oxide layer and attacks the grain boundaries of the waterwall fireside surface. The corroded grain boundaries act as thermal stress concentrators, resulting in the formation of the waterwall cracks.

1.2.4. Cold-end corrosion:

Cold-end corrosion results from the formation of sulphuric acid (H_2SO_4) on metal surfaces. It occurs in the cooler regions of the combustion system, such as economisers and air-heaters (Southwest Research Institute 1989: 4-6).

1.2.4.1. Causes:

Condensation of sulphuric acid on metal surfaces occurs under the following circumstances (Singer 1981: 3-29):

- (1) Operation with boiler tube metal temperatures below the acid dew point temperature so that condensate will form on the metal.
- (2) Operation with the gas temperature below the acid dew point temperature so that condensate will form on the fly ash particles and produce acid smuts.

(ii) Sulfidation corrosion:

Corrosion is considered to occur in several stages (French 1983: 203):

- (1) Sulphur in the fuel is oxidized in the flame to sulphur dioxide (SO_2):



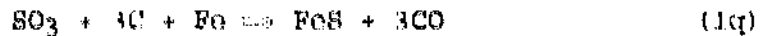
- (2) Sulphur dioxide (SO_2) is converted to sulphur trioxide (SO_3) by a catalytic process occurring near the furnace wall:



- (3) Carbon is deposited in the ash either from unburnt coal or carbon monoxide as:



- (4) Tube wastage occurs by either:



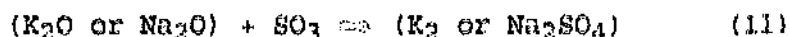
Investigations by Smith and Marder (1992), revealed that circumferential cracking in waterwall boiler tubes had two components, namely corrosion and thermal stress.

1.2.3.2. Corrosion mechanism:

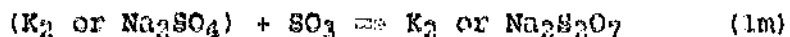
The following corrosion mechanisms are described (Batelle-Columbus Division 1987: 3-6; and Port and Herro 1991: 135):

(i) Formation of alkali pyrosulphates:

Potassium and sodium volatilize from the mineral matter in coal to form K_2O and Na_2O which react with SO_3 in the gas stream to form potassium sulphate (K_2SO_4) and sodium sulphate (Na_2SO_4) respectively:



Potassium pyrosulphate ($K_2S_2O_7$) or sodium pyrosulphate ($Na_2S_2O_7$) is formed by reaction of the alkali sulphates with sulphur trioxide (SO_3) in the gas stream:



The pyrosulphates then react with the iron exposed to the flue gas stream or with the iron oxides that have formed on the fireside surface. Precipitation of the alkali pyrosulphates takes place between 370°C and 430°C (Cutler et al., 1978). The molten slag fluxes the external protective Fe_3O_4 layer on the tube surface, causing rapid metal wastage.

The sodium-vanadium complexes are corrosive when molten. Oxidation of the metal reduces wall thickness which results in an increase in stress through the thinned region. The combined influence of increased stress and high metal temperatures result in final failure by creep rupture (Port and Herro 1991: 124; and Babcock and Wilcox 1978: 15-23).

1.2.3. Waterwall fireside corrosion:

Waterwall fireside corrosion is found in the burner area of the boiler and is caused by insufficient oxygen in the burner zone (Port and Herro 1991: 135).

1.2.3.1. Causes:

Poor combustion conditions produce a fuel-rich corrosion environment (Port and Herro 1991: 136). This fuel-rich condition in a reducing atmosphere contains high levels of carbon monoxide (CO) and delivers unburnt coal particles to the tube surface.

The deposited incomplete burnt coal particles release chloride compounds and volatile sulphur in the form of sodium pyrosulphate ($\text{Na}_2\text{S}_2\text{O}_7$) and potassium pyrosulphate ($\text{K}_2\text{S}_2\text{O}_7$) (Southwest Research Institute 1985: 4-8).

1.2.2.1. Characteristics of oil ash corrosion:

Oil ash corrosion occurs by the fluxing action of molten sodium-vanadium compounds on the protective oxide scale on the tube steel. The corrosion process is the catalytic oxidation of the metal by the reaction with vanadium pentoxide (V_2O_5) or complex vanadates (Southwest Research Institute 1985: 4-23 to 4-24; and Port and Herro 1991: 124).

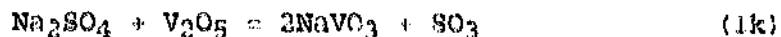
1.2.2.2. Corrosion mechanism:

The following corrosion mechanisms are described:

- (1) Vanadium compounds in the fuel are oxidised in the flame to V_2O_5 (Port and Herro 1991: 123).
- (2) Sodium, as chloride, vaporises to Na_2O and reacts with sulphur oxides in the flue gas:

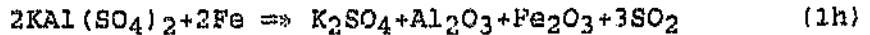


- (3) The vanadium and sodium compounds then react to form complex vanadates having melting points lower than those of the parent compounds:

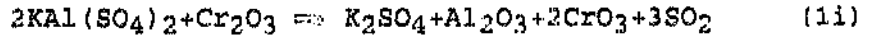


(Babcock and Wilcox 1978: 15-21 to 15-22).

or



or



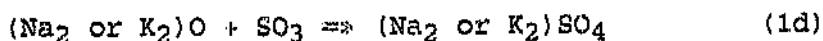
The reaction products shown in reaction (1g) tend to slow down the corrosion rate. If the deposit spalls, the reaction begins anew. The spalling rate, then, controls the overall rate of corrosion.

Reduction of the tube wall thickness is caused by accelerated oxidation of the protective oxide covering the tube. Stress rupture is then caused by the combination effects of high metal temperatures and increased stress through the thinned tube wall (Port and Herro 1991: 129, 130).

1.2.2. High temperature oil ash corrosion:

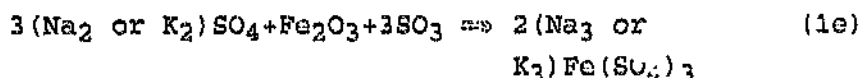
High temperature oil ash corrosion results when a molten slag containing vanadium and sodium compounds forms on superheater and reheater tube surfaces. The sodium vanadate compounds, whose melting points are as low as 525°C, are mainly responsible for this type of corrosion (Needham and Jones 1984: 32; and Port and Herro 1991: 123).

- (3) The Na_2O and K_2O then react with SO_3 either on the tube or in the gas stream to form sodium or potassium sulphate, a low-melting material that deposits on the tube:

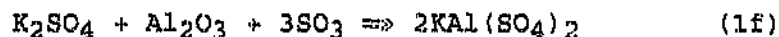


The low-melting material attracts other ash particles, building up a thick deposit on the tube.

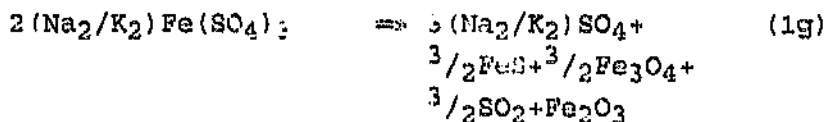
- (4) The alkali sulphates, iron oxide, and SO_3 then react to form the complex sulphate:



Adams and Raask (1963: 196), showed that the main constituent of the deposit was a potassium aluminium sulphate, $\text{KAl}(\text{SO}_4)_2$, rather than the iron-containing sulphates:



- (5) The complex sulphates in the molten phase then reacts with the tube metal:



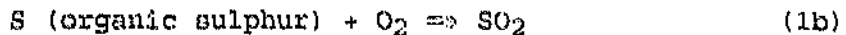
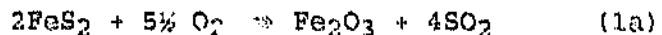
1.2.1.1. Generation of corrosive ash deposits:

The deposition rate of alkali-metal sulphates in coal-fired boilers depends on the amount of volatile sodium chloride in the coal (Raask 1985: 202, 203). Sodium and potassium sulphates are vapor species that diffuse through a porous matrix of silica ash deposits and condense on cooled boiler tubes (Halstead and Raask 1969: 344).

1.2.1.2. Corrosion mechanism:

The following sequence of events is representing the actions occurring during the corrosion process (Reid 1971: 106; Borio and Hensel 1972: 142 to 148; Borio, Plumley and Sylvester 1977: 168 to 169; and Simons, Browning and Liebhafsky 1955: 17):

- (1) Sodium and potassium are volatilized in part from the mineral matter in the high-temperature flame forming Na_2O and K_2O .
- (2) SO_2 and some SO_3 are formed by the reaction of pyrites (FeS_2) and organic sulphur with oxygen:



If CO is formed, the coal is not (completely) burnt under oxidizing conditions and, in pulverised fuel burners, some unburnt carbon is entrained in the ash.

2.4.2.2. Hydrogen:

The hydrogen in coal is burnt to water vapor during the combustion process (Singer 1981: 3-14).

2.4.2.3. Nitrogen:

Practically all coals contain less than 2% of nitrogen on an air-dry basis (Kirner 1985).

2.4.2.4. Sulphur:

Sulphur occurs in coal as pyrite or marcasite (FeS_2), as organic sulphur and combined with calcium and iron as sulphates (Perry, Green and Maloney 1985: 9-5). In South African coals, only traces of calcium sulphate (<0,05%) and no iron sulphate is found.

2.4.2.5. Oxygen:

Oxygen is calculated by subtracting from 100 the sum of the percentages of the hydrogen, nitrogen, total carbon and organic sulphur contents of coal (Singer 1981: 3-14).

subjected to a standardized temperature test. Volatile matter includes the volatile matter of the inorganic material such as crystal water from clay minerals, carbon dioxide from carbonate minerals and sulphur from pyrite. A high organic volatile content is preferred for ignition, flame stability and coal burnout.

2.4.1.4. Fixed carbon:

The fixed carbon is the combustible residue left after driving off the volatile matter (Singer 1981: 2-10). It is calculated by subtracting from 100 the sum of the percentages of inherent moisture, volatile matter and ash content (Perry, Green and Maloney 1985: 9-4).

2.4.2. Ultimate analysis:

The ultimate analysis of coal is expressed in terms of its organic carbon, hydrogen, nitrogen, organic sulphur and oxygen contents (Singer 1981: 2-14; and Perry, Green and Maloney 1985: 9-4).

2.4.2.1. Total carbon:

Total carbon includes both the carbon in the fixed carbon and in the volatile matter but excludes the carbon from the carbonate minerals (Singer 1981: 2-14). All this carbon appears in combustion products as carbon monoxide (CO) and carbon dioxide (CO₂).

2.4.1. Proximate analysis:

The proximate analysis of coal is expressed in terms of its moisture, ash, volatile matter, and fixed carbon contents (Anderson, Didlick, Turner, Gemmill, Godfrey, Jackson, Huntington, Kennedy, Musgrave and Varley 1971: 48 to 51). Values are calculated to the nearest 0.1%.

2.4.1.1. Inherent moisture:

Inherent moisture is the moisture retained in the pores of the coal when the surface moisture has evaporated when in equilibrium with the relative humidity of its surroundings (Anderson *et al.*, 1971: 48).

2.4.1.2. Ash:

Singer (1981: 3-11) defined ash as the solid, non-combustible residue which remains after the complete combustion of coal. Ash is derived from the mineral matter in coal (Perry, Green and Maloney 1985: 9-4).

2.4.1.3. Volatile matter:

Singer (1981: 3-11) described the volatile matter as the material, other than the the inherent moisture, which is driven off in vapor form when coal is

Coal supplied to Hendrina power station is supplied by Optimum Colliery, of which the coal deposit is contained within the Vryheid formation of the Becca Group of the Karoo Sequence. Only the No. 4 Lower, No. 2 and No. 2A seams are economically mineable in the Optimum Coalfield.

- C. No. 4 seam: The No. 4 seam contains approximately 26% of the coal resources of the Witbank Coalfield. It contains dull to dull lustrous coal with numerous shale and sandstone partings.
- D. No. 5 seam: The No. 5 seam consists of mixed banded coal with shale and mudstone partings in some areas. This seam contributes only approximately 4% of the coal resources in the Witbank Coalfield.

2.3.2. The Highveld Coalfield:

The Highveld Coalfield lies in the south-eastern Transvaal, south of the Witbank Coalfield. The No. 3 and 4 seams largely contain low grade bituminous coal. Mining from the thicker areas of the No. 4 seam includes Matla Colliery and Amcoal's Kriel Division (Anhaeusser and Maske 1986: 1990-1993).

2.4. COAL ANALYSIS:

Perry, Green and Maloney (1985: 9-4) reported the composition of coal in two different ways, namely the proximate analysis and the ultimate analysis.

It is postulated that the susceptibility to deposit formation is a function not only of the phosphorus, but also of the boron and fluorine content of South African coals (Dutkiewicz 1990).

Results obtained from Neutron Activation analysis by Hart, Leahy and Falcon (1981) revealed average arsenic levels of 3,75% in the No. 2 seam of the Witbank Coalfield. Arsenic may originate from the pyrite mineral, mispickel ($\text{FeS}_2 \cdot \text{FeAs}_2$) in coal. The formation of highly aggressive arsenic sulphide (As_2S_3) could drastically increase the corrosion rate of boiler steel.

2.3. DESCRIPTION OF COALFIELDS IN THE SOUTH EASTERN TRANSVAAL:

2.3.1. The Witbank-Middelburg Coalfield:

The Witbank-Middelburg Coalfield consists of four mineable coal seams (Anhaeusser and Maske 1986; 1969-1984):

- A. No. 1 seam: The No. 1 seam consists of lustrous to dull coal with shaly sandstone.
- B. No. 2 seam: The No. 2 seam contains some of the best quality coal and contributes to approximately 69% of coal resources of the Springs-Witbank Coalfield. Power stations receiving coal mined from this seam include Arnet, Duvha and Hondrina.

The most notable differences between these coals are the high calcium levels in the South African coal and the higher iron oxide levels in the German and English coals. The sodium and potassium levels are also higher for the overseas coals. The South African coals contain high levels of kaolinite, a clay mineral composed of aluminium silicate. According to Pollmann (1981), the exceptionally high calcite (CaCO_3) levels in the South African coal, in combination with the kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), produces anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), a slag mineral which crystallizes to form the main component of the porous slag.

2.2.3.2. Trace elements in coal:

Phosphatic bonded deposits in boilers using South African coals are more prevalent than in boilers using northern hemisphere coals. It would appear that phosphatic deposit problems are caused by coal containing more than 0,01% phosphorus. This means that 30% of South African coals have the potential for phosphatic deposition. Hoffmann and Hoffmann (1948) claim that 33% of phosphorus in the apatite mineral ($\text{CaF}_2 \cdot 3\text{Ca}_3\text{P}_2\text{O}_8$) can be transferred into the vapor phase. The metal vapor readily oxidises in the flue gas where oxygen is present in excess:



The oxide depositing together with ash can function as a high-temperature cement in bonded deposits.

TABLE 2.2 Composition of some local and overseas coals
(Boshoff 1986; Pollmann 1981; and Hadrill 1979).

Coal ash analysis	Country		
	South Africa (Kriel)	Germany (Ruhr)	England
Mineral matter:	Siderite Kaolinite Quartz Calcite Dolomite		
Ash elemental:			
%Si (as SiO ₂)	44,8	48,8	47,0
%Al (as Al ₂ O ₃)	30,4	31,8	26,3
%Fe (as Fe ₂ O ₃)	3,3	10,7	13,7
%Ca (as CaO)	11,6	1,4	2,3
%Mg (as MgO)	0,3	0,7	2,2
%Na (as Na ₂ O)	0,6	0,7	1,3
%K (as K ₂ O)	0,6	4,2	3,3
%Ti (as TiO ₂)	1,5		
%S (as SO ₃)	4,8		
%P (as P ₂ O ₅)	1,5		
Ash fusion temperatures (°C)			
Deformation	1360	1240	1200
Softening	1390	1490	1340
Fluid	1450	1510	1400
Ratios:			
Base/acid ratio	0,22	0,22	0,31
Slagging factor	0,2	0,4	0,8
Slagging tendency	low	low	high

TABLE 2.1 Classification of coal by rank
(Singer 1981: 2-2 to 2-6).

Rank	Physical properties
Anthracites	Hard, brittle coals
Bituminous	Normally a sticky mass when heated
Subbituminous	Brownish black or black coals
Lignites	Brown coals

2.2.3. Chemical and mineralogical composition of some local and overseas coals:

The qualities of some local and overseas coals are compared to evaluate the slagging and fouling tendencies of the different coal ashes.

2.2.3.1. Composition of a typical South African and some overseas coals:

The chemical and mineralogical composition of typical South African, German, English and American coals are compared in Table 2.2.

peat to the various stages of coal ranks (Elliott 1961).

The Northern Hemisphere coals and the Southern Hemisphere coals formed under different conditions. In the Northern Hemisphere, the vegetation accumulated in great swamps which were surrounded by fairly even and low lying terrain. The Southern Hemisphere coals were formed by vegetation growing in great shallow lakes which were fed by rivers flowing from the elevated terrain surrounding the lakes.

The coal seams from the South African coals are deposited in a continental depression, known as the Karoo Basin. These coal seams are relatively low and geologically undistributed.

2.2.3. Classification of coal:

Snyman, Van Vuuren and Barnard (1984: 1) classify coal into three independent methods:

- coal grade: classification based on the degree of purity (quantity of inorganic material);
- coal type: classification based on the macerals (vitrinite, exinite and inertinite); and
- coal rank: classification based on the degree of metamorphism (properties of the maceral vitrinite in a coal). Table 2.1 shows the classification of coal by rank.

CHAPTER 2

COAL: ITS PROPERTIES AND CONTRIBUTION TO FIRESIDE BOILER TUBE FAILURES

2.1. INTRODUCTION:

Coal, by its combustion, is the primary fuel used in steam generation. Combustion gases formed during combustion (CO and CO_2 ; SO_2 and SO_3 ; NO_2 and NO_3 ; and water vapor) rarely remain as individual oxides, but interact to form new complexes with fusion temperatures lower than those of the substances from which they were formed. Accelerated oxidation of the protective oxide which covers the tube, leads to a reduction in the tube wall thickness. Deterioration and final failure of the tube is then caused by the combination effects of the increased stress through the thinned wall and high tube metal temperatures (Port and Herro 1991: 121 to 129).

2.2. THE FORMATION AND CLASSIFICATION OF COAL:

2.2.1. Formation of coal:

Coal originated from the arrested decay of the remains of trees, bushes, mosses and other forms of plant life. The precursor of coal was peat, which was formed by bacterial and chemical action on the plant debris. Subsequent actions of heat metamorphosed the

1.6.3. Material defects:

Whenever a metal's thermal stability is exceeded by the environment in which the metal is used, material defect may be evident (Port and Herro 1991: 254).

1.5. THERMAL FATIGUE:

Thermal fatigue is a process which leads to tube fracture under repeated or fluctuating thermally induced stresses having a maximum value less than the tensile strength of the material (Port and Herro 1991: 176, 275-276).

1.6. DEFECTS:

Defects resulting from poor quality control, human error or poor workmanship can also cause the failure of a tube section.

1.6.1. Forming defects:

Incomplete fusion of the weldment during the manufacturing process may lead to deficient welds in welded tubes (Port and Herro 1991: 227).

1.6.2. Welding defects:

Many weld defects occur in the superheater and reheater sections. An accepted weld is one which forms smoothly flowing surface contours and is free of residual welding stresses, nonmetallic inclusions and significant porosity (Port and Herro 1991: 237).

potassium, sulphur and manganese. The elements were reported in their highest oxidation state, and their concentrations were calculated as the oxide.

Approximately 1.0 g ash sample was accurately measured, milled, dried and combusted at 850°C. The sample was cooled and mixed with lanthanum oxide and lithium metaborate. The mixture was fluxed in the LECO FX-100 fluxer.

Analyses were performed according to an ESKOM developed procedure No. 121, Rev. 1, using the Philips PW 1404 sequential X-ray Fluorescence Spectrometer with digital micro BDP 11/23 computer. Secondary X-rays which were produced by the elements present in the ash sample, were measured and the data recorded on a computer.

3.3.2.2. Mineralogical analysis of coal ash (XRD method):

X-ray diffraction is a technique in which an X-ray beam is diffracted by a sample to identify the phases or compounds present in a solid by classifying the size and type of their crystal structure. The diffracted X-rays are detected by a goniometer and recorded. The crystal lattice spacing can be calculated, and the phases or compounds present in a mineral identified by classifying the size and type of their crystal structure.

The calorific value of coal was determined according to ESKOM procedure No. 105, Rev. 1, using the DPH CP500 calorimeter. The coal was ground to a nominal topsize of 212 μm and prepared according to SABS 0135 methods.

Lower calorific values may be due to the higher sulphur contents which reduce the gross calorific value in the final calculation. During the final calculation, when determining the calorific value, a correction for sulphur content was made (0,095 MJ/kg per 1% sulphur).

3.3.2. Coal ash analysis:

Coal ash analysis and ratio calculations were performed on the laboratory-prepared coal ash from all three power stations. This was done to determine and evaluate the different coal ash qualities and to assess the slagging and fouling propensities of the coals.

3.3.2.1. Elemental analyses of coal ash (XRF method):

X-ray Fluorescence Spectrometry is a technique which uses the wavelengths or energies of X-rays emitted by a sample to identify the elements present in a solid. This method was used to determine the concentrations of major elements in the ash, namely silicon, aluminium, iron, titanium, phosphorus, calcium, magnesium, sodium,

The determination of the different forms of sulphur in coal was performed according to an ESKOM modified procedure, using the Philips PW 1404 sequential wavelength dispersive X-ray Fluorescence Spectrometer.

3.3.1.1.4. Trace elements:

The determination of trace elements in coal was performed according to an ESKOM method No. 135 Rev. 1, using the Philips PW 1414 sequential X-ray Fluorescence Spectrometer.

The coal was ground to less than 53 micron in a swing mill. The coal was then mixed with wax and milled to a fine powder and pressed with a hydraulic press into a pellet. The surface of the powder pellet was radiated with primary X-rays. Secondary X-rays were produced by the elements present in the powder pellet. Secondary X-rays were detected by the spectrometer, converted to electronic pulses and submitted to the computer where data reduction was done.

3.3.1.1.5. Calorific Value (or heating value):

The calorific value is mainly determined by its carbon and hydrogen contents and to a lesser extent by its sulphur and nitrogen contents. The better the coal quality, the higher its calorific value and the lower the ash content (Fenton, Adams and Rumsby 1962: 494).

3.3.1.1.2. Ultimate analysis:

The ultimate analysis of coal is expressed in terms of the five main constituents, namely carbon, hydrogen, nitrogen, sulphur and oxygen.

For the ultimate analysis, the coal was ground to a nominal topsize of 212 μm , prepared according to SABS 0135 methods. Carbon, hydrogen and nitrogen were determined according to an ESKOM procedure No. 110, Rev. 1, using the LECO-600 analyser. The total sulphur was determined according to an ESKOM procedure No. 104, Rev. 1, using the LECO SC-43 analyser. The oxygen content was calculated by subtracting from 100 the carbon, hydrogen, nitrogen and total sulphur contents.

The titrimetric determination of the carbonate content of coal was carried out according to an ESKOM procedure No. 100, Rev. 1, using the British Standard 1016 guidelines.

3.3.1.1.3. Form of Sulphur:

The percentages of pyritic, organic and sulphate sulphur in coal were determined. This was done to investigate the presence of fireside deposits which are caused by certain sulphur containing species.

Moisture:

Moisture is the amount of water physically associated with coal and is removable by heating to 105-110°C for 1.5 hours under standard conditions. The moisture content is then calculated from the loss in mass.

Ash:

Ash content is determined by combusting 1g of coal in a muffle furnace. The coal is heated to 815°C ($\pm 10^\circ\text{C}$) and kept at this temperature until constant mass is attained. The ash content is calculated from the mass of the residue after incineration.

Volatile matter:

Volatile matter is calculated from the loss of mass obtained by heating 1g of coal at 900°C ($\pm 10^\circ\text{C}$) for 7 minutes.

Fixed carbon:

The fixed carbon content is obtained by subtracting the sum of moisture, ash and volatile matter, expressed as percentages, from 100.

Finally, boiler tube samples were collected from different operating units from three power stations (A, B and C) for visual inspection, chemical and metallurgical analyses. Slag deposit samples were removed from the tubes for chemical analysis to determine the chemical composition of such deposits.

3.3. ANALYTICAL METHODS:

3.3.1. Coal analysis:

3.3.1.1. Proximate and ultimate analyses of coal:

The proximate and ultimate analyses were performed to determine the characteristics of the different coals supplied to the various power stations to identify any obvious problems associated therewith. This was also done to compare the coal qualities from the different coal seams.

3.3.1.1.1. Proximate analysis:

The proximate analysis of coal involves determining the percentages of four main constituents, namely moisture, ash, volatile matter and fixed carbon content.

The proximate analysis of coal was performed according to ESKOM procedures Nos. 101 to 103, Rev.1, following SARS guidelines. Coal was ground to a nominal topsize of 212 μm and prepared according to SARS 0135 methods.

CHAPTER 3

EXPERIMENTAL AND ANALYTICAL METHODS

3.1. INTRODUCTION:

Various samples were collected from three power stations for chemical and metallurgical evaluations to determine the causes and extent of associated boiler tube failures. The data was then used to establish a systematic guideline for the evaluation and investigation of fireside boiler tube failures.

3.2. SAMPLE COLLECTION:

Approximately 25 kg of raw coal sample was collected from the mills from Power Station A, Unit number 4. This was taken in increments over a period of three months to obtain a representative sample. Various analyses were performed to determine the qualities and properties of the different coals.

A fly ash sample prior to the air heater and a coarse ash sample from the ash hopper were also collected from Unit 4. This was done to determine the ash qualities and slagging propensities of the ash (possible effect on boiler tube failures) and the combustion efficiency.

2.5.5. Coal ash deposition and slagging:

Ash deposits on boiler superheater tubes are removed by sootblowers which are installed in the boiler surface. As these deposits grow and become thicker, the heat exchange potential of the tube is hampered. This could, in severe cases, lead to overheating and failure of the tube. Depending on their hardness, these deposits are often difficult to remove and sootblowing thus becomes less effective. Bryers (1988: 1-13) defined slagging as the formation of fused or sintered deposits on heat transfer surfaces in the boiler furnace. It is the result of reactions occurring when the mineral matter is heated above some critical temperature, so that a liquid phase is produced in a portion of the material.

Alkali-metal sulphates constitute a liquid phase in ash deposits. The molten sulphates wet and spread on boiler tube surface. Sulphates, in a reducing atmosphere and when in contact with carbon, are reduced to sulphides which wet and spread on any surface (Bortozzi and Soldani 1967: 1536).

The significance of the differences between Southern and Northern hemisphere coals (relatively high ash, inertinite and ash fusion temperatures, and low iron, sulphur, sodium, potassium, and chloride contents) lie in the combustion performance of the coals from the different regions. For maximum combustion, the Gondwana coals, burning well in hot, strong flames, require finer pulverising, higher secondary air temperatures and longer residence times in the boiler furnace. These modifications contribute to enhanced combustion performance (Falcon and Ham: 1988).

2.5.4. Conversion of minerals during coal combustion:

The amount of mineral matter passing through the milling and boiler plant has an inverse relationship with the heat content of coal, and the increased amounts of ash can markedly enhance furnace slagging.

The conversion of the mineral matter in coal during the combustion process is illustrated in Table 2.3 New crystalline phases (slag minerals) are formed through decomposition and reaction.

TABLE 2.3 Conversion of minerals during coal combustion (Pollmann 1967).

Mineral	Conversion	Product
FeS ₂ (Pyrite)	FeS	Hematite (Fe ₂ O ₃)
	FeS+Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	Fayalite (Fe ₂ SiO ₄)
	FeS+Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	Mercurite (FeAl ₂ O ₄)
SiO ₂ (Quartz)		Slag glass (SiO ₂)
CaCO ₃ (Calcite)	CaO+SO ₂	Anhydrite (CaSO ₄)
	CaO+Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	Anorthite (CaAl ₂ Si ₂ O ₈)
Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O (Kaolinite)		Mullite (3Al ₂ O ₃ ·SiO ₂)

2.5.3. Fusibility of coal ash:

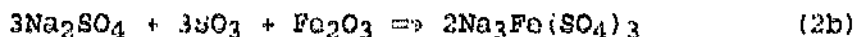
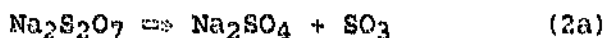
Ash fusibility is a measurement of the performance of coals related to slagging and deposit build-up (Barrett 1945: 496 to 571). Ash fusion temperatures are performed on the laboratory prepared ash in a reducing atmosphere.

Singer (1981: 3-5), Reid (1971: 106), and Winegartner (1974) observed the following characteristic fusion temperatures:

1. Deformation Temperature (DT) is the temperature at which the tip of the ash pyramid begins to show evidence of deformation.
2. Softening Temperature (ST): The softening temperature is the temperature at which the test cone under observation has deformed to a spherical form where the height is equal to the width.
3. Hemispherical Temperature (HT) is the temperature at which the ash sample fuses into a hemispherical shape. This temperature is related to conditions at which the ash shows a tendency to mass together and stick in large quantities to heat-exchange surfaces.
4. Fluid Temperature (FT) is the temperature at which the test cone flattens out to a pancake shape. This temperature is related to the temperature at which the coal ash flows from furnace walls.

Phase diagrams show which slag minerals are formed from the coal ash at certain furnace temperatures and at what temperatures they melt. The three phase diagram ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$) of Kriel bituminous coals showed that the slag mineral formed was anorthite which crystallizes and imparts great rigidity to the slag (Albrecht and Pollmann 1980). The test also revealed that all South African coals form slags when the temperature difference between the initial deformation and softening point is less than 100°C . Such ashes are particularly sensitive to low temperature differences because in a closely limited range they change their state from the solid to the liquid phase and vice versa. The ashes also crystallize rapidly out of the molten state, a characteristic feature of Kriel coal containing high calcium ashes (Pollmann 1981).

Differential Thermal Analysis (DTA) results (Shigeta, Hamao, Aoki and Kajigaya: 1987) of a synthetic ash indicated a $\text{Na}_2\text{S}_2\text{O}_7\text{+Fe}_2\text{O}_3$ sample mixture undergoing the following reaction:



The DTA curve revealed endothermic peaks at 380°C (decomposing of $\text{Na}_2\text{S}_2\text{O}_7$ by reaction (2a)) and 640°C (fusion point of $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ formed by reaction (2b)). The steep slope beyond 600°C on the Thermogravimetric (TG) curve was due to the decomposition of $\text{Na}_3\text{Fe}(\text{SO}_4)_3$.

2.4.3. Calorific value:

The calorific value of coal is the amount of heat released during combustion. Heating values as determined in calorimeters are termed high or gross heating values, and include the latent heat of the water vapor in the products of combustion (Singer 1981: 3-12).

2.5. COAL ASH:

2.5.1. Introduction:

Coal ash is the inorganic non-coal residue left after complete combustion of coal. Coal ash consists mainly of the oxides of aluminium, iron, silicon, titanium, calcium, magnesium and alkali metals. These normally account for at least 99% of the ash. The remaining 1% of coal ash contains other elements in trace amounts (Singer 1981: 3-1).

2.5.2. Chemical analysis of ash and three phase diagrams:

According to Albrecht and Pollmann (1980), the laboratory-prepared ash does not resemble either the fly ash or the slag in the furnace as both of them have been subjected to different temperature, gas and time conditions. The alkali and sulphur contents in superheater deposits may therefore be several times that of the laboratory-prepared ash.

4.2.1. Tube number 1: A/4/Sec SH In/E45/R33

4.2.1.1. Introduction:

A tube section was removed from the Unit 4 Secondary Superheater Inlet, Element 45, Row 33, from Power Station A.

Although this tube did not fail at the time, or showed no signs of having been affected by fireside corrosion, it was removed because of an extensive deposit build-up on the fireside of the tube. This tube was also seen as a good example for various analysis and investigations.

Because of the intensive deposit build-up, it was decided to perform a comprehensive study of the feed coal to Power station A, the tube metal, and also the fireside deposits.

4.2.1.2. Coal investigations:

4.2.1.2.1. Proximate and ultimate analyses, and calorific value of coal:

The proximate analysis and calorific value were performed to determine the characteristics of the coal and the amount of heat released during combustion. The results of the proximate analysis and calorific value are given in Table 4.2.

- (iii) Studies reported in the literature of other researchers applying various analytical techniques to investigate the deposit layers on the fireside of boiler tubes.

4.2. RANDOM REMOVAL OF SELECTED TUBES FOR CHEMICAL AND METALLURGICAL INVESTIGATIONS:

Three tubes were removed from different operating units from three power stations. The identification and location of the tubes are listed in Table 4.1.

TABLE 4.1 Particulars of boiler tubes investigated.

Tube #	Station	Location	Identification
1	A	Superheater	A/4/Sec SH/E45/R33
2	B	Economiser	B/1Eco/EE/R117
3	C	Side Wall	C/2/LH SW/26m

Power Station A is a 200 MW station receiving opencast coal while Power Station C is a 600 MW station also receiving coal from an opencast mine. Power Station B is a 600 MW station receiving both opencast and underground coal.

CHAPTER 4

BOILER TUBE INVESTIGATIONS

4.1.1 INTRODUCTION:

In order to propose a root cause for boiler tube failures, the causes and mechanism of such failures must be established. This can be achieved by a thorough investigation of the failed/degraded tube section and knowledge of the boiler operating conditions at the time of failure.

For the purpose of this study, fireside boiler tube investigations were based on:

- (i) Tubes selected at random from different ESKOM operating units. These tubes did not fail at the time of investigation but were selected because of ash/deposit build-up or signs of external corrosion.
- (ii) Case studies of failed/degraded tubes removed for chemical and metallurgical analyses performed by ESKOM Technology, Research and Investigations. To illustrate the complexity of the different failure mechanisms, these case studies were used to illustrate a framework for tube failure investigations. Each case study is discussed separately.

to a prescribed temperature programme, of two samples of equal mass under identical conditions, eg. heating rate, furnace atmosphere, composition, shape and size. The reference sample is an inert material which heats up in response to the furnace.

Two deposit samples from Tube number 1, the white layer and the red layer, were analysed using the Perkin Elmer Series 7 DTA (ESKOM, TRI, Report number R/00001). The furnace was connected to a Perkin Elmer TAC 7 control module which controls the heating of the furnace and the sample environment. A controlled dynamic nitrogen atmosphere of 50 cc.min^{-1} and a heating rate of 10°C was used during the investigation.

The deposit samples were subjected to a standard DTA test procedure in order to "fingerprint", on DTA curves, the thermal events undergone by each sample under the given set of conditions. The conditions of each run were as follows:

Initial temperature ($^\circ\text{C}$)	: 35
Final temperature ($^\circ\text{C}$)	: 1600
Scan rate (heating rate) ($^\circ\text{C.min}^{-1}$)	: 10
Gaseous environment	: Nitrogen

The DTA tests were performed using alumina as a diluent and also without alumina as diluent. The thermal properties before and after grinding of the white layer sample were compared and finally the DTA curves of the white layer and the red layer were evaluated.

3.5.4. Carbon analysis:

The determination of the total carbon in the deposit layers was performed according to an ESKOM procedure No. 119, Rev. 1, following the LECO CS 125 method.

The deposit samples were heated in an induction furnace in an oxygen atmosphere. The carbon in the samples oxidised to carbon dioxide, which was detected by infrared detectors. The final results were displayed as a percentage carbon.

3.5.5. Thermal analysis (TA):

3.5.5.1. Introduction:

Thermal Analysis covers a series of techniques which study the chemical and physical properties of a mixture or substance as a function of temperature or time. The sample is subjected to a controlled temperature programme.

3.5.5.2. Differential Thermal Analysis (DTA):

The difference in temperature between the sample and a reference material is recorded while both are subjected to the same heating programme. The technique involves the simultaneous heating or cooling, according

3.5.3.2.2. EDS analysis:

Energy Dispersive X-ray Spectroscopy is a microscopic chemical analysis technique which measures the characteristic energies of X-rays emitted by the atoms of an element. The separated sample layers were individually analysed with the EDS technique, using the Phillips PV9100 Energy Dispersive X-ray Analyser. This was done to identify the elements present in each sample layer and to compare these to the major and minor mineralogical phases.

3.5.3.3. Combined Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS):

The mounted, polished and gold plated specimens were studied at high magnification with a scanning electron microscope (Phillips SEM 515). High magnification photographs were taken, showing the different layers formed on the tube surfaces. While mounted in the SEM, EDS (using a Phillips PV9100 Energy Dispersive Analyser) was used to determine the concentrations of certain elements at points on the sample.

Three areas of the sample were analysed, namely the inside edge where the deposit was attached to the surface of the tube, an area from the middle of the deposit, and the outside edge which represents most recently deposited material.

3.5.3. Elemental Analyses:

3.5.3.1. X-ray Fluorescence Spectroscopy (XRF):

XRF analysis of the deposit samples was performed using a Philips PW1404 X-ray Spectrometer. This was done to identify the elements present in the different deposit layers which were removed from the tubes. These elements were matched with the mineralogical analysis results to identify the mechanism for deposit formation on the fireside of boiler tubes.

3.5.3.2. Energy Dispersive X-ray Spectroscopy (EDS):

3.5.3.2.1. Introduction:

The tubes were cut carefully in cross-section to prevent the deposit from dislodging at the edges. The samples were then mounted in clear acrylic metallographic resin and the mounted samples were then ground to expose the deposits.

The samples were then covered with a low viscosity cellulose acetate solution which was allowed to penetrate and bind the loose deposits before final grinding and polishing to a 1μ surface finish. Finally, the samples were gold sputter coated for use in the scanning electron microscope.

(ii) Tube number 2:

The deposit samples were removed for mineralogical analysis (XRD) and elemental analysis (XRF). For SEM-EDS analysis, the layers were not removed or separated from the tube.

(iii) Tube number 3:

The deposit samples were removed for elemental analysis (XRF) and mineralogical analyses (XRD).

3.5.2. Mineralogical Analysis (XRD Method):

Mechanical separation of tube deposits were carried out by scalpel. In each case the deposits were divided in portions in an attempt to separate the deposits in the respective layers. The finely ground samples were mixed with an internal standard and pressed in the form of a pellet. The samples were individually mounted on double sided adhesive tape for X-ray diffraction analysis.

The determination of major and minor phases of ash deposit layers was performed according to an ESKOM Procedure No. 116 Rev. 1. Analysis was performed by using the Philips Automated X-ray Power Diffraction System (APD PW 1700) backed up by the Philips analytical software (Version 3.5).

3.4.4. Determination of alloying elements in solid steel (XRF method):

The alloying elements in the boiler tube samples were determined according to an ESKOM procedure No. 106, Rev. 1, using the Philips PW 1404 sequential XRF spectrometer.

The polished surface of the steel specimen was radiated with primary X-rays. Secondary X-rays were produced by the elements present in the steel sample and the data recorded on the digital micro PDP 11/23 computer.

3.5. BOILER TUBE DEPOSIT ANALYSIS:

3.5.1. Introduction:

Slag deposit samples were removed by manually separating the layers from the tubes. The following approach was followed to analyse the tube deposit samples:

(1) Tube number 1:

Portions of each dried, ground and homogeneous deposit sample were used for mineralogical analysis (XRD method) and elemental analysis (EDS method). Sample portions were also used for carbon analysis, trace elemental analysis, differential thermal analysis (DTA) and pH determination.

3.4.1. Material identification:

Material identification is an important step to verify that the tube material conforms to the manufacturer's specification. A section was cut from each tube and analysed by X-ray fluorescence. The analyses results were then matched with standard boiler tube material specifications. This was done to determine the elemental composition of each tube.

3.4.2. Tube hardness evaluation:

Samples from each tube were ground and polished to a 1 μ m finish. The ground and polished samples were then subjected to the Vickers hardness measurement. A test load of 20 kg was used to determine the hardness of each tube. The tube hardness is inherently related to the material's resistance to deformation.

3.4.3. Microstructure evaluation:

The microstructure of a failed/degraded tube provides information about the thermal condition the tube was exposed to. The tube surface was prepared and polished to a 1 μ m finish. After etching with an appropriate etchant, (eg. 3% solution of nitric acid and alcohol, Nital), the samples were inspected with an optical microscope at magnifications of 50-400 times.

3.3.2.4. Ash fusion temperatures:

Coal was ground smaller than 212 micron while the coal ash, fly ash and deposits were ground to obtain a particle size of less than 75 micron. Ash fusion temperature measurements were performed according to an ESKOM method No. 125, Rev. 1, using the LECO AF 600 bomb calorimeter. The instrument has been automated by employing an electronic video system to obtain the initial deformation, softening, hemispherical and flow temperatures of coal ash, fly ash and ash deposits.

The method consists of the controlled raising of the temperature of an ash specimen, moulded in a standard pyramid shape. The tests were performed in a mildly reducing atmosphere which should always result in slightly lower (approximately 20 to 50°C) results.

3.4. BOILER TUBE INVESTIGATIONS:

Various tube samples were removed from different locations in the operating units. The main purpose of the tube investigation was to determine whether the tube complied to the manufacturer's specification at the time of failure/inspection.

The tube samples removed were subjected to material identification, hardness evaluation, microstructural examination and X-ray analysis.

The determination of the mineral phases of coal ash was performed according to an ESKOM procedure No. 116 Rev. 1, using the Philips Automated X-ray Powder Diffraction system (APD PW 1700) backed up by the Philips analytical software. (Version 3.5).

3.3.2.3. Slagging and fouling parameters:

Gray and Moore (1974), have proposed a slagging index which originates from the Nicholls and Selvig ratio where the so-called slagging index is given by the acid/base ratio (R):

$$R = \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}} \quad (1)$$

The index is given by %S/R in coal, which explains the influence of sulphur on slagging.

Incedently, the fouling index is given by:

$$\frac{\% \text{Na}_2\text{O in ash}}{R} \quad (2)$$

It must be stressed that these ratios are standards for overseas coals and only serves as a guideline to calculate or to predict the slagging and fouling propensities of the South African coal investigated.

4.2.1.4.2. Tube microstructure:

(ESKOM, TRI, OT 940 KLR/cn)

The microstructure of the tube was found to be ferrite ASTM grain size No. 8 with spheroidised pearlite and carbide dispersion. Discontinuous carbide dispersion at the grain boundaries was present.

4.2.1.4.3. Determination of the alloying elements in solid steel (X-ray Fluorescence method):

A section of the superheater tube metal was analysed to determine the elements present in the steel. The results of the most prominent alloying elements in the tube material are reflected in Table 4.12.

Although the elements detected in the coal ash (Table 4.6) are expected in a coal ash, the presence of carbon (Table 4.14) in the tube deposit suggests incomplete combustion of the coal.

Upon removal of the ash deposit, surface filings were taken from the outer 5 mm for carbon analysis. The carbon content of these filings was found to be 0,22%. This is a marked increase from the maximum specified carbon content of 0,15% (BS 3059 HPS 622). This is an indication that carbon has diffused into the tube material during service.

4.2.1.4. Boiler tube investigations:

4.2.1.4.1. initial on site inspection:

The superheater bank was visually inspected to ascertain the condition of the adjacent tubes and the tube identified for removal. The fireside of the tubes showed a thick, friable ash deposit throughout the entire tube bank (Plate 1). Upon removal of the ash deposits, a hard and more adherent inner layer was observed. These tubes were in operation for some 2.5 years.



**PLATE 1: Tube bank from a Secondary Superheater inlet,
Element 45, Row 33.**

TABLE 4.11 Trace elemental analysis.

Trace elements	ppm
Vanadium (as V)	85,3
Niobium (as Nb)	26,9
Chromium (as Cr)	186,3
Manganese (as Mn)	163,4
Cobalt (as Co)	10,6
Nickel (as Ni)	49,7
Copper (as Cu)	50,2
Zinc (as Zn)	82,3
Gallium (as Ga)	25,3
Germanium (as Ge)	14,4
Arsenic (as As)	66,8
Selenium (as Se)	7,9
Rubidium (as Rb)	32,2
Strontium (as Sr)	710,1
Yttrium (as Y)	82,9
Zirconium (as Zr)	263,5
Barium (as Ba)	888,0
Tungsten (as W)	6,7
Lead (as Pb)	78,6
Bismuth (as Bi)	11,9
Thorium (as Th)	6,0
Uranium (as U)	6,9

When the trace elemental results of coal ash and fly ash are compared, a high level of chromium, arsenic, strontium, zirconium, barium and lead enrichment in fly ash is evident.

4.2 1.4.2. Ash fusion temperatures:

The ash fusion temperatures of fly ash are listed in Table 4.10.

TABLE 4.10 *Ash fusion temperatures of fly ash.*

Parameter	Ash fusion temperature (°C)
Initial deformation	1500
Softening	1533
Hemispherical	1550
Fluid	1600

The ash fusion of the fly ash were generally higher than the fusion temperatures of the coal ash.

4.2.1.4.3. Trace elements:

According to Kirch *et al.* (1968), and Raack *et al.* (1970), the arsenic and lead content in ash is usually between 10 and 100 ppm, whereas in boiler deposits the elements may be present in concentrations of 1-5%. Lead has been found in boiler deposits in concentrations over 100 times higher than the average value in ash. The trace elemental analysis results of fly ash are listed in Table 4.11.

4.2.1.4.1. Elemental analysis:

The elemental analysis of fly ash was performed to determine the major elements present in fly ash and to compare the fly ash quality to the coal ash quality. The elemental composition of fly ash is listed in Table 4.9.

TABLE 4.9 *Elemental analysis of fly ash.*

Parameters	(%)
Silicon (as SiO_2)	47,8
Aluminium (as Al_2O_3)	29,5
Iron (as Fe_2O_3)	6,8
Titanium (as TiO_2)	1,5
Phosphorus (as P_2O_5)	0,9
Calcium (as CaO)	6,0
Magnesium (as MgO)	1,5
Sodium (as Na_2O)	0,2
Potassium (as K_2O)	0,5
Sulphur (as SO_3)	0,4

The composition of ashed coal (as analysed in the laboratory) differs from the composition of fly ash produced when the same coal is burnt in the boiler. This is due to the difference in temperature and physical conditions of burning, and fractionation of the mineral matter. When comparing the Fe_2O_3 levels in the coal ash and the fly ash, a high degree of iron enrichment is evident.

4.2.1.3.3. Ash fusion temperatures:

Ash fusion tests are empirical methods performed in a reducing atmosphere to determine the different melting temperatures of a coal ash. Ash fusion temperatures are listed in Table 4.8.

TABLE 4.8 Ash fusion temperatures of coal ash.

Parameter	Fusion temperature (°C)
Initial deform	1484
Softening	1527
Hemispherical	1546
Fluid	1565

As the difference between the deformation and softening temperatures is less than 100°C, the possibility of slagging exists for the coal tested.

4.2.1.4. Fly ash:

The fly ash was analysed to compare its quality with the coal ash quality. Fly ash results are reflected in Tables 4.11 to 4.13.

The results from the ash elemental composition indicate no obvious problems in terms of ESKOM standards. The levels of the abrasive elements in the ash is also regarded as normal for ESKOM coals.

4.2.1.3.2. Slagging and fouling parameters:

Results from coal analysis and coal ash analysis are applied to calculate the slagging and fouling parameters of coal. The calculated slagging and fouling parameters are listed in Table 4.7.

TABLE 4.7 *Slagging and fouling parameters.*

Parameter	Percentage
Acid/base ratio	9,09
Slagging index	0,091
Fouling index	0,011

The slagging and fouling indices indicate a low slagging potential of the coal tested. It is however important to note that these ratios are calculated for northern hemisphere coals and only serve as guidelines for South African coals.

4.2.1.3. Coal ash:

Analyses of ash were performed to determine the quality and properties of the ashed coal and the fly ash, i.e. the differences in major elemental composition, ash fusion temperatures and trace elemental composition.

4.2.1.3.1. Elemental analyses of coal ash (XRF method):

Ash elemental composition provides information on the abrasive properties and slagging propensity of the ash. The elemental composition of the coal ash is listed in Table 4.6.

TABLE 4.6 Ash elemental composition.

Elemental composition	
Element	(%)
Si (as SiO ₂)	58,9
Al (as Al ₂ O ₃)	27,8
Fe (as Fe ₂ O ₃)	3,8
Ti (as TiO ₂)	1,5
P (as P ₂ O ₅)	0,4
Ca (as CaO)	4,0
Mg (as MgO)	1,3
Na (as Na ₂ O)	0,1
K (as K ₂ O)	0,5
S (as SO ₃)	2,4
Mn (as MnO)	0,03
Combustible matter	2,97

4.2.1.2.4. Forms of Sulphur:

The different forms of sulphur were performed to determine the percentages of pyritic sulphur, organic sulphur and sulphate sulphur in the coal. The results of the different forms of sulphur are listed in Table 4.5.

TABLE 4.5 *Different forms of sulphur in coal.*

Sulphur form (Air-dry Basis)	Percentage (%)
Pyritic sulphur (as S)	0,54
Organic sulphur (as S)	0,06
Sulphate sulphur (as S)	0,23
Total sulphur (as S)	0,83

The total sulphur content in the coal (0,83%) is low according to ESKOM standards. Although also regarded as low, the pyritic sulphur and volatile organic sulphur are captured in the gaseous form and contribute to fireside deposits. Generally, the propensity of sulphur to form deposits is aggravated by high calcium, potassium and sodium levels.

TABLE 4.4 Trace elements in coal.

Elements	Results (ppm)
Vanadium (as V)	24,9
Niobium (as Nb)	9,0
Chromium (as Cr)	35,0
Manganese (as Mn)	32,9
Cobalt (as Co)	45,8
Nickel (as Ni)	39,0
Copper (as Cu)	30,1
Zinc (as Zn)	18,3
Gallium (as Ga)	8,3
Germanium (as Ge)	3,8
Arsenic (as As)	18,3
Selenium (as Se)	5,7
Rubidium (as Ru)	7,2
Strontium (as Sr)	168,2
Yttrium (as Y)	17,9
Zirconium (as Zr)	56,9
Barium (as Ba)	227,7
Tungsten (as W)	8,1
Lead (as Pb)	14,5
Bismuth (as Bi)	N/D
Thorium (as Th)	4,6
Uranium (as U)	5,7

According to Kirsch et al. (1968), and Raask et al. (1970), arsenic and lead have been found occasionally to be present in high concentrations in boiler deposits. Other elements, such as lithium, may play a role in the formation of aggressive deposits, but there is a lack of published data for an appraisal.

TABLE 4.3 Ultimate Analysis of coal.

Ultimate Analysis (Air-dry basis)	Results (%)
Inherent Moisture	2,9
Ash	29,1
Carbon	59,45
Hydrogen	3,61
Nitrogen	1,37
Total Sulphur	0,83
Carbonate (as CO ₂)	0,79
Oxygen (by difference)	6,95

Results from ultimate analysis proved to be within the ESKOM limits. The presence of oxygen in coal can be taken as an indication of the degree of partial oxidation of the fuel, thus reducing the amount of heat released on combustion.

4.2.1.2.3. Trace elements in coal:

In addition to the major constituent elements that make up the mineral impurities in coal, there are also a number of trace elements present in the f. 1. Trace elemental analysis were performed to determine the levels of these elements in coal and the enrichment of certain trace elements in superheater deposits. Results from trace elemental analysis are listed in Table 4.4.

TABLE 4.2 Proximate analysis and calorific value of coal.

Parameters (Air-dried-basis)	Results
Proximate analysis:	
%Inherent Moisture	2,9
%Ash	29,1
%Volatile Matter	24,4
%Fixed Carbon (by difference)	48,6
Calorific Value (MJ/kg):	23,32

Proximate analysis results show no abnormalities, although the ash content (29,1%) can be regarded as relatively high in terms of Eskom standards. The coal also has a medium calorific value (23,32 MJ/kg).

4.2.1.2.2. Ultimate analysis:

The ultimate analysis of coal was performed to determine the percentages of the basic elements in the coal, namely the sulphur, carbon, hydrogen, oxygen, and nitrogen content. The ultimate analysis results are given in Table 4.3.

XRD results showed that aluminium and silicon in the deposit layers were present as non-crystalline phases in the form of aluminosilicates or in the crystalline form as mullite. Molten aluminosilicate fly ash particles strike and react with the sticky layers on the superheater tube. Deposit layers are therefore often comprised of aluminosilicate glass. Calcium was present in the form of anhydrite which plays a vital role in the formation of the initial deposit layer. Iron was present as hematite.

EDS results revealed high levels of iron, possibly from hematite, while calcium and sulphur in the layers could be from gypsum. Chromium in the base of the metal was likely to originate from the tube material. Chromium diffuses slowly through iron oxides and therefore remains in the inner layer.

TGA results (Appendix A) showed that the peak at approximately 1358°C represents the melting of hematite in both samples. Hematite has a melting point of 1350°C to 1360°C. α -Quartz undergoes a reversible inversion at 573 °C which could not be observed because this transition is known to produce a weak peak even for the pure mineral. Anhydrite inverts to α -CaSO₄ at 1300°C and melts at 1450°C. This means that the first peak observed on both curves might correspond to the inversion of anhydrite. The third peak might correspond to the melting point of mullite or the unidentified crystalline phase detected with XRD.

4.2.1.6. Conclusion:

(1) Coal and coal ash evaluation:

Although the coal results and the coal ash elemental results were normal, the ash fusion temperatures and the slagging index indicate the possibility of slag formation.

(2) Tube metal evaluation:

The carbon content in iron fillings from the fireside surface of the tube was well above the design carbon specification. This indicates that diffusion of carbon into the tube material took place during service. This carburization phenomenon is significant in that the carbon combines with chromium present in the tube material, thereby reducing the corrosion resistance of the tube steel. The presence of carbon in the deposit layers resulted from incomplete combustion of coal.

(3) Tube deposit evaluation:

Results of tube deposit analyses showed that the ash particles were not exposed to extremely high temperatures. Also, the pH values of all the layers were above 3.5 which indicated the absence of corrosive complex sulphates such as $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ and $\text{K}_3\text{Fe}(\text{SO}_4)_3$.

The samples showed a distinct colour change when they were ground in a mortar. However, no change in the thermal properties of the samples before and after grinding could be observed. A possible explanation for this phenomenon could be that mullite, normally white in colour, encapsulates the hematite so that the red colour becomes invisible. When the sample is ground, it actually breaks the mullite encapsulation structures and the red colour of hematite becomes visible.

When comparing the results of the red layer and the white layer it was clear that three thermal events occurred above 1200°C in both samples. There appeared to be a definite relationship between the temperatures where the first and second peaks were observed in both samples while the third peak was observed at slightly different temperatures in both samples (Table 4.18)

TABLE 4.18 Peak onset temperatures of the red and white layers.

Peak #	Peak temperatures (°C)	
	White layer	Red layer
1	1207	1212
2	1357	1368
3	1387	1396

4.2.1.5.5. Determination of pH:

The pH determinations of the sample layers were performed to determine the acid or water soluble constituents within each distinct layer. Results of the pH determinations are reflected in Table 4.17.

TABLE 4.17 pH Values of deposit layers.

Deposit layer	pH value (25°C)
Black top	8,67
White bottom	8,50
Black crust	7,12
White layer	7,99
Red layer	7,70
Base	7,08

The measured pH levels of the outer layers are all in the alkaline region, thus indicating the absence of corrosive complex sulphates.

4.2.1.6.6. Thermal analysis:

(ESKOM,TRI, Report number R/00001)

DTA was used to determine the melting temperatures of the white and the red layers from tube number 1. The results proved to be more successful without using alumina as diluent.

TABLE 4.16 EDS results of deposit layers.

Element	Deposit layer (%)					
	Black top	White bottom	Black crust	White layer	Red layer	Base
Al (as Al_2O_3)	18,9	25,5	21,6	24,0	26,8	20,6
Ca (as CaO)	5,0	2,7	2,9	2,6	3,2	1,9
Cr (as Cr_2O_3)	N/D	N/D	N/D	N/D	N/D	0,7
Fe (as Fe_2O_3)	40,0	16,1	34,5	26,8	15,2	40,2
Mg (as MgO)	1,3	0,6	1,1	0,7	0,5	N/D
K (as K_2O)	0,3	0,8	0,5	0,4	1,0	0,5
Si (as SiO_2)	31,3	49,8	34,6	41,9	49,0	30,6
S (as SO_3)	1,4	2,0	3,0	1,7	2,4	2,6
Ti (as TiO_2)	1,7	2,6	1,9	2,0	2,9	1,9

Elemental results show a typical fly ash structure for all the layers. Relatively high calcium, magnesium and potassium levels were found occasionally in some of the layers.

Exceptionally high iron concentrations were found in all the layers, especially in the black top layer (40,0%) and in the base area (40,2%) of the tube.

The chromium in the base area (0,7%) could have originated from the tube metal.

The distribution of the mineral matter in the deposit layers is consistent throughout the entire ash deposit. The presence of α -quartz (SiO_2) and the absence of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) in all the samples indicates that the ash particles were not exposed to extremely high temperatures. At very high temperatures, α -quartz is converted to cristobolite while calcium oxide (CaO) combines with kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) to form anorthite. Kaolinite can also be transformed into mullite ($3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), which is regarded as a slag mineral.

Calcium in the samples was present mainly in the form of sulphates (as anhydrite, CaSO_4). The CaSO_4 plays a vital role in the formation of the initial deposit layer on superheater tubes.

Iron in the samples was found mainly as hematite, Fe_2O_3 .

4.3.1 5.4 Elemental analysis (EDS method):

Energy Dispersive X-ray Spectroscopy was also applied to determine the elemental composition of the different deposit layers. It is also useful to compare the results with the XRD results in Table 4.15. EDS results of the deposits layers are shown in Table 4.16.

TABLE 4.15 XRD results of deposit layers.

Deposit layer	Phase identified	
	Major	Minor
Black Top	Mullite Non-crystalline Hematite Alpha quartz	Anhydrite
Black Crust	Mullite Non-crystalline Hematite Alpha quartz	Anhydrite
Red Layer	Mullite Non-crystalline Hematite Alpha quartz	Anhydrite
Base	Mullite Non-crystalline Hematite Alpha quartz	Anhydrite

The ash fusion temperatures of the deposit layers were much lower than those of the coal ash and fly ash.

4.2.1.5.2. Carbon analysis:

The carbon analysis was performed to determine the carbon levels in certain deposit layers. Results of the carbon analysis are reflected in Table 4.14.

TABLE 4.14 Carbon content of deposit layers.

Deposit layer	Carbon content (%)
Black top	0,231
White layer	0,078
Red layer	0,12
Base	0,043

The presence of carbon in all the layers indicates that incomplete combustion of coal took place.

4.2.1.5.3. Mineralogical analysis (XRD):

The mineralogical analysis was performed to determine the major and minor phases present in the deposit layers. The mineralogical results of the tube deposit layers are illustrated in Table 4.15.

4.2.1.5. Chemical analysis of boiler deposits:

The fireside deposits were chemically analysed to identify the major elements present in such deposits. This was done to derive compounds or complexes which are formed during the slegging/corrosion process.

4.2.1.5.1. Ash fusion temperatures:

The melting temperatures of the deposit layers from the tube were performed to determine at which temperatures the layers melted, and also to compare these to the melting temperatures of the coal ash and the fly ash. The melting temperatures of the deposit layers are given in Table 4.13.

TABLE 4.13 Ash fusion temperatures of deposit layers.

Parameter	Ash fusion temperature (°C)					
	Black top	White bottom	Black crust	White layer	Red layer	Base
Deformation	1100	1144	1054	1093	1138	1196
Softening	1120	1148	1088	1132	1141	1197
Hemisphere	1160	1151	1134	1154	1144	1199
Fluid	1185	1213	1179	1200	1161	1220

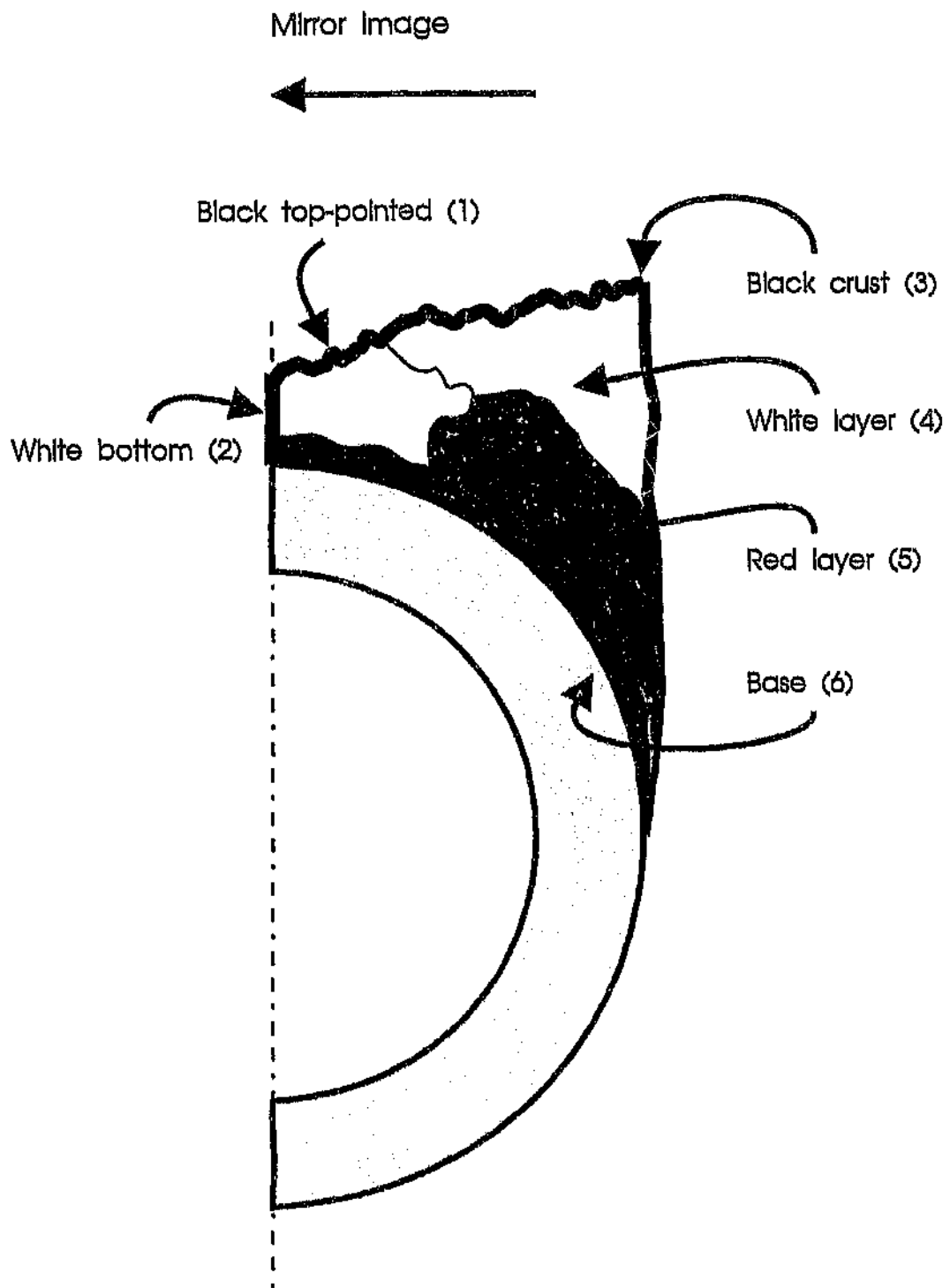


Figure 1:
Secondary Superheater Inlet,
Element 45, Row 33

a 10 mm thick ash deposit, lightly adherent and friable with no hard or glassy phase present, was observed on the fireside of the tube (Plate 2). A schematic diagram showing the accumulation and structure of the deposit layers on the tube fireside is illustrated in Figure 1.

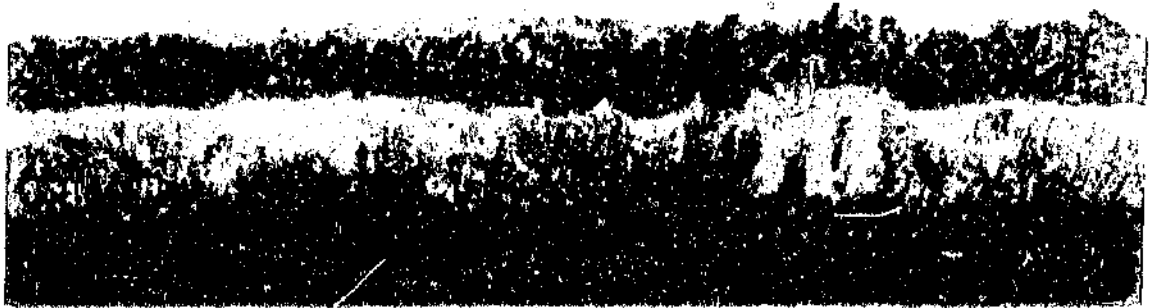


PLATE 2: Fireside surface of a Secondary Superheater inlet tube, Element 45, Row 33.

TABLE 4.12 Alloying elements in tube sample.

Element	(%)
Carbon	0,12
Chromium	2,18
Nickel	0,04
Manganese	0,45
Molybdenum	0,94
Vanadium	0,01
Silicon	0,32
Copper	0,02
Tungsten	<0,01
Titanium	<0,01
Tin	<0,01

The results of the alloying elements in the tube steel were matched with the material specification to determine the structure of the tube. This was found to be BS 3059 HFS 622, which is accepted as a very good quality steel in superheaters.

4.2.1.4.4. Tube microscopic evaluation:
(ESKOM, TRI, OT 940 KLR/cn)

The microscopic evaluation of the fireside surface revealed an oxide layer of 50-200 μm . No signs of tube metal degradation (tube cracking or oxide penetration) or metal loss were present. However, some pitting with pit depths of approximately 100 μm was observed.

Table 4.25 Case studies of failed boiler tubes.

Tube #	Identification	Reference
1	A/5/Prim SH/T24/E28	7762M2721 TN/5028/en
2	A/3/Nose tube	7762M2721 MEJ/5066/en
3	A/8/SH2/TH/F26	7762M2721 MEJ/7027/en

4.3.2. Case study number 1: A/5/Prim SH/T24/E28
(TRI, Project No. 7762M2721, TN/5028/en)

4.3.2.1. Introduction:

ESKOM, TRI performed various analyses on a section of a failed primary superheater tube from Power Station A unit 5, Tube 24, Element 28.

4.3.2.2. Tube technical specifications:

The technical data and specifications of the tube at the time of failure is as follows:

Tube operating time (hours) : 153000
Material specification : BS 3604 HFS 140

4.2.3.5. Conclusion:

The fireside of the tube was extensively corroded and the oxidation of the metal has in some areas caused a reduction of up to 50% in tube wall thickness. This observation may well indicate the relatively low resistance to corrosion of this tube structure. This is supported by XRF results which showed high iron levels in all three layers which could be from the tube metal.

4.3. CASE STUDIES:

4.3.1. Introduction:

Because of the wide variety of possible tube leaks and a combination of factors which might contribute to the failure mechanism, it is virtually impossible to cover the entire topic of boiler tube failures and their mechanisms in this study. The study will however attempt to cover some of the most common failure types occurring on ESKOM power stations.

To supplement the investigation of tubes randomly removed and analysed as described in Section 4.2, various case studies of failed tubes are discussed in this section (Table 4.25). These tubes were removed and analysed by ESKOM, Technology, Research and Investigations.

4.2.3.4. Elemental analysis of tube deposits (XRF method):

The elemental analysis was performed to determine the elements present in the tube deposits. Results of the elemental analysis are reflected in Table 4.24.

TABLE 4.24 Elemental results of tube deposits.

Elements	Deposit layer		
	Outer	Middle	Inner
Sodium (as Na ₂ O)	N/D	N/D	N/D
Magnesium (as MgO)	1,1	0,7	0,7
Aluminium (as Al ₂ O ₃)	18,3	17,4	23,0
Silicon (as SiO ₂)	24,5	24,3	34,2
Phosphorus (as P ₂ O ₅)	0,6	0,6	1,0
Sulphur (as SO ₃)	1,3	2,5	1,7
Chlorine (as Cl ₂)	N/D	N/D	N/D
Potassium (as K ₂ O)	0,4	0,3	0,5
Calcium (as CaO)	3,3	3,4	3,0
Titanium (as TiO ₂)	0,9	0,9	1,3
Chromium (as Cr ₂ O ₃)	N/D	0,6	N/D
Manganese (as MnO)	0,3	N/D	N/D
Iron (as Fe ₂ O ₃)	49,5	50,0	34,3
Arsenic (as As ₂ O ₃)	N/D	N/D	N/D

XRF results showed that all three layers had a typical fly ash composition while the high iron levels could be from the tube metal.

4.2.3.3. Mineralogical analysis of tube deposits (XRD method):

Analysis of the deposit layers was performed to determine the major and minor phases present in the deposits. The results of the mineralogical analysis are listed in Table 4.23.

TABLE 4.23 Mineralogical analysis of tube deposits.

Deposit layer	Phase identified	
	Major	Minor
Top	Magnetite Non-crystalline	Mullite Hematite Alpha quartz Gypsum
Middle	Magnetite Non-crystalline	Mullite Hematite Alpha quartz Gypsum
Inner	Magnetite Non-crystalline	Mullite Hematite Alpha quartz Gypsum

XRD results showed that magnetite and non-crystalline phases were the major phases detected while mullite, hematite, alpha quartz and gypsum were the minor phases detected in all three layers.

4.2.3.2. Alloying elements and tube microstructure:

The tube section was analysed to determine the chemical composition of the tube steel. The results of the alloying elements are reflected in Table 4.22.

TABLE 4.22 Alloying elements in tube sample.

Element	(%)
Carbon	0,14
Chromium	0,01
Nickel	0,03
Manganese	0,60
Molybdenum	0,28
Sulphur	0,018
Phosphorus	0,021
Silicon	0,27
Copper	0,01
Cobalt	0,01
Tungsten	0,01

The tube material was identified as 1,5415 15Mo3. The microstructure was a ferritic matrix with ASTM No. 8 grain size and slightly spheriodized pearlite with strings of carbides along the grain boundaries.

PLATE 4: Polychaete tubes, 30m level.

Fig. 10. Left hand side wall tube.

The top of the tube is at the left hand side of the photograph. The tube is composed of a series of segments, each of which is a single tube. The segments are separated by a series of small gaps. The tube is composed of a series of segments, each of which is a single tube. The segments are separated by a series of small gaps. The tube is composed of a series of segments, each of which is a single tube. The segments are separated by a series of small gaps.



PLATE 5: Left hand side wall tube, 30m level.

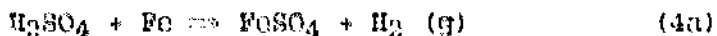
The top of the tube is at the left hand side of the photograph. The tube is composed of a series of segments, each of which is a single tube. The segments are separated by a series of small gaps. The tube is composed of a series of segments, each of which is a single tube. The segments are separated by a series of small gaps. The tube is composed of a series of segments, each of which is a single tube. The segments are separated by a series of small gaps.

4.2.3.4. Conclusions:

The spaces between the heat fins of the economiser element were covered with an adherent white deposit. Upon removal of the deposit, corrosion of the tube fireside surface was evident while slight pitting corrosion was also observed.

XRD results of the deposit layers showed that aluminium and silicon were present as non-crystalline phases in the form of aluminium silicates while calcium in the inner layer was present as gypsum (CaSO_4). Iron was present in the form of hematite (Fe_3O_4) and magnetite (Fe_2O_3) while metallic iron (Fe) in the inner layer was most probably part of the tube metal. This is supported by the visual observations that corrosion and slight pitting did indeed occur.

The XRD results of the deposit layers are complimented by the EDS results which indicated that corrosion was likely to be caused by sulphuric acid attack of the tube surface according to the following reaction:



This type of corrosion occurs in the cooler regions of the combustion system such as economisers and is caused when the tube metal temperatures or gas temperatures in the furnace are controlled below the acid dew point temperature. The presence of corrosion is also supported by a high chromium concentration in the inner layer, possibly from the tube metal.

EDS results of the deposit layers are listed in Table 4.21.

TABLE 4.21 EDS results of deposit layers.

Element	Deposit layer (%)		
	Top	Middle	Inner
Aluminium (as Al_2O_3)	8,5	7,2	N/D
Silicon (as SiO_2)	12,1	10,2	1,8
Phosphorus (as P_2O_5)	9,0	4,1	N/D
Sulphur (as SO_3)	4,3	7,2	6,2
Potassium (as K_2O)	0,2	0,1	N/D
Calcium (as CaO)	3,4	3,5	N/D
Titanium (as TiO_2)	1,0	0,9	N/D
Chromium (as Cr_2O_3)	N/D	1,3	5,6
Manganese (as MnO)	N/D	0,8	0,5
Iron (as Fe_2O_3)	61,6	64,6	85,9

The high iron concentrations in all three layers could be from hematite (Fe_2O_3) and magnetite (Fe_3O_4). The high sulphur content (6,2%) and iron content (85,9%) in the inner layer may indicate that iron sulphate (FeSO_4) might have originated from reaction of sulphuric acid (H_2SO_4) with iron (Fe) from the tube metal.

The chromium in the inner layer (5,6%) could also be from the tube metal due to corrosion of the fireside tube surface.

4.2.2.3.2. Elemental analysis (combined SEM-EDS method):

While mounted in the scanning electron microscope, Energy Dispersive X-ray Spectroscopy was used to determine the elemental composition of the deposit layers. A high magnification photograph was taken of the outer layers on the tube (Plate 4).

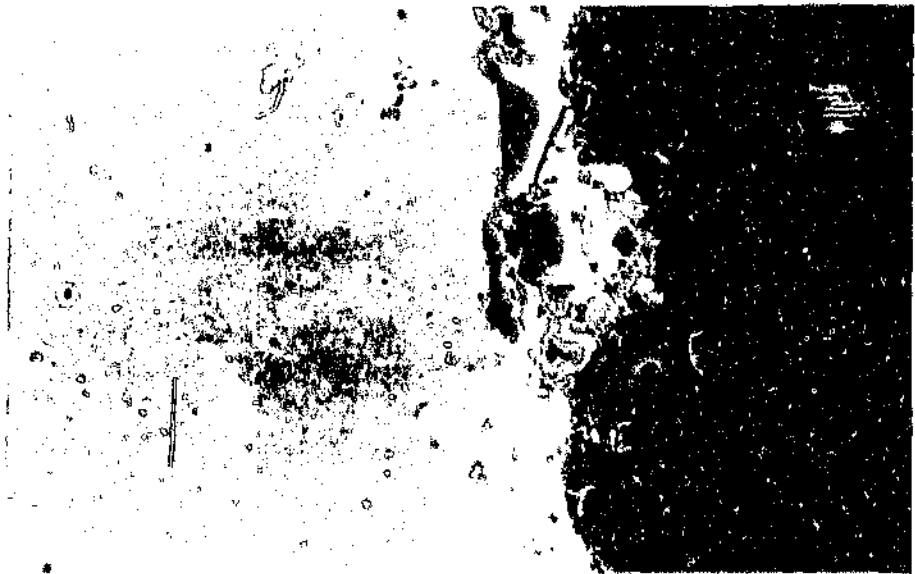


**PLATE 4: Scanning Electron Microscope image-
Economiser, Element E, Row 117.**

A thick, white fly ash deposit (left hand side) is observed on the fireside of the tube.

4.2.2.3. Chemical analysis of tube deposits;

4.2.2.3.1. Mineralogical analysis (XRD method):

The mineralogical analysis was performed to determine the major and minor phases present in the deposit layers as shown in Table 4.20.

TABLE 4.20 XRD results of deposit layers.

Deposit layer	Phase identified	
	Major	Minor
Top	Magnetite Hematite	Non-crystalline Alpha quartz
Middle	Magnetite Hematite	Non-crystalline Alpha Quartz
Inner	Magnetite Hematite	Metallic iron Gypsum Non-crystalline

XRD results show that the major phases in all three layers were identified as magnetite (Fe_2O_3) and hematite (Fe_3O_4). The minor phases in the top and middle layers were identified as alpha quartz and non-crystalline phases while the inner layer contained gypsum (CaSO_4) and metallic iron (Fe).

4.2.2.2. Alloying elements and tube microstructure:

The determination of the alloying elements in the tube steel was performed to identify the chemical composition of the tube. The results of alloying elements in the tube are listed in Table 4.19.

TABLE 4.19 Alloying elements in tube sample.

Elemental composition	
Element	(%)
Carbon	0,16
Chromium	0,02
Nickel	0,03
Manganese	1,07
Molybdenum	<0,01
Vanadium	<0,01
Sulphur	0,018
Phosphorus	0,024
Silicon	0,26
Copper	0,01
Cobalt	0,01
Tungsten	<0,01

The tube material was identified as BS3602 HF410. The tube microstructure was a ferritic matrix with ASTM No. 7 grain size and partly spheriodized pearlite with carbide dispersion along the grain boundaries.

4.2.2. Tube number 25011-B-20-23-1117

4.2.2.1. *Inspection*

The tube section was removed from the Economiser section Row 117, Unit 1, from Power Station B (Plate 3).



**PLATE 3: Fireside surface of an Economiser tube,
Element E, Row 117.**

An adherent white deposit has blocked up most of the space between the heating. Corrosion of the tube was evident beneath the deposit while slight pitting corrosion was also observed.

(iii) Corrosion mechanism:

The severe intergranular corrosion attack on the fireside surface of the waterwall tube was caused by the sulphur-bearing combustion gases in the burner furnace atmosphere. The sulphur-laden gas was also responsible for the multilayer scale on the surface and within the cracks. The composition of the scale was determined by the partial pressures of oxygen and sulphur gases. A phase stability diagram explained that iron oxide was the first deposit to form. Because of the high oxygen partial pressure required for coal combustion, a stable oxide formed in the combustion chamber, resulting in the formation of Fe_2O_3 . The decrease in oxygen/sulphur partial pressure ratio and the subsequent sulphide scale formation resulted from sulphur transportation through scale defects (sulphidation).

4.4.3. Publication number 2:

Kärner, Zygarlicka and Brodke (1994) have used scanning electron microscopy and electron microprobe analysis (SEM/EMPA) to expose the size, shape and chemistry of the individual ash particles formed when coal burns. The data was then used to predict combustion behaviour and its impact on ash deposition and tube deposits.

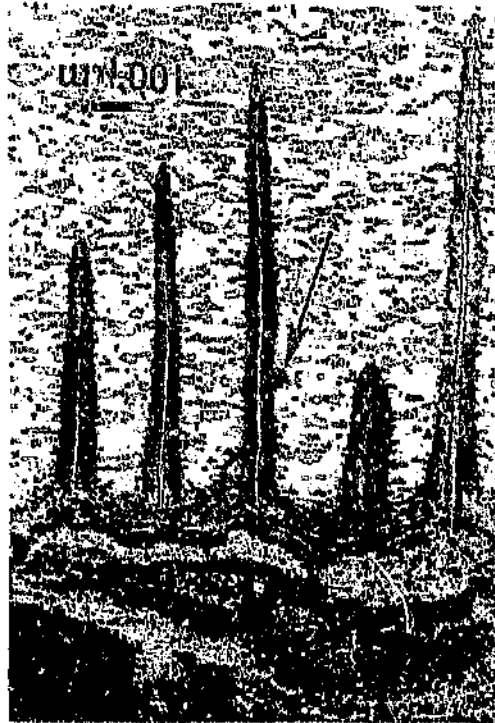


**PLATE 9: Cross-section of a circumferentially
cracked waterwall tube.**

(Smith and Mardon: 1992, from National Association
of Corrosion Engineers).

4.4. OVERSEAS PUBLICATIONS:

4.4.1. Introduction:

The investigation into boiler tube failures was further extended to research findings by overseas researchers. Publications in this regard is used to supplement and support research within ESKOM.

4.4.2. Publication number 1:

Investigations into the contribution of corrosion to circumferential cracking in waterwall boiler tubes (Smith and Marder: 1992) revealed the following:

(i) Circumferential crack macrostructure:

A circumferentially cracked boiler tube was removed from the waterwall and the fireside surface scale removed. The cracking was oriented around the outside circumference and originated at the fireside surface.

(ii) Circumferential microstructure:

A cross-sectional view of the circumferentially oriented cracks and the corrosion products on the surface and within the cracks is shown in Plate 9. A white layer in the etched microstructure and a second, darker in colour layer are observed.

4.3.4.6. Hardness evaluation:

The Vickers hardness (30 kg) of the tube was found to be 127 Hv.

4.3.5. Conclusions:

The tubes investigated were all exposed to overheating for some time. The following conclusions are made for each tube:

(1). Tube number 1:

Tube number 1 failed due to creep damage resulting from long term overheating, probably caused by partial blockage of the tube.

(2). Tube number 2:

Tube number 2 failed due to severe overheating, caused by steam starvation or external factors.

(3). Tube number 3:

Carbon-molybdenum (15Mo3) steels, as opposed to chromium containing steels (B83059/620), are susceptible to graphitization. The tube was Al killed (0,25% Al) instead of B83059/620 preselected. The 15Mo3 was susceptible to graphitization.

Wall thickness (mm) · 3,6
Design temperature (°C) : 479
Design pressure (MPa) : 13,3
Operating hours : 140 000

4.3.4.3. Visual examination:

The failure resembled three parallel wall cracks about 30 mm to 50 mm from a butt weld. The cracks also resembled brittle failure and no evidence of erosion damage was observed. Also, no pitting was observed on the inside or outside of the tube.

4.3.4.4. Chemical analysis:

Chemical analysis of the tube indicated that the tube material complied to 15Mo3 instead of BS 3059/620.

4.3.4.5. Metallography:

Examination of the parent metal with an optical microscope revealed a ferritic matrix of ASTM No. 8 grain size with a fine carbide dispersion and coarse globular carbides on the grain boundaries. The pearlite was spheroidised and fairly decomposed.

A2 (400 mm remote of rupture) showed small grained ferritic matrix with globular carbides on the grain boundaries and partly spheriodised pearlite. No creep voids were observed.

4.3.3.6. Tube hardness evaluation:

The Vickers hardness (20 kg) of the tube (remote of rupture) was found to be 162 Hv.

4.3.4. Case study number 3: A/8/SH 3/TH/E26 (TRI, Project No. 7762M2721, MBEJ/7027/en)

4.3.4.1. Introduction:

A failed tube section of Unit 8, Superheater 3, tube H (in the dead space near the outlet header), Element 26, from Power Station A, was analysed by ESKOM, TRI.

4.3.4.2. Tube design dimensions:

The tube design dimensions and operating conditions of the tube at the time of failure are as follows:

Material specification : BS 3059/620
Outside diameter (mm) : 31,8

4.3.3.3. Optical microscopic evaluation:

An optical microscope was used to measure the penetration depths of some pits on the steamside of the tube. Pit depths of up to 1,1 mm have been measured.

4.3.3.4. Tube wall thickness measurement:

A vernier caliper was used to measure the outside diameter and minimum wall thickness of the tube (remote of rupture). This was given as 66,7 mm and 5,5 mm respectively.

4.3.3.5. Metallographic evaluation:

The two areas, A1 and A2, were evaluated with an optical microscope:

Area A1 (at the thin lip rupture) revealed a decomposed microstructure consisting of a small grained ferritic matrix with coarse globular carbides on the grain boundaries and spheroidised pearlite. No evidence of martensite could be found at the fracture edge. This indicates that temperatures did not rise above austenitization temperatures. It is believed that temperatures were in the region of 600°C to 700°C where the yield stress of the material is low.

The remainder of the failed section consisted of thick shear lips (Plate 3). No signs of corrosion damage in this area were evident. The remainder of the tube showed several pittings in the area of the largest pitting leading to reduced wall thickness resulting in local failure since the tube was stressed to higher levels in the pitted area, by the internal pressure.



PLATE A: Failed boiler nose tube. Note the thick fracture l.p.

(PPD), Project 90, 17042, 21, 1134, 5000, etc)



PLATE 6: Failed boiler nose tube.

(PPL) Project No. 17642/24, MRB 60667011

4.3.2.6. Tube hardness evaluation:

The Vickers hardness (30kg) of the tube was given as 117 Hv in the locality of the crack, and 136 Hv on the undamaged part of the tube.

4.3.3. Case study number 2: A/3/Nose tube (TRI, Project No. 7762M272I, MEJ/5066/cn)

4.3.3.1. Introduction:

ESKOM, TRI performed various analyses on a section of a failed nose tube section from Unit 5, Power Station A. The tube technical data and specifications at the time of failure is as follows:

Tube operating time (hours)	: +156000
Material specification	: BS 3059/440
Outside diameter (mm)	: 63,5
Wall thickness (mm)	: 5,89
Operating temperature (°C)	: 326
Operating pressure (MPa)	: 11,7

4.3.3.2. Visual examination:

A longitudinal burst, ±250 mm long and ±200 mm from a bend in the tube was present in the tube section (Plate 6).

Outside diameter (mm) : 57,15
Wall thickness (mm) : 5,385
Operating temperature (°C) : 410
Operating pressure (MPa) : 13,1

4.3.2.3. Visual examination:

Visual examination of the tube section revealed fine cracks in the longitudinal direction, some penetrating the tube wall. The cracks extended over a distance of approximately 23 cm. The cracked side also showed thick ash deposits.

4.3.2.4. Metallographic evaluation:

A replica at the cracked area showed a decomposed microstructure consisting of a ferrite matrix of ASTM grain size, with a fine carbide dispersion in the grains and globular carbides on the grain boundaries.

4.3.2.5. Creep exhaustion calculations:

Creep exhaustion calculations showed little anticipated creep exhaustion, whilst the microstructure at the cracked area revealed extensive creep damage resulting from long term overheating, probably caused by partial blockage of the tube.

The coal seam data, in conjunction with previous experience with coal from the same source, can be used in efforts to avoid both slagging or fouling problems. The following information is recorded to evaluate the coal quality and to identify the impurities in coal:

Overview of coal seams

Proximate and ultimate analyses of coal

Mineralogical content of coal

Forms of sulphur in coal

Calorific value of coal

Trace elements in coal

Coal petrographic analysis

The coal information is imperative in building up a coal data base, especially for power stations with a history of slagging and foiling problems. The data base will also assist in the prediction of future coal qualities where trends are available.

5.2.4. Slagging and fouling experience and data:

5.2.4.1. Coal ash quality:

The following data is recorded to assess the slagging and fouling propensities of coal ash:

Ash elemental analysis

Ash fusion temperatures

Frequency of occurrence of slagging or fouling.

5.2.2. Tube failure background information:

To determine the cause(s) of boiler tube failures/deterioration, the following information regarding the failed or degraded tube is recorded:

Date of tube failure

Previous failures in this section

Sectional sideview with tube location

Tube operating hours (since commissioning date)

Material specification

Dimensional specification

Tube metal temperature

Tube metal stress

Tube metal thickness

Tube metal microstructure

Tube design and operating pressure

Major modifications performed in the area concerned.

5.2.3. Coal supply and quality:

In this step the quality of the coal supplied to the operating unit is evaluated to determine any obvious problems associated therewith or any changes in quality over a certain period. According to Hatt (1986: 79 to 87), variations in the composition of the feed coal can lead to a variety of boiler problems.

Fouling tendencies are aggravated when operating at full load. This is a result of more intense combustion at higher flame temperature caused by firing more coal. Parameters frequently identified as being important are the following:

- Unit load and pressure*
- Boiler steam flow*
- Boiler outlet steam pressure*
- Boiler outlet steam temperature*
- Levels of carbon monoxide (CO) in flue gas*
- Excess oxygen*
- Fineness of pulverized coal*
- Fuel burner maintenance*
- Proper coal and air distribution among burners*
- Condition and position of fuel burners*
- Wall blower operating frequency*
- Condition and position of wallblowers and sootblowers.*

The following boiler parameters are influenced by coal properties and should also be recorded:

- Furnace exit gas temperature*
- Heat release per unit furnace plan area*
- Spacing of convection tubes*
- Flue gas flow pattern and velocity*
- Flue gas temperature*
- Number of wall and sootblowers.*

5.2.1.1. Boiler design parameters and operating conditions at the time of failure discovery:

Boiler design and boiler operating conditions are important parameters for predicting the performance of different coals more accurately than conventional fouling and slagging indices based on coal quality characteristics alone. These include:

*Number of operating units
Manufacturer and type of boiler
Operating hours of boiler
Number of boiler start-ups.*

5.2.1.2. Boiler operating conditions at time of failure discovery:

Apart from the mineral matter content in coal, the deg sitional behaviour of coal ash is also influenced by boiler operational parameters. Incomplete combustion of coal results in a loss of coal energy in the form of unburnt carbon and carbon monoxide (CO) in the flue gas. The CO content of the flue gas increases rapidly when the excess oxygen falls below 3%.

Coal burning rate can influence fouling which can be due to the particle size distribution of the coal, the excess air and the fuel-air distribution. The fouling behaviour of coal is also influenced by the boiler load.

5.1.6. Tube packaging and transportation:

The section of the failed or degraded tube is wrapped in plastic sheeting with the tube ends covered with sealing tape. The tube is then transported to the chemical and metallurgical laboratories in such a way that the integrity of deposits is preserved. A covering letter with tube information or any unusual conditions or events which were noted prior to, during, or after the failure, must accompany the tube to the laboratory.

5.2. STEP 2: BACKGROUND INFORMATION AND TUBE FAILURE HISTORY

This step requires data of the boiler where the tube degradation/failure occurred as well as background information of the tube removed. Other information include the quality of fuel supplied to the operating unit and a history of past boiler tube failures.

5.2.1. Boiler data:

Boiler data and operating conditions provide information on processes and environments to which the coal and ash may have been exposed.

5.1.4. Initial on-site examination:

Visual examination of the surrounding tubes not only provides data on the causes of degradation or failure, but determines where repairwork is to be done. This is also done to determine whether any tubes adjacent to the failed tube were damaged as a result of a secondary failure mechanism. A careful examination of adjacent tubes is warranted to assure that steam cutting has not occurred and that another tube failure is not imminent. Details of failure appearance on the tube include:

Appearance of fracture surface

Appearance and texture of fire-side deposits.

Repetitive failures in the same local area warrant further failure investigation, and failed tube specimens are required for laboratory examinations.

5.1.5. Removal of failed or degraded tube:

Approximately one metre of tubing is removed from the boiler, using electric grinders or saws. The tube should be protected against overheating. Once the sample has been selected, it should be handled with care to preserve as much information about the failure mechanism as possible.

5.1.2. Location of failed or degraded tube:

The location of the tube is identified and logged into a computer data sheet or boiler tube log sheet.

Power Station

Unit number

Boiler section

Elevation

Assembly

Row number.

5.1.3. Labelling and codification of failed or degraded tube:

The tube is clearly marked by placing an identification tag on the tube. Identification codes characteristic to that specific power station unit is useful, eg.:

Power Station/Unit #/Section Assembly/Row #.

The sample orientation is marked on the tube prior to removal:

Gas flow direction

Water flow direction.

Photographs of the entire tube bank or adjacent tubes can provide useful information regarding the specific boiler section.

CHAPTER 5

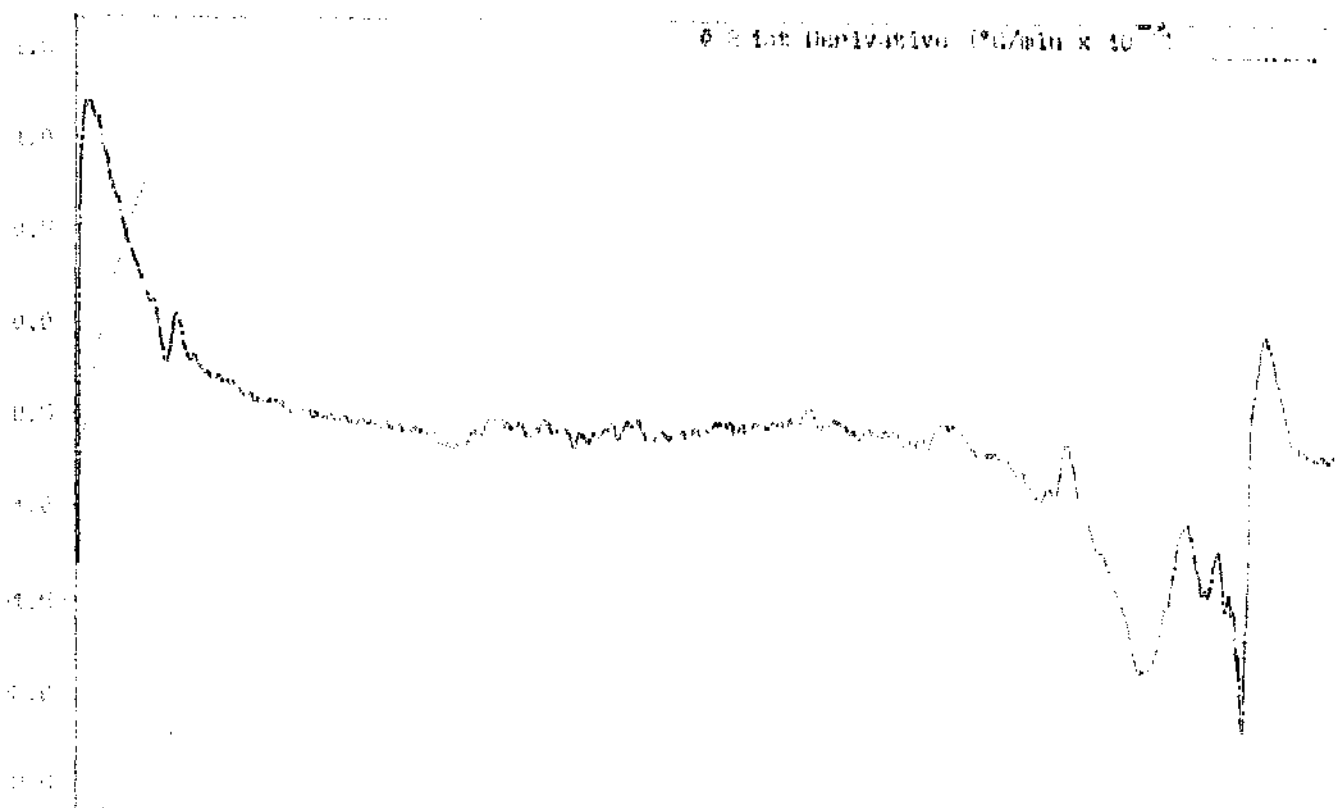
ROOT CAUSE FOR FIRESIDE BOILER TUBE FAILURES

In order to identify the possible causes of fireside boiler tube failures, a comprehensive set of results and observations must be available to the investigator for meaningful conclusions and recommendations. The boiler tube failure root cause verification method include the gathering of physical evidence or data by determination of critical parameters or the studying of the available facts through a systematic problem analysis. By combining the information from the literature studies, the tube investigation results and the case studies, the following steps and guidelines for fireside boiler tube investigations are presented:

- Step 1: Removal of the failed or degraded tube and the documentation of available data and observations
- Step 2: Documentation of background information and the current status of the plant
- Step 3: Chemical and metallurgical evaluation of the tube sections removed
- Step 4: Identification of the failure mechanism.

It is important to note that the abovementioned steps are based on some of the general, most frequent fireside tube failures studied, and will thus not necessarily suit the need of all investigations.

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4.5. FINAL CONCLUSION:

It is clear from the tube investigations, case studies and overseas publications that a thorough investigation is required to identify the failure mechanisms of fireside boiler tube failures. The investigation needs to be structured and a systematic approach must be followed to gather the relevant data and to prevent duplication of analyses.

Different tube failure mechanisms occurred on the power stations researched. These varied from corrosion/erosion to overheating, tube defects and thermal fatigue. In most cases, each tube failure required its own individual investigation.

Modern analyses techniques are recommended for studying ash deposits and slags on the fireside surface of boiler tubes. SLM is regarded as a useful tool for viewing fracture surfaces and for determining the mode of fracture. EDS is used to identify the elements present in fireside deposits through analysis of the bulk deposit. This is done by performing EDS directly on a large area of the tube surface or a cross-section through the deposit. X-ray analyses are used for elemental and mineralogical analyses of deposits while SEM/EMPA are effectively applied to analyse complex ash fouling products.

SEM/EMPA has outstanding potential for analysing complex ash-fouling materials in the deposition stage. The products of ash-fouling processes are easily identified, quantitatively described and traced through combustion systems.

Karner et. al. have suggested four steps to solve the problems of deposit formation on boiler tubes:

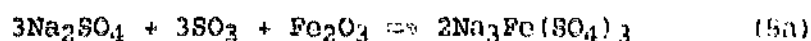
- (i) Step 1: The critical boiler zones where ash deposition occurs, is identified.
- (ii) Step 2: Micro-analysis is used to determine the fouling mechanisms by identifying key inorganic coal components that interact in the combustion environment to form ash deposits.
- (iii) Step 3: Operational parameters are optimised through the mechanistic insights gained through micro-analysis. The causes of potential and, actual fouling when combined with combustion experience, is effectively highlighted with SEM/EMPA.
- (iv) Step 4: Computer models are used to solve complex boiler fouling mechanisms as well as in cases where deposit buildup is severe. This technique is used to integrate relevant information which is then used to select the appropriate coal and changes in operating conditions.

indicates the presence of corrosive complex sulphates.

The thin middle layer, white to yellowish in colour, contains complex alkali-iron sulphates such as $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ and $\text{K}_3\text{Fe}(\text{SO}_4)_3$, identified by X-ray analysis. This layer often contains higher levels of sodium, potassium and sulphur than does the parent coal ash.

The tightly bonded black, inner layer is composed primarily of corrosion products, i.e. oxides, sulfides and sulphates of iron, and other alloying elements in the boiler tube steel.

The presence of sulphur in the ash deposits indicates that the propensity for coal ash corrosion exists. Liquid ash corrosion involving alkali-iron trisulphates would be expected of coal ash constituents having melting points between 552°C and 621°C. An endothermic peak at 640°C on a DTA curve indicates the fusion point of $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ formed by reaction (5a).



A steep slope beyond 600°C on a TG curve indicates the decomposition of $\text{Na}_3\text{Fe}(\text{SO}_4)_3$.

Corrosion rates are high on superheater and reheater tubes where the temperature ranges between 593°C and 704°C. Upon removal of the fireside deposit, the corroded regions will have a pitted corrosion pattern

Metallographic examinations of the failed tube may also reveal that impingement of the high velocity fly ash particles has caused microscopic plastic deformation on thinned tube surfaces.

5.4.3.2.2. Sootblower erosion:

Metal surfaces are normally smooth and only a thin oxide layer (if any) normally occurs if attack is fresh. Deposits and oxides will cover thinned surfaces if attack is old or intermittent. Thinned surfaces often show shallow wavelike striations, aligned perpendicular to steam flow across the fireside surface. Bulging is usually absent while rupture edges are normally thin and ragged.

5.4.3.3. Fireside corrosion:

5.4.3.3.1. Coal ash corrosion:

Overheating may lead to accelerated oxidation of the tube fireside to produce thickened, hard scales. Corrosion is associated with deposits that are strongly bonded to the metal surface. Such deposits consists of three distinct layers:

The outermost outer layer is a bulky layer with elemental composition similar to that of fly ash. A measured pH of this layer around 3,5 positively

5.4.3.1.2. Short term overheating:

Metallographic examinations are normally applied to identify the presence of short term overheating. Sectioning of the tube is required for microscopic examination. The following factors are often present in failures caused by short term overheating:

- bulging
- uniform tube expansion
- violent rupture: A thick-walled longitudinal rupture may be caused by very rapid overheating. Virtually identical tube circumferences can be present at the rupture and away from the burst. Such failures sometimes occur when temperatures exceed 730°C. Short term overheating in which bulging occurred before rupture may also produce a longitudinal fish-mouth rupture
- absence of thick waterside deposits and magnetite layers
water chemistry should not play a significant role in this type of tube failure.

5.4.3.2. Erosion:

5.4.3.2.1. Fly ash erosion:

Inspection of the rupture site of the tube reveals no overheating or corrosion while fireside deposit layers are often much thinner on wasted regions.

5.4.3.1.1. Long term overheating:

The occurrence of long term overheating can best be ascertain by metallographic examination of the failed tube while visual inspection is required to identify bulging, oxidation, or spalling.

Tubes subjected to long term overheating are either ruptured or bulged. The rupture is almost always longitudinal with a fish-mouth shape. Bulging and a thin-lip rupture indicate severe overheating. The absence of martensite at the edge of the thin lip fracture indicates that the temperatures did not rise above austenitization temperature. Metal temperatures are generally higher at bulges than in the surrounding metal area.

A thick, brittle magnetite layer near the failure indicates that deposits have insulated the tube wall from cooling effects of the water. Internal deposits are often hard and stratified and tend to show multiple layers of different colour and texture. The inner layer attached to the tube surface is harder and more tenacious.

Cracking of the fireside scale and deformation of the grains on the fireside indicate the deformation of the fireside of the tube. Spalling of the oxide layer at the bulge results in tube wall thinning in the failed area.

the main component of the porous slag. Quartz, under very high temperature conditions, becomes part of the aluminosilicate glass.

Phosphorus in the apatite mineral ($\text{CaF}_2 \cdot 3\text{Ca}_3\text{P}_2\text{O}_8$) can volatilize under suitable conditions to form P_2O_5 , a high temperature cement in slag deposits. Deposit formation is also a function of the boron and fluorine contents in the coal.

5.4.3. Tube failure mechanism:

The following most frequent failure mechanisms experienced in ESKOM boilers were derived from the literature, chemical and metallurgical investigations, case studies and overseas publications (Southwest Research Institute 1985: 5-1 to 5-14; Port and Harro 1991: 29 to 55, 192 to 202; and ESKOM, Technology, Research and Investigations):

5.4.3.1. Creep rupture (Stress rupture):

Failure due to creep exhaustion is revealed by the microstructure of the tube. Creep rupture usually produces a thick-lipped rupture at the apex of a bulge. The rupture will be large with a fish-mouth shape or a small longitudinal fissure at the apex or a oxidized bulge will be present. The microstructure and magnetite layer at the bulge indicate that extremely high temperatures were experienced in this area.

5.4. STEP 4: IDENTIFICATION OF FAILURE MECHANISMS

5.4.1. Introduction:

The investigation into boiler tube failures has the potential to determine the root cause of slagging problems or specific tube failures/deterioration. Furthermore, the root cause can lead to the implementation of corrective measures which could eliminate or reduce the possibility of a recurrence.

5.4.2. Slag formation:

Where deposits are present on the fireside of a tube, distinction must be made between slag deposits (molten deposits) and fouling deposits (deposits bonded by sulphate salts).

Slag formation can normally be expected when the temperature difference between the initial deformation temperature and the softening point of the coal ash is less than 100°C. A high acid/base ratio, calculated from the ash elemental composition, indicates a high slagging index for the same coal ash.

The absence of quartz (SiO_2) and the presence of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) in slag deposits indicate that the coal ash particles have been exposed to extremely high temperatures. Anorthite is only formed under very high temperature conditions and crystallises to form

5.3.9.2. Chemical analysis of boiler deposits:

Different analyses techniques for tube deposits are listed in Table 5.2.

TABLE 5.2 Analyses techniques for fireside boiler deposits.

Analysis Technique	Determination
X-ray Diffraction (XRD)	Mineral or crystal (minor/major) phases
X-ray Fluorescence (XRF)	Elemental content
Scanning Electron Microscopy (SEM)	Specimen surface topography
SEM combined with Energy Dispersive X-ray Spectroscopy (Combined SEM-EDS)	Elemental content of elements with atomic numbers above ten
Spectrochemical analysis	Major, minor and trace elements
Atomic Absorption	Acid or water soluble constituents
Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)	Melting temperatures, phase identification of each layer
Electron probe microanalysis (EPMA)	Deposit composition
Wavelength Dispersive Spectroscopy (WDS)	Deposit elemental distribution

In slags, bonding is produced by melting or fusion of the ash particles. In fouling deposits the ash particles are bound together by sulfate salts (Babcock and Willcox 1973; and Hatt and Rimmer 1989: 40 to 44).

TABLE 5.1 Megascopic deposit classification system
(Hatt and Rimmer 1989: 41).

Deposit	Category	Properties
Molten deposits	Metallic	Commonly derived from pyrites during combustion under reducing conditions
	Amorphous	Found in high temperature zones of the boiler and with low fusion coal
	Vesicular	Amorphous slag
	Sintered	Partially fused particles commonly found in boiler convection zones
Fouling deposits	Very strong	Cannot be broken with the hands, only with a tool
	Strong	Can be broken with hands but does not crumble
	Weak	Deposits crumble when handled
	Unconsolidated	Dust accumulation

5.3.7. Removal of the fireside deposits and separation of the different layers for analysis:

The objective of sampling and analysis of boiler deposits is to determine their formation mechanism. Where a specific deposit is constituted of various layers, special care must be taken to separate these layers as accurate as possible.

5.3.8. Surface morphology of the tube fireside surface:

The morphology of the fireside deposits provides key information about the mechanisms responsible for erosion and corrosion.

5.3.9. Characterization and chemical analysis of deposits:

It is advisable to obtain more information about the physical nature of a deposit before the various analyses of the deposits are performed.

5.3.9.1. Deposit classification system:

Visual examination of the fireside deposit provides the first clues of the cause and extent of the deposit. Table 5.1 classifies deposits as either slag deposits or fouling deposits.

5.3.4. Removal of a tube section for material identification:

Tube material identification is an important step in order to verify that the tube material conforms to the manufacturer's specification. This also determines whether the designed tube material was installed during boiler construction, and whether the designed material is appropriate for the boiler operating conditions. The X-Ray Fluorescence Spectrometry (XRF) technique is normally applied for tube material identification.

5.3.5. Metallographic evaluation of tube sections:

The following tube data is required for metallographic evaluation:

Microstructural degradation
Pitting (pit shape and pit depth)
Crack or cavity morphology
Tube wall thinning
Presence of welds and bends
Texture and thickness of fireside deposits.

5.3.6. Tube hardness evaluation;

Tube hardness evaluation provides information regarding the changes in the tube material structure. The Vickers hardness tester can be used for this measurement.

5.3. STEP 3: CHEMICAL AND METALLURGICAL EVALUATION OF TUBES SECTIONS

This section describes the features of the tube and its fireside deposits which uniquely identify the dominant damage modes which were active.

5.3.1. Tube log-in:

On its arrival at the chemical laboratory, the boiler tube section is provided with a tag containing its serial number and other useful information.

5.3.2. Chemical and metallurgical examination route:

A systematic boiler evaluation plan is developed to ensure that all required analyses are accurately performed by following a logic route through the laboratory and also to prevent duplication of analysis.

5.3.3. Visual examination and photo documentation of the as-received tube:

Visual examination of the failed tube can give the investigator a rough idea of the most likely causes of the failure. This can then be verified by further investigations. Colour photographs are taken to highlight a specific area of interest, eg. bulging, rupture, ash build-up or pitting.

5.2.4.2. Calculation of slagging and fouling indices:

Slagging and fouling problems that occur in coal boilers are complex because the mechanisms by which the deposits are formed are complex. Deposit problems can also originate from the coal, the boiler design, or boiler operating conditions. The following ratios can predict slagging and fouling tendencies:

Base/acid ratio

Slagging index

Fouling index.

5.2.5. Boiler tube failure history:

A record of previous tube failures for each unit should be kept and updated for each power station, eg.:

Power station	Unit #	Area of failure	Cause of Failure	Date of failure

By logging this information, a tube failure trend can be established for each unit as well as the total failure per annum per power station.

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Borio, R.W., Drumley, A.L., and Sylvester, W.R., "Control of High-Temperature Metal Wastage in Pulverized Coal-Fired Steam Generators." Combustion Engineering Publication, from "Ash Deposits and Corrosion due to Impurities in Combustion Gases," R.W. Bryers, Livingston, New Jersey, 168 to 169, 1977.

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Cold-end corrosion:

Normal location in boiler: Air heaters/economisers
Most common primary features: Presence of fireside deposits/corrosion products

Common examination techniques: XRD

Possible causes/contributing factors: Acid attack due to condensation of H_2SO_4

Usual remedial actions: Control excess air, control metal temperatures and flue gas temperatures.

Defects:

Normal location in boiler: Boiler tube sections

Most common primary features: Internal voids/cracks, pin hole burns, material deficiency (tube rupture)

Common examination techniques: Nondestructive testing techniques, visual examination

Possible causes/contributing factors: Defective/wrong tube material, poor workmanship, tube contraction or expansion

Usual remedial actions: Good workmanship, tube material comply to designed specification, proper quality control/quality assurance.

Coal ash corrosion:

Normal location in boiler: Superheaters and reheaters
Most common features: Typical fireside deposit, tube metal wastage, pitted corrosion patterns, tube microstructural degradation (tube rupture)
Common examination techniques: XRD, XRF, DTA, SEM EDS
Possible causes/contributing factors: High levels of Na, K, S, and Fe in coal [Na_2 or $\text{K}_2\text{Fe}(\text{SO}_4)_3$ complex], high tube metal temperatures
Usual remedial actions: Fuel treatment additives, pad welding or thermal spray coatings.

Oil ash corrosion:

Normal location in boiler: Superheaters and reheaters
Most common primary features: Presence of corrosive slag
Common examination techniques: Measurement of melting points of fireside constituents
Possible causes/contributing factors: High levels of Na, V and S in oil, excess amounts of excess air for V_2O_5 formation, high tube metal temperatures
Usual remedial actions: Fuel treatment additives, low excess air to retard V_2O_5 formation, control tube metal temperatures below 593°C .

Water wall corrosion:

Normal location in boiler: Burner/windbox area
Most common features: Circumferential cracks, carbon particle impingement or direct flame impingement
Common examination techniques: XRD, DTA, EDS, IOM, NPM, WDS
Possible causes/contributing factors: High CO levels in flue gas, high carbon content in ash, and high chloride levels in coal
Usual remedial actions: Improve burning efficiency.

Short term overheating:

Normal location in boiler: Superheaters and reheaters
Most common primary features: Uniform tube expansion, bulging, violent rupture
Common examination techniques: Tube metallographic and microscopic examinations
Possible causes/contributing factors: High tube metal temperatures (caused by steam starvation)
Usual remedial actions: Optimal boiler operation.

Fly ash erosion:

Normal location in boiler: Economisers, superheaters and reheaters
Most common primary features: Polished flat spots, reduction in tube wall thickness
Common examination techniques: Tube metallographic examination and visual inspection
Possible causes/contributing factors: High velocity fly ash particles striking the tube
Usual remedial actions: Pad welding or spray coating, installation of baffles or screens.

Sootblower erosion:

Normal location in boiler: Tubes near wall entrance or wall blowers
Most common primary features: Thin, ragged rupture edges, smooth metal surfaces (flat spots), absence of bulges
Common examination techniques: Visual examination and ultrasonic tube wall thickness measurements
Possible causes/contributing factors: Malfunction of sootblowing system
Usual remedial actions: Alignment of sootblowers, spray coating or pad welding.

5.4.4. Conclusion:

By combining all the conclusions, case studies, publications, and literature information referred to in chapters 1 to 5, some important information required for fireside boiler tube investigations are summarised in Table 5.3:

TABLE 5.3: Summary of fireside boiler tube information

Slag formation:

Normal location in boiler: Superheaters and reheaters

Most common primary feature: High slagging index

Common examination techniques: XRD, XRF, DTA, EDS, SEM, SEM-EDPA

Possible causes/contributing factors: Buildup of molten coal ash deposits on fireside boiler surfaces

Usual remedial actions: Effective sootblowing and sootblowing programmes.

Long term overheating:

Normal location in boiler: Mostly wall tubes, reheaters, and superheaters

Most common primary feature: Tube rupture is normally preceded by single or multiple bulges

Common examination techniques: Visual inspection and metallographic examination

Possible causes/contributing factors: Overheating caused by deposits insulating the tube

Usual remedial actions: Good water chemistry to prevent internal deposits, optimal boiler operation.

5.4.3.4. Defects (Port and Herro 1991: 227-254):

5.4.3.4.1. Welding defects:

Sharp edges at the weld-tube interfaces, which remained after the welding process, act as stress raisers which could initiate cracking. A failed tube may also show a pin hole burnt through the tube wall from the outside to the inside, caused during welding of adjacent tubes. Weld failures in a heat affected zone may be caused by contraction and expansion of the tube.

5.4.3.4.2. Forming defects:

Seam or lap defects in seamless tubing may occur in unwelded tubes as a result of internal voids or cracks, or as a result of faulty methods or steel rolling in the steel mill.

5.4.3.4.3. Material defects:

The sealing temperature and the susceptibility to creep are the two critical factors in materials deficiency. This typically involves the use of unalloyed carbon steel in superheaters and reheaters where low-alloy steels would be required (Port and Herro 1991: 254).

(iii) Wavelength Dispersive Spectroscopy (WDS):

WDS element X-ray mapping showed the iron and sulphur elemental distribution in the two layers. The region of the crack possessed a high sulphur concentration while the centre region also contained iron but not to the degree of the surrounding scale.

(iv) Energy Dispersive X-ray spectroscopy (EDS):

EDS results of both layers revealed that iron and sulphur dominated the corrosion product with minimal contribution from other elements, eg. chromium and aluminium.

(v) X-ray Diffraction (XRD):

XRD results of deposit samples indicated that the outer scale contained mullite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and hematite, Fe_2O_3 . No sulphur was detected, probably due to the large background intensity, resulted from contaminants in the outer layer, eg. unburnt coal particles.

S.4.3.3.4. Cold-end corrosion:

By using XRD, cold-end corrosion may be revealed by the presence of fireside deposits and corrosion products as hydrated iron sulphate (Port and Herro 1991: 149). The fireside of the tube will be pitted where corrosion has occurred.

5.4.3.3.3.2. Circumferential cracking:

Circumferential cracking with deep, finger-like penetrations may occur if corrosive ash and cyclic thermal stresses are both present. The cracking is oriented around the outside circumference of the tube and originates on the fireside surface (Electric Power Research Institute 1993: 3 - 156, TR- 102433-VI; and Smith and Marder: 1992).

Smith and Marker (1992) used the following analytical techniques to study the fireside of a 0,5Cr-0, 5Mo and 2,25Cr-1Mo low alloy waterwall tube:

(i) Light optical microscopy (LOM):

A cross-section view of the circumferentially oriented cracks showed that the crack in the centre of the micrograph had a secondary crack branch propagating perpendicular to the original crack. Two layers were identified on the fireside surfaces. The one layer appeared white in the etched microstructure, while the other layer was significantly darker in colour.

(ii) Electron probe microanalysis (EPMA):

Secondary electron image (SEI) of a circumferential crack tip, as recorded from the EPMA, showed that the composition of the dual products on the tube surface and within the cracks were distinctly different.

(Na_2O) to vanadium oxide (V_2O_5) ratio is about 1:5 (French 1983: 203).

5.4.3.3.3. Waterwall fireside corrosion:

Two sub-sections of waterwall fireside corrosion are described, viz:

5.4.3.3.3.1. Reducing atmosphere corrosion:

The signs of potential reducing atmosphere fireside corrosion problems are listed as follows (Southwest Research Institute 1985: 4-10):

- (i) Carbon monoxide levels greater than 10 ppm in flue gas,
- (ii) Carbon content greater than 3% in the coal ash, and
- (iii) Chloride levels greater than 0,6% in the coal.

Carbon particle impingement or direct flame impingement may be revealed during visual inspection of those waterwalls experiencing fireside corrosion. The presence of sulphur, carbon, sodium and potassium can be detected by EDX analysis of metallographic tube cross sections. The melting points of compounds present in the slag deposits can be determined by DTA.

while wastage flats will be located at the 2 o'clock and 10 o'clock sectors when viewed in cross-section. (Babcock and Wilcox 1978: 15-19 to 15-20; Battelle Columbus Division 1987: 2-11; Southwest Research Institute 1985: 4-16; Port and Herro 1991: 130-131; Cain and Nelson 1961: 468; Electric Power Research Institute TR-102433-VI; and Pollmann 1994: Unpublished).

5.4.3.3.2. Oil ash corrosion:

A corrosive slag may develop under the following circumstances (Port and Herro 1991: 124):

- (i) The use of fuel oil that contains high levels of sodium, vanadium or sulphur, or combinations of these elements,
- (ii) Availability of excess amounts of excess air for the formation of V_2O_5 , and
- (iii) Operation that produces tube metal temperatures above 593°C.

The presence of a liquid ash can be confirmed by measuring the melting points of fireside constituents. Severe oil ash corrosion is likely when the vanadium/sodium ratio is near 2:1 (Needham and Jones 1984: 32). The greatest wastage occurs when the sodium oxide

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