

PF-Fired Supercritical Boilers Operational Issues and Coal Quality Impacts

Technical Note 20

Prepared by:

**B. J. P. Buhre
R. Gupta
S. Richardson
A. Sharma
C. Spero
T. Wall**

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CRC for Coal in Sustainable Development
University of Newcastle
Department of Chemical Engineering
University Drive
Callaghan, NSW 2308

Summary

The use of super-critical (SC) steam conditions has been applied in recent Australian, European and Japanese coal fired power stations. For example, recent Australian units use conditions of 566°C and 25 MPa, Japanese units have used 600°C, 24.1 MPa and associated with 40% efficiency, and a European project aims to develop 700°C technology and 50% efficiency.

These developments indicate that SC units are, and will be, leading the way to higher efficiency plant in these countries even though coal gasification does offer higher efficiencies in the long term.

The coal related issues in the operation of such power stations are therefore of interest to Australian power generators using and contemplating SC units and also to exporters selling coal to be used in SC units. A literature review was prepared to provide background information for CCSD to help develop an appropriate research project to establish information lacking.

The literature was found to contain many references on the properties of steels developed to allow the higher steam temperatures of SC plant and the fireside corrosion associated with increased metal temperatures. At SC conditions the corrosion of ferritic steel is known to increase with temperature, with high Ni steels required as temperatures approach 600°C and even higher Ni steel now being developed for advanced plant.

The major impact of coal quality on the operation of SC boilers reported is due to the effect of ash deposition on corrosion of the water wall and super heater and reheaters.

Corrosion is influenced by

- Coal properties, and the properties of any cofired fuel
- Combustion conditions, particularly fuel-rich regions in the furnace
- Metal type and temperatures

Some purchasers limit S levels in coal due to its association with corrosion and correlations between corrosion rate and H₂S are provided in the literature. In fact, other inorganic components are known to influence corrosion. The use of biomass cofiring with coal has also been associated with corrosion, necessitating low metal temperatures with some biomass types. Locally reducing conditions associated with fuel staging using low-NO_x burners exacerbates the problem, particularly when overfired air is also used for staging, consistent with an expectation based on corrosion mechanisms presented in the report.

Based on this information, CCSD should consider initiating a research project on coal quality impacts on supercritical and ultra-supercritical technologies in order to better understand the matching of appropriate coals with the technology.

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1 Introduction

Concerns about CO₂ emissions and the need to improve the environmental acceptance of coal utilisation for electricity production have led to the worldwide development of advanced coal fired power stations with higher efficiencies. New coal utilisation technologies such as fluidised bed combustion, gasification and combinations of these, such as coal gasification integrated with gas combined cycles (IGCC) and fuel cells are being developed. One of these developments is the so-called IGCC 98 design, an initiative of the European Union. The design is a follow-up of existing IGCC power stations and would achieve an efficiency of 51.5 % (LHV). From this starting point, a program has been set up to increase the efficiency up to 58 %. This is achieved by development of high temperature gas cleaning devices, materials allowing higher turbine inlet temperatures, and eventually, integration of fuel cells with the design (Pruschek, 2001).

Introduction of these “advanced” technologies involves technical risk, and generators are installing more conventional technologies but using steam cycles involving supercritical steam, in order to increase efficiency.

With the current expansion of supercritical power plants worldwide and within Australia, a fundamental understanding of these power plants and its implications for coal use and operation are necessary.

The aim of this report is to provide a survey of plant and operational differences between subcritical and supercritical boilers with a review of the reported impacts of coal quality on operational issues.

2 Sub- and Super-Critical Steam Cycles

2.1 Sub-critical Boilers

Water when heated at sub-critical pressure (less than 22.1 MPa) increases in temperature until it starts to boil. While the water is boiling it exists as two phases, liquid and gas that have different mass densities, and remains at a constant temperature known as the *saturation temperature* for the given pressure. Once all of the liquid has boiled off to steam (evaporated) the temperature of the steam will continue to rise, at constant pressure, and is then referred to as superheated steam.

Sub-critical boilers typically have a means of separating the two phases, liquid and steam, to allow the process to be continuous. The separated liquid is recirculated through the evaporating section of the boiler and steam passes through to the superheating section. This separation typically occurs in the *boiler drum*, a heavy thick walled steel pressure vessel with a series of cyclones and baffles to separate liquid from steam.

It is the mass of this boiler drum which limits the rate at which a sub-critical boiler can be brought on line and how well it responds to load changes which results in fuel being consumed for no energy output compared with a more responsive boiler. Too great a firing rate will result in damaging thermal stresses in the heavy boiler drum.

2.2 Super-critical Boilers

When water is heated at a constant pressure above the critical pressure its temperature is never constant and no distinction between gas and liquid can be made, the mass density of the two phases is the same. Properties of the water in the super-critical boiler continuously change from liquid to gas (steam), for example:

- Temperature rises steadily.
- Specific heat and rate of rise changes considerably.

Liquid in the super-critical boiler is assumed to have changed to steam after the critical temperature for the super-critical pressure, as the steam is heated further it continues to gain temperature in a superheated state.

With the super-critical boiler there is no stage where the water exists as two phases and requires separation, so the boiler is constructed without a drum. Typically super-critical boilers are *once through boilers* where water pumped in at pressure by the Boiler Feed Pump passes progressively through the heating stages of the boiler and is delivered to the turbine at final temperature with no recirculation.

The actual location of the transition from liquid to steam in a once through super-critical boiler is free to move with differing conditions. This means that for changing boiler loads and pressures the process is able to optimise the amounts of liquid and gas regions for efficient heat transfer keeping the high boiler efficiency over a wider range than sub-critical boilers with drums.

2.3 Operational Aspects

Supercritical boilers operate at a pressure where there is no transitional phase between water and steam. This has some implications and raises some operating issues.

In subcritical boilers, drums are used to separate the steam from the water phase. After separation, the steam is led into the heat exchangers in the boiler for further heating. In supercritical boilers, the drum is eliminated.

During start-up, the supercritical fluid must be heated before it is led into the steam turbine. A flash tank is therefore required until the appropriate steam feed is achieved. During start-up and partial load, the steam pressure can also be decreased to subcritical pressures. In the past, supercritical boilers were intended for base load only (Smith, 1998). Electric utilities now have a need to efficiently run supercritical boilers at lower loads when the plant efficiency drops for constant pressure operation. However, when variable pressures are used, high efficiencies are achieved even when operating at partial load (Miyazawa, Yamamoto et al., 1997). Figure 2-1 shows the trend of the two types of power plants under partial load.

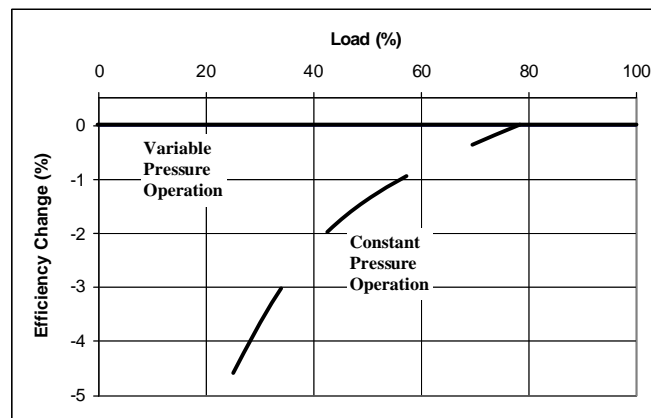


Figure 2-1: Trends in Plant Efficiencies at Partial Load

Although constant pressure boilers are not inherently designed to operate at partial load, development of operating procedures enables a more efficient operation of these plants at partial load (Vera, 2000).

In order to reduce start-up and partial load problems inclined boiler tubes may be used. However, application of this design, where boilers are helically surrounding the flame, requires higher capital costs and more auxiliary power. Another method to minimize these problems is the use of rifled tubes in the waterwall, a method applied extensively in Japan (Miyazawa, Yamamoto et al., 1997). A scientific approach to the hydrodynamic instabilities which occur during start-up has been made by Tian and others (Tian, Chen et al., 1992). In their study, a model has been developed to calculate the hydrodynamic instability boundaries of a 600 MW supercritical boiler.

2.4 Process Characteristics

The differences between sub- and super-critical processes are shown in Figure 2-2 and Figure 2-3 below.

The Temperature versus Entropy diagram (TS diagram) charts the temperature of the process water with its changing state of energy as it passes through the boiler and turbine plant.

Features of the TS diagram are as follows:

- Horizontal lines on the TS diagram represent water changing state to steam (evaporating) or steam changing state to water (condensing) at constant temperature.
- Inclined lines represent the fluid gaining temperature at constant pressure. The vertical lines are changes in pressure (the pumps and turbines).
- The saturation line represents the point at which water begins to boil (when approaching from the left) or when steam begins to condense (when approaching from the right).

The numbered locations in the schematic diagrams correspond with the numbering of the TS diagrams.

Both plants utilise feed heating of condensate (the boiler water taken from the condenser prior to being fed to the boiler point 5 on Figure 2-2 and Figure 2-3). Heating of the condensate is achieved in heat exchangers with higher temperature steam bled from the turbine stages (10) and (11). Both sub- and super-critical plant will use seven and up to eight stages of condensate feed heating depending on the specific design of the plant.

2.4.1 Sub-critical Boiler Process

The Condensate Extraction Pump (CEP) and Boiler Feed Pump (BFP) of the sub-critical plant deliver the feedwater to the drum after passing through low and high pressure feed-heaters and economisers at the saturation temperature. The feed-water is circulated through the evaporation stages of the boiler at its constant saturation temperature until it returns to the drum in two phases, liquid and steam (9) to (9') Figure 2-2. (The energy required to boil the liquid at this constant temperature is often called *latent heat of evaporation*.) The drum separates the liquid and steam, recirculating liquid through the evaporation stages and directing steam to the superheaters. After the drum (9') the steam is considered as a *dry gas* and further heat input contributes to superheating the steam (9') to (1) Figure 2-2.

The superheated steam at full pressure and temperature is expanded in the High Pressure (HP) turbine to deliver mechanical energy to the generator. Steam exhausted from the HP turbine is returned to the boiler (2) to be superheated again (3) and is referred to as *reheat*. The reheated steam is again expanded in a Low Pressure (LP) turbine before being exhausted to the condenser (4) to continue its cycle through the feed heating process.

Reheating the steam after the HP turbine improves process thermal efficiency by fully utilising the energy in the boiler from combustion of coal and maximising the difference between LP turbine inlet and outlet steam temperatures. Theoretically, duplicating the reheating process continues to improve the process cycle efficiency.

The number of reheat stages used in practice is limited by:

- The economics of the cost of extra plant required for each reheat stage compared with the benefits from improved efficiency.
- The available pressure in the exhausted steam is reduced through each stage of reheater tubing. As the steam pressure reaches the saturation line water droplets form which can badly erode steam turbine internals.

Current best practice sub-critical plants utilise only a single reheat stage.

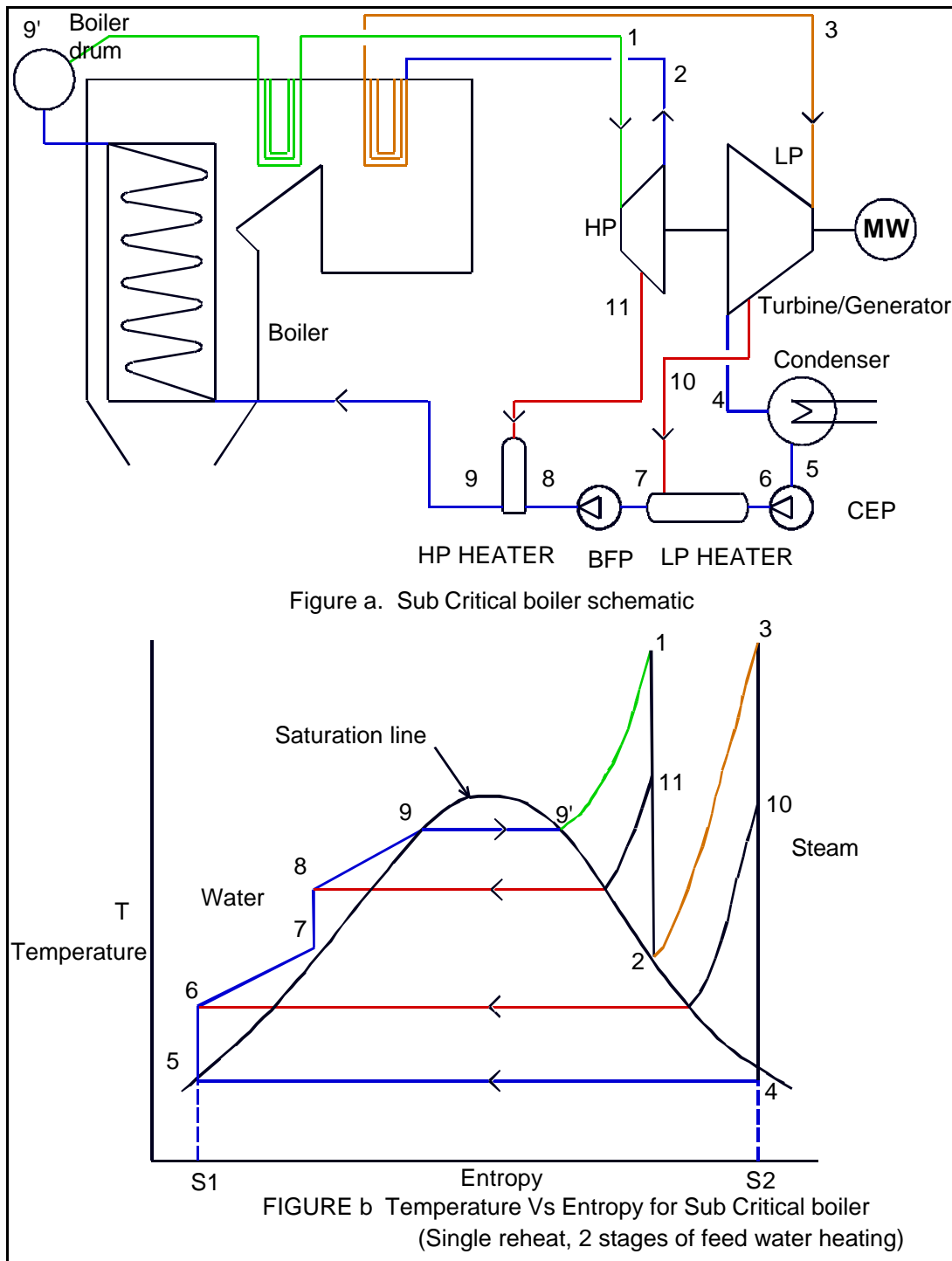


Figure 2-2: Sub-critical plant schematic and process description

2.4.2 Super-critical Boiler Process

The super-critical plant process, Figure 2-3, utilises similar condensate feed heating plant, boiler plant and turbine plant to the sub-critical plant with the following differences:

The CEP and BFP raise the pressure of the boiler feed water above the critical pressure.

As the boiler water in the super-critical plant does not exist as a two-phase fluid it does not require any separation or recirculation of liquid through the evaporation stage, hence no drum. The steam is considered to be superheated after it passes the critical temperature (9) for the cycle pressure.

As can be seen from the TS diagram for the super-critical plant, Figure 2-3b, the process line does not cross the Saturation Line as does the sub-critical plant avoiding *Latent Heat of Evaporation* to boil the water as seen between (9) and (9') in Figure 2-3b.

The steam at final temperature is expanded through the HP turbine in the same way as the sub-critical plant operates. Steam exiting the HP turbine is again reheated before further expansion to improve cycle efficiency. With the higher process pressure multiple stages of reheat become practical and current best practice super-critical plant is utilising two stages of reheat.

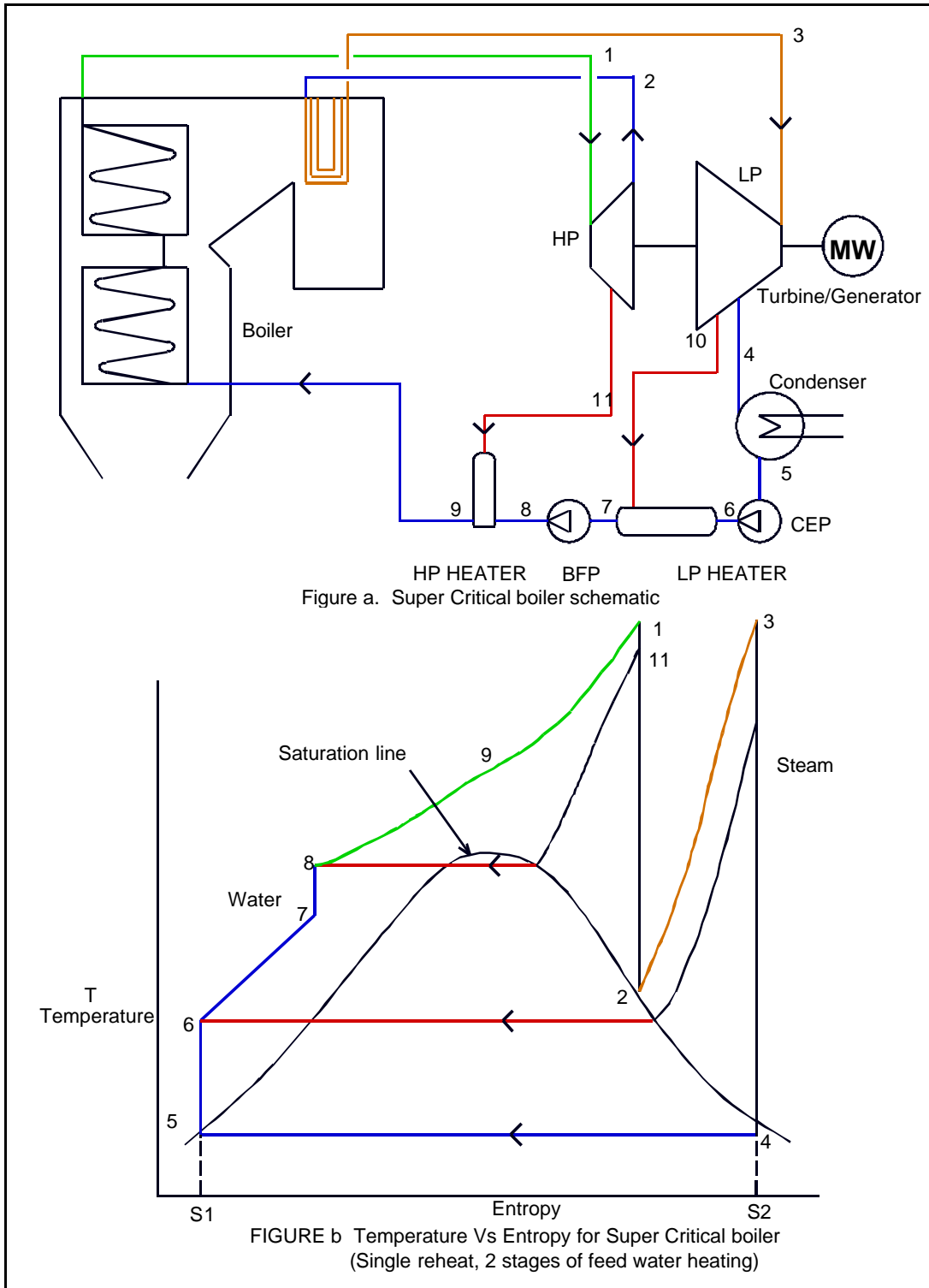


Figure 2-3: Super-critical plant schematic and process description

2.5 Illustrative Plant Efficiency Gains

The improvement of plant efficiency of super-critical over sub-critical plant is a function of a superior cycle thermal efficiency. Thermal efficiency can be represented on the TS diagram as a function of the area bound by the process line 1-2-

3-4-5-6-7-8-9-1 and the total area under the process line $S_1-5-6-7-8-9-1-2-3-4-S_2-S_1$ in Figure 2-2b and Figure 2-3b. Both sub- and super-critical plants have the same process base point, condensing steam (4) to (5), but increasing the top points with pressure and temperature results in the super-critical plant having a greater ratio of useable energy to unusable energy ($S_1-5-4-S_2-S_1$) hence the greater cycle efficiency.

With the same steam temperatures super-critical plants, with pressures of 24.1 MPa, show an improvement in net efficiency of two to three percent over sub-critical plants with pressures of 16.5 MPa. An “ultra super-critical” plant with 29 MPa main steam pressure and two stages of reheat shows a relative improvement in net efficiency of 15% over the standard sub-critical boiler with only a single reheat stage. The relative gains in plant efficiency of super-critical over sub-critical plant for constant steam temperatures are shown in Figure 2-4.

The International Energy Agency (IEA) indicate an expected improvement in net efficiency of at least 18 percent for super-critical plants over world standard sub-critical boilers given normalised plant conditions (Couch, 1997).

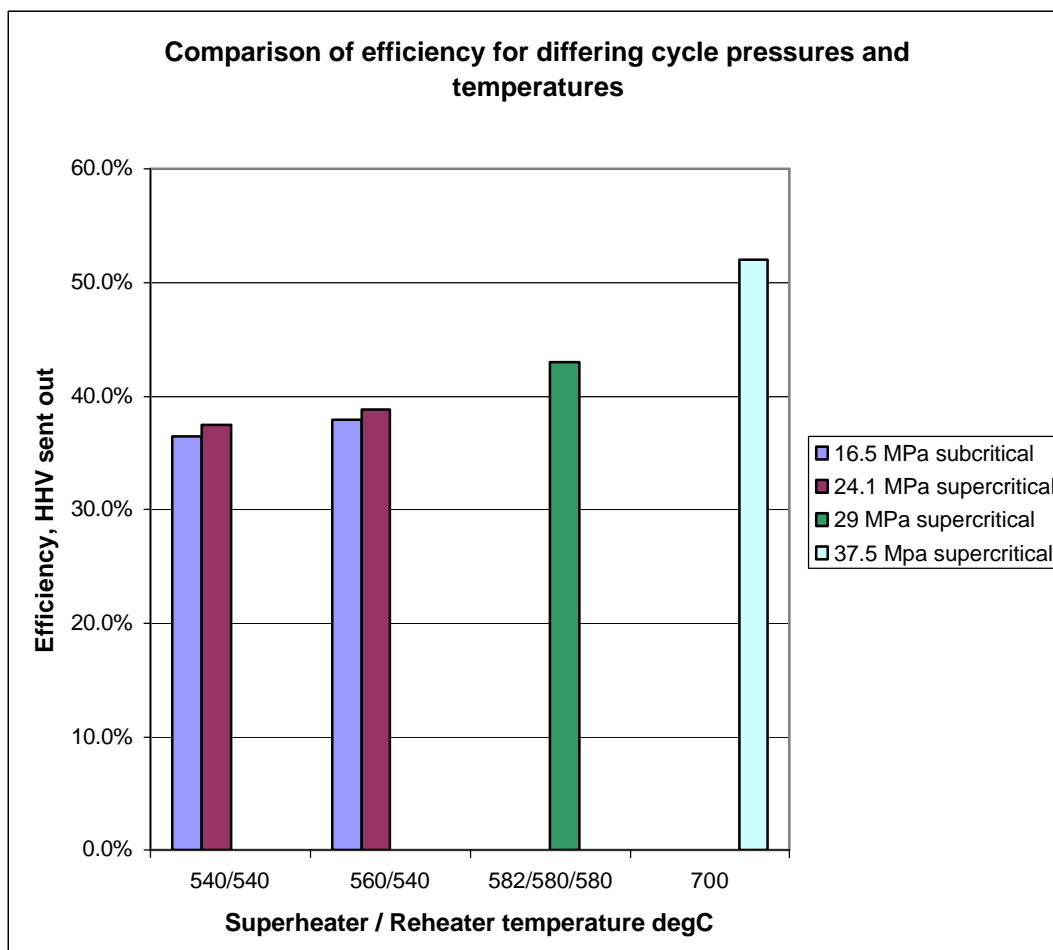


Figure 2-4: Variations in sent out efficiency with cycle pressures and temperatures

2.6 Observed Trends

Sub-critical plant development has been limited since the 1970's with the achievement of system pressures below the critical pressure and temperatures limited by material properties. Typical steam conditions for sub-critical plant are shown in Table 2-1.

Table 2-1: Typical steam conditions for sub-critical plant

Main steam pressure, MPa	16.5 to 18
Main steam temperature, °C	540
Reheat steam temperature, °C	540 to 560
Efficiency, sent out HHV, %	36

For super-critical plant gains in plant efficiency are more open to advances in cycle steam conditions. Typical commercial super-critical plant installed during the 1990's has had the steam conditions shown in Table 2-2.

Table 2-2: Typical steam conditions for current super-critical plant

Main steam pressure, MPa	25
Main steam temperature, °C	540
Reheat steam temperature, °C	565
Efficiency, sent out HHV, %	37.5

Future trends in super-critical plant have been labelled "ultra" super-critical with pressures of 30 to 40 MPa and final temperatures of 700 °C (Couch, 1997; Spero, 2002).

ELSAM, a Danish electricity utility, have recently reported on the progress of their research into "ultra" super-critical technology with the target steam conditions shown in Table 2-3.

Table 2-3: Target steam conditions for "ultra" super-critical plant

Main steam pressure, MPa	37.5
Main steam temperature, °C	700
First Reheat steam temperature, °C	720

Second Reheat steam temperature, °C	720
Efficiency, sent out HHV, %	52

Note: Data for electric feed-water pumps, and cooling water 10⁰C (sea water cooled)

Table 2-4 reports on the progress of the *EU Advanced (USC 700⁰C) PF Power Plant*.

Table 2-4: Progress of the EU Advanced (USC 7000C) PF Power Plant. Progress of the EU Advanced (USC 700⁰C) PF Power Plant.

Commission date		Live steam pressure MPa	Live steam temperature °C	Reheat 1 °C	Reheat 2 °C	Feedwater temperature °C	Condenser pressure mbar	Auxiliary power (%P _e)	Sum of Dh (%)	Net efficiency (%) HHV
1998	Parameters	29	582	580	580	300	23	7.5		45
2000	Parameters	30	582	600	-	310	23	6.8		46.2
2005	Parameters	32.5	612	630	630	330	21	6.8		
	Δη-relative (%)	0.25	0.90	0.75	2.8	0.50	0.20	-	5.4	48.8
2010	Parameters	37.5	700	720	720	350	21	6.8		
	Δη-relative (%)	0.50	1.85	1.20	1.20	0.55	0.0	0.0	6.3	52.0

(Spero, 2002)

Notes: Data based on:

- Electric boiler feed-water pumps
- Boiler efficiency = 93.5% HHV
- Cooling water temperature = 10⁰C (sea water cooled)

2.7 Experience with Supercritical Boilers

The expansion in installation of supercritical boilers has been based on experience operating these boilers. The first of these boilers was installed in the 1960s and since then many improvements have been made. In the United States alone, 86 GW of this type is installed (Gorokhov, Ramezan et al., 1999). The majority of this capacity operates with steam conditions that are just supercritical, it was built in the sixties and seventies, and has not increased substantially since 1991. Of these 162 units, 121 units are pf coal fired plants and during this time, the efficiency of power stations in the US has increased from approximately 33% in the 1960's to an average of over 40% in the 1990's. A selection of installed supercritical boilers in the United States is given in Table 2-5.

EP Company	Station	Unit	Cap.	Steam Press	ST (Main)	ST (Reheat)	Built
			MW	MPa(g)	°C	°C	
Philadelphia El. Company	Eddystone 1		350	34.4	694	566	1958
Ohio Edison	W.H. Sammis	6	623	26.1	541	541	1969
Detroit Edison	Monroe	1	800	26.2	541	541	1971
Tennessee Valley	Cumberland	1	1300	25.2	539	539	1972
Dayton/Cincinnati/Col.	J.M. Stuart	3	610	26.2	541	541	1973
Cleveland el Illuminating	Eastlake	5	680	26.1	541	541	1973
Tennessee Valley	Cumberland	2	1300	25.2	539	539	1973
Kansas City	La Cygne	1	844	26.4	543	541	1973
Duke	Belews Creek	1	1100	25.2	542	538	1974
Dayton/Cincinnati/AEP	J.M. Stuart	4	600	26.2	541	541	1975
Duke	Belews Creek	2	1100	25.2	542	538	1975
AEP-Ohio	Gavin	2	1300	26.5	543	538	1975
AEP-Ohio/Buckeye	Cardinal	3	650	26.6	541	541	1977
TU Electric-Generating D.	Monticello	3	775	26.6	543	541	1977
AEP-Appalachian	Montaineer	1	1300	26.5	543	538	1980
AEP-Indiana & Michigan	Rockport	1	1300	26.5	543	538	1984
AEP-Indiana & Michigan	Rockport	2	1300	26.5	543	538	1989
Cincinnati/Dayton/AEP	Zimmer	1	1300	26.5	543	538	1990

Table 2-5: Installed Supercritical Boilers in the U.S. (Smith, 1998)

Japan has seen the greatest expansion of installed supercritical power plants and also the use of ultra cupercritical conditions. (Gorokhov, Ramezan et al., 1999). A list of existing and planned supercritical power plants is provided in Table 2-6, together with some of their efficiencies (Ashizawa, 2001; Isherwood, 2001).

EP Company	Station	Unit	Cap.	Steam Press	ST (Main)	ST (Reheat)	Built	?
			MW	MPa(g)	°C	°C		%
Hokkaido	Tomato-	2	600	24.1	538	566	1985	

	atsuma							
Tohoku	Haramachi	1	1000	24.2	566	593	1997	39.9
		2	1000	24.2	600	600	1998	40.3
Chubu	Hekinan	1	700	24.1	538	566	1991	37.1
		2	700	24.1	538	566	1992	38.6
		3	700	24.1	538	593	1993	38.4
		4	1000	24.1	566	593	2001	
		5	1000	24.1	566	593	2002	
Hokuriku	Tsuruga	1	500	24.1	566	566	1990	39.9
		2	700	24.1	593	593	2000	40.9
	Nanao-ohta	1	500	24.1	566	593	1995	
		2	700	24.1	593	593	1998	
Chugoku	Misumi	1	1000	24.2	600	600	1998	40.0

Table 2-6: Installed Capacity of Supercritical Boilers and Efficiencies in Japan (Ashizawa, 2001)

Europe is also expanding the use of supercritical steam pressures in pf coal fired boilers. New black coal power plants in the planning phase have steam temperatures of 600 °C at 290 bar (29.4 Mpa) and superheated steam temperatures of 620 °C at 61 bar (6.2 Mpa). For example, six supercritical power plants are operating in Denmark, with net efficiencies between 42.9 and even 47 % (LHV) (Scott and Carpenter, 1996). These efficiencies are higher than commonly obtained efficiencies because of the exclusion of the flue gas desulphurisation plant in the calculation and the availability of cold seawater.

In the European network project “700 °C Power Plant” approximately 40 enterprises European-wide have joined to develop plant efficiencies higher than 50 % using steam pressures over 700 °C with pressures up to 350 bar (35.5 Mpa) (Bassier, 2001).

In Australia, CS Energy has installed one supercritical boiler, unit 1, at the Callide power station. The operating temperatures and pressures of this unit are provided in Table 2-7. Another supercritical unit is expected to be operational in December 2001. Tarong Energy is also planning to operate a supercritical boiler in the near future.

EP Company	Station	Unit	Cap MW	Steam Press MPa(g)	ST (Main) °C	ST (Reheat) °C	Built
CS Energy	Callide	B	350	25.0	566	566	1989
		C	350	25.0	566	566	2001
Tarong Energy	Tarong North	5	450	25.0	566	566	2001-2003

Table 2-7: Installed and Planned Supercritical Boilers in Australia (Ashizawa, 2001)

2.8 Economics

The final reason favouring supercritical plants is the economical attractiveness of the installations. In recent years, reduction of SO_x, NO_x, and CO₂ emissions combined

with the improved availability and reduction of capital cost of supercritical boilers, has made installation of these boilers economically attractive (Campbell, McMullan et al., 2000; Sondreal, Benson et al., 2001). This has been associated with the cost reduction of high temperature non-corrosive steels.

2.9 Advantages of Super-critical Plant Over Sub-critical Plant

The advantages of super-critical boiler plant over sub-critical boiler plant in terms of reduced greenhouse gas emissions per MWh sent-out:

- Greater plant efficiency – reducing CO₂ emissions per MWh electricity sent out during normal operations.
- Greater plant efficiency over wider range of part loads than sub-critical boilers with drums.

Quicker start-up times than for sub-critical boilers with drums due to reduced boiler materials, reduces CO₂ emissions over the life of the power station due to start-ups.

Other advantages favouring the use of supercritical boilers over other are:

- Operating experience obtained with supercritical boiler plants has shown that supercritical boiler plants are reliable.
- Using modern steel technologies, supercritical boiler plants are price competitive with sub critical boiler plants.

3 Material Requirements

Supercritical boilers have different operational characteristics because of the higher steam temperatures and require more stringent material characteristics than subcritical boilers. The four key components are high-pressure steam piping and headers, superheater tubing and waterwall tubing (Viswanathan and Bakker, 2000).

For universal steam pressure boilers as supplied by Babcock and Wilcox, all steam pipes are held at the supercritical high pressures (Smith, 1998). Since these pipes will transport steam over larger distances, the self-weight-induced stresses in these pipes are considerable. The high temperatures and pressures cause the pipes to be subject to creep. In addition, the pipes are subject to fatigue induced by thermal stresses, making steels with low thermal expansions more preferable.

When steam is heated in the waterwall or in convective or radiative heat exchangers, it is divided over a number of pipes or tubes, so not all steam will have to pass through one pipe. This reduces the volume flow through the pipes and increases the heat transfer. When steam is fed to a heat exchanger, the steam flows into a so-called inlet header. The inlet header is connected to the heat exchanger tubes pendant in the heat flow. When the steam has passed through the heat exchanger, it is collected and mixed with the steam coming from the other tubes in the outlet header. The location and typical configuration of the headers are shown in Figure 3-1 (picture obtained from (Smith, 1998)).

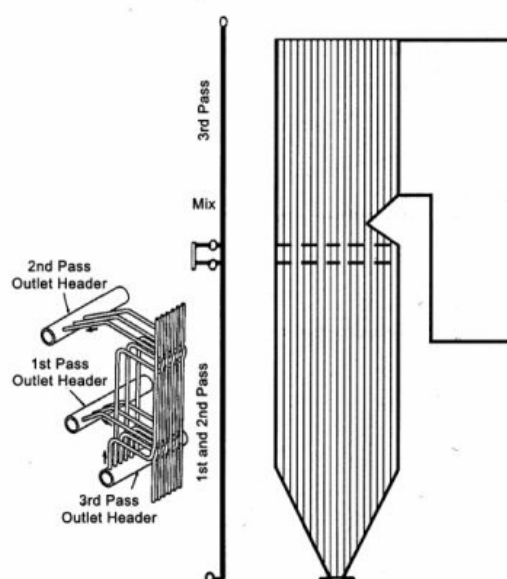


Figure 3-1: Position of Inlet and Outlet Headers in a Supercritical Once Through Boiler

There are several characteristic material selection criteria for headers and steam pipes. Although great similarities can be found between the two, the steam temperatures will be time and location dependent in headers, as opposed to the more constant temperatures occurring in steam pipes. The major difference is that headers have many welded attachments to inlet stub tubes and from reheaters and superheaters and intersections of outlet nozzles connecting pipework. These connections can cause

large stresses and therefore creep strength requirements have to be met. The thermal stresses can cause fatigue of the material of the connected components and dissimilar-welded joints therefore care must be taken to ensure a solid connection is established that is able to withstand these thermal stresses.

When steam is led into superheaters (SH) and reheaters (RH), the pressure is kept constant, while the temperature is increased. Some pressure loss will occur due to friction in the tubes, but the main difference will be on the temperature side. The superheaters and reheaters can be classified as two types according to their heat source:

- Convection type – These heaters are placed in the gas passage of the boiler where the heat is transmitted by convection,
- Radiant type – These heaters are placed where the heat source is dominated by the radiation from the flame.

The tubing in SH/RH requires resistance to high creep, thermal fatigue, demands special requirements regarding weldability, fireside corrosion/erosion, and steam side oxidation and spallation. In the next chapter, the corrosion/erosion effects on the fireside will be discussed in more detail.

A steel wall of tubes through which water is transported, the so-called waterwall, encases the flame in a boiler. In a US boiler, the tubes are typically 50 mm outside diameter, and are joined together by strips of steel approximately 10 mm wide. Approximately one-third of the way up the combustion chamber, pulverized coal is pneumatically injected into the boiler. The exact positioning of the burners varies significantly, but in general the objective of the arrangement is to create a ‘fireball’ in the furnace. Heat is transferred to the water in the tubes by radiation. When steam is fed into the waterwall tubes, a large temperature gradient is obtained between the fireside and waterside of the tube. In supercritical boilers, the medium temperature of the waterwall is higher than in subcritical boilers, since the temperature of the cooling medium will be higher. These higher average temperatures require higher resistance to creep.

In the design of ultra-supercritical boilers, material cost, material reliability and longevity should be considered. In Japan, Electric Power and Development Co. LTD., and IHI carried out application tests of various candidate alloys and trial manufacturing of full size models of pressure components for an USC boiler that operates at 30 MP/630oC. Usually, steel for boilers can be classified to low alloy steel, ferritic steel and austenitic steel. Advanced 9-12 Cr alloys of high strength leading to reduce weight and thermal stress have been recently developed. Austenitic steel has superior corrosion resistance properties but is expensive. (Kajigaya et al., a)

The other concern for supercritical boilers is fireside erosion and corrosion. Recent results in the USA on boilers retrofitted with low NO_x burner systems, using overfire air, indicate that low alloy steels can suffer from excessive corrosion rates, as high as 2 mm/yr (Bakker and Stringer, 1997). Helical or straight tube design effects material choice. In helical tube design, the heat absorption is more uniform, decreasing the internal stresses due to thermal expansion and thus makes the requirements less stringent.

In the following table, a summary is given of the characteristic requirements needed for the identified key components.

Component	Material Requirements
Steam pipes	Creep strength Thermal expansion
Headers	Creep strength Thermal expansion Weldability
Superheater / Reheater	Creep strength Thermal expansion Weldability Fireside corrosion / erosion Steamside oxidation / spallation
Waterwall tubing	Creep strength Fireside corrosion / erosion Weldability

Table 3-1: Identified Key Components in Supercritical Boiler and their Specific Requirements

4 Erosion and Corrosion

Metal loss is associated with the material, its temperature and environment. For the key components in a supercritical boiler, both water / steam side oxidation, and fireside oxidation occurs. However at the high temperatures occurring in the boiler, fireside corrosion can be rapid. Furnace wall tubes situated near staged burners have shown wastage rates of 1.5 mm per year and higher (Brown and Tanzosh, 1996). Typically, ferritic steels subject to a steam temperature of 610 °C show corrosion rates between 0.33 mm per year to 0.57 mm per year (McDonald, Meisenhelter et al., 1999).

Inorganic material is injected into the furnace together with pulverised coal. This determines the corrosive components present in the flue gas. With boilers applying overfire air, the reducing conditions have a strong impact on waterwall corrosion (Bakker and Stringer, 1997; Stringer, 1998; Kung and Bakker, 2000). In Figure 4-1 a typical corrosion pattern is given for a waterwall from a corner-fired boiler with an overfire low NO_x burner system.

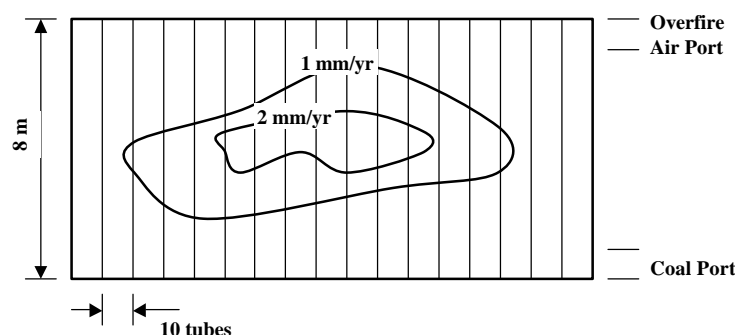


Figure 4-1: Corrosion Pattern from a Corner Fired Boiler with an Overfire Low NO_x Burner System (Bakker and Stringer, 1997).

4.1 Observed Effects of Temperature on Corrosion

The corrosion rate has exponential increase in rate of corrosion with temperature. It appears to be important to establish the corrosion mechanism and estimate the rate constants and kinetic parameters in order to assess the corrosion in super critical boilers for a given metal surface. The reaction parameters may vary dramatically by change in tube material. The metal temperature has primary importance in aggressive gas corrosion and the gas temperature is irrelevant.

Since the mechanism causing corrosion is determined by reaction kinetics, higher temperatures will increase corrosion rate. In general, a fireside material temperature of 35 °C higher than the design steam temperature can be assumed (Sondreal, Benson et al., 2001). However, the temperature gradient through the wall and deposits is strongly dependent upon the character and thickness of the deposit. Temperature gradients through a waterwall with significant deposits are shown in Figure 4-2.

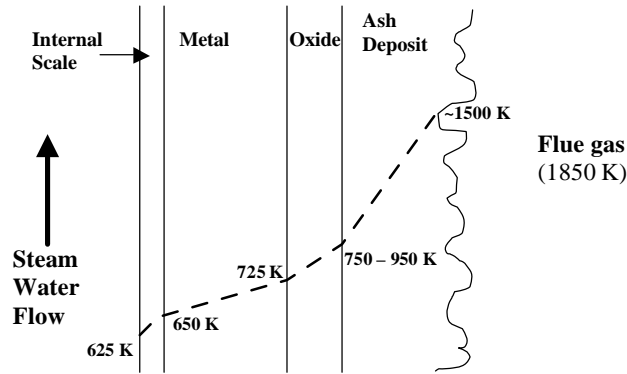


Figure 4-2: Temperature Gradient through the Evaporator Tube Wall in the Furnace Section of a Boiler (Cutler and Raask, 1981).

The difference between corrosion rates of ferritic and austenitic steels is well known. Ferritic steels show linearly increasing corrosion rates with increasing steam / flue gas temperatures, while austenitic steels show a peak in corrosion rates at steam temperatures of around 680 °C. In

Figure 4-3, the general trends in corrosion rates for fireside corrosion for the two material types are shown. The causes for the peak in corrosion rate is the formation of corrosive alkali-iron-trisulfates (McDonald, Meisenhelter et al., 1999). As can be seen in

Figure 4-3, at high temperatures, the corrosion rates of austenitic steels are lower than those of ferritic steels. However, austenitic steels have a lower thermal conductivity and high thermal expansion resulting in high thermal stresses and fatigue cracking. These problems and the general low availability of many supercritical plants were the reason for many of the teething problems of supercritical power plants (Viswanathan and Bakker, 2000).

The relationship between corrosion rates as a function of metal wall temperature shown in Figure 4-3, suggests that reducing the tube wall temperature would lead to low corrosion rates. Temperature was reduced by first, adopting an intermediate header for reheater. This reduced the metal temperature to that of conventional boiler. Second, a parallel arrangement wherein steam and gas flows are made to coincide with each other. (Kuwahara et al., b)

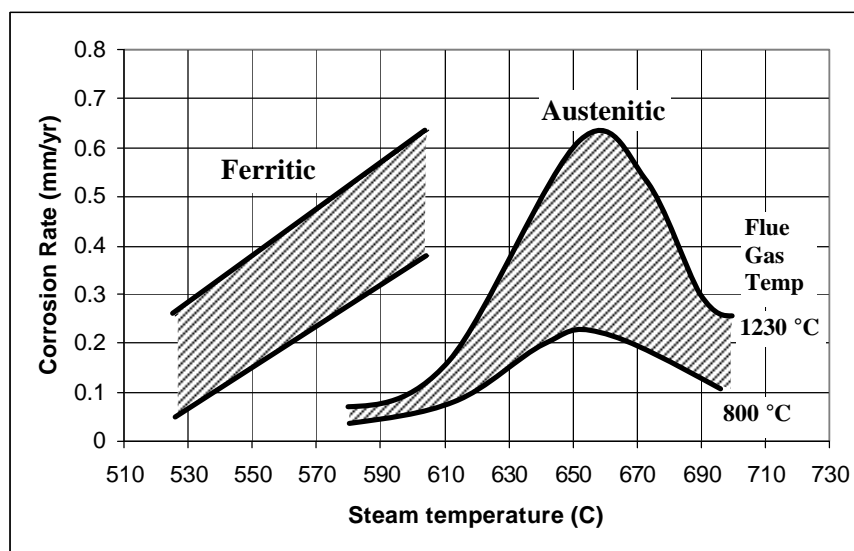


Figure 4-3: General Trends Observed in Waterwall Corrosion Rates at Various Temperatures (McDonald, Meisenhelter et al., 1999)

The Bell-shaped curve of corrosion rates of austenitic steels can be explained by the behaviour of the ash deposited on the tube surfaces and the effect of the temperature gradient in the deposit. At relatively low metal temperatures of around 550 °C, the ash deposit consists of a porous layer which allows diffusion between the tube surface and the bulk flue gas. Corrosion occurs relatively slowly, at a rate similar to the gas-phase oxidation of metal. At higher metal temperatures, the ash deposit turns molten and forms a molten layer of alkali-metal-trisulfates on the tube surface. This molten layer changes the oxidation potential at the outer surface of the oxide layer and allows the dissolution of the scale as metal sulfates. SO₃ is more soluble than O₂ in molten alkali sulfate. Furthermore, oxygen is consumed in the oxidation of the metals at the metal-scale interface. This increases the sulfidation potential to increase and allows sulfidation of the metal to occur (Nielsen, Frandsen et al., 2000).

In the previous paragraph, the role of sulphur in corrosion mechanisms is described. Under normal oxidizing operating conditions, low alloy steel or carbon steel waterwalls are protected from rapid wastage by the formation of an iron oxide layer, usually magnetite, Fe₃O₄ and a relatively thin layer of hematite, Fe₂O₃. This scale is dense, impermeable to gases and strongly adheres to the tube. Such a scale grows slowly and the growth rate decreases with time. An example of such a layer is shown in Figure 4-4 (Devir, 2001).

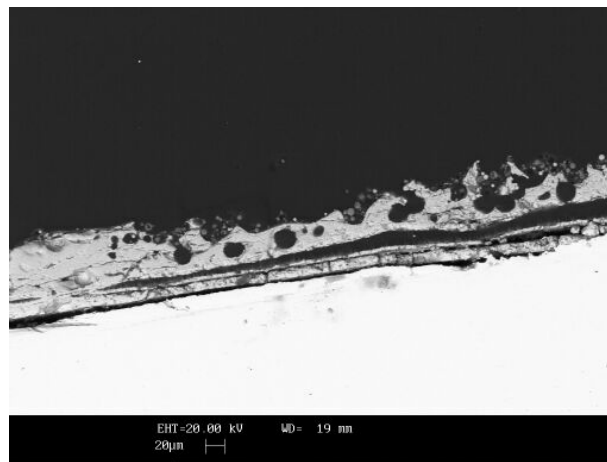


Figure 4-4: Typical Magnetite / Hematite Layer on a Waterwall Tube

The magnetite / hematite layer protects the metal from (further) oxidation and reaction of the metal with the surrounding gasses. On alloyed steels with a high chromium content, a layer of chromium oxide is created protecting the steel from further corrosion. Scheffknecht and Chen examined the effect of chromium content on its high temperature corrosion behaviour. In the experiments, different alloys were covered with synthetic coal ash and heated to 650 °C. The general trend observed is given in Figure 4-5, and is also noted in other studies (Ouden and Korevaar, 1996; Viswanathan and Bakker, 2000).

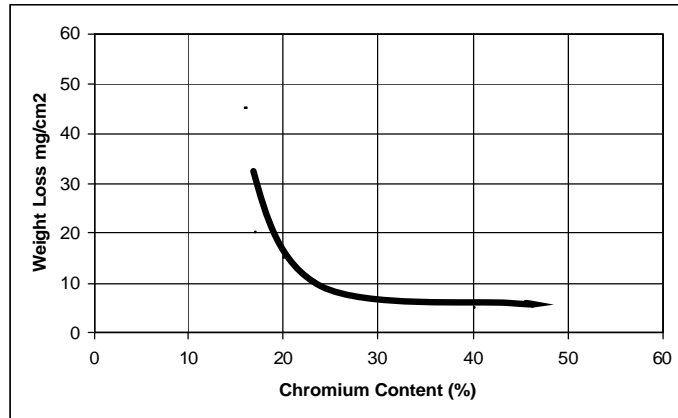


Figure 4-5: High Temperature Corrosion Behaviour Trend in Relationship with Steel Chromium Content (adapted from (Scheffknecht and Chen, 2000)).

An alloy with over 25% Cr has satisfactory corrosion resistance. Nickel also plays an important role in corrosion resistance. Nickel is an austenite forming constituent and is used in combination with chromium to create austenitic steels at low temperatures, increasing its corrosion resistivity. The addition of nickel improves the toughness, but at the expense of creep strength (Viswanathan and Bakker, 2000). In general, austenitic steels for boilers contain more than 8 % Ni and high Cr- high Ni steels can contain up to 54 % Ni (Viswanathan and Bakker, 2000). New promising alloys possessing high creep strength and corrosion resistance are: 23Cr-34Ni-1.25Mo-0.4Ng (Mod. Alloy 800H), 30Cr-50Ni-2Mo-0.2Ti-0.02Zr (CR30A), 25Cr-20Ni-Nb-N (HR3C), 20Cr-25Ni-1.5Mo-0.25Nb-0.05Ti-0.15N (NF709) (Kihara et al. c). To reduce corrosion in boilers co-fired with biomass, high Ni and high Cr content steels have been tested. It was concluded that high Ni and high Cr alloys were promising superheater materials in co-combustion environments with biomass (Eriksson, 2001).

The combustion chamber and the high temperature superheater and reheater sections of coal-fired boilers do not usually suffer from tube erosion by ash impaction in that attached deposits prevent erosion. No specific effect of erosion wear on supercritical boilers has been found (Raask, 1985).

4.2 Fireside Corrosion Mechanisms

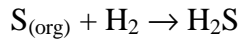
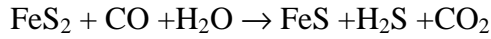
Two of the components of a supercritical boiler, the waterwall and the superheater / reheater, are subject to fireside corrosion. The corrosion rate is related to the coal chemistry, firing conditions, metal composition and temperatures. Sulphur and chlorine species in coal are primarily responsible for fireside corrosion. Coal purchases therefore may impose coal composition limits for these elements.

4.2.1 Effect of sulphur

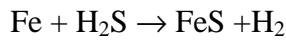
When firing a high sulphur coal, sulphur present as pyrite corrodes the metal surface. Although, firing low sulphur coals reduced the corrosion rates significantly, appreciable corrosion rates were observed even with low sulphur coals under reducing conditions. The reducing conditions leads to formation of corrosive gases, H₂S and

COS. Significant quantities of H₂S and COS can form if the O₂ level is below 0.2%. (Kajigaya et al., d)

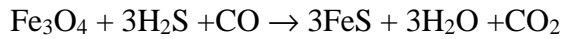
When low NO_x firing is applied by the combustion of coal in a sub-stoichiometric flame, a low oxygen partial pressure and a significant amount of CO will be present. Under these conditions, there is also some H₂ present in the flue gas and the reactions



are likely to occur. When H₂S is present in the flue gas, it can react with iron in the waterwall tubes to form FeS.



Already formed Fe₃O₄ may also be transformed to FeS by the following reaction:



This mechanism describes how FeS becomes part of the scale on waterwall tubes. The presence of FeS decreases tube strength, and increases growth rate and permeability of the scale. This results in increased metal wastage, which becomes the dominant factor in tube life. Kung and Bakker have carried out laboratory corrosion experiments concentrating on this aspect, and they indicated that FeS rich deposits could increase corrosion rates up to tenfold. This generally occurred during oxidizing, mildly reducing, or alternately reducing and oxidizing conditions (Kung and Bakker, 2000). However, the presence of sulphur in the flue gas alone could not explain the observed differences in corrosion rates. In the same study, a correlation between the corrosion rate of steel with varying amounts of chromium content and the effect of temperature and H₂S content in the gas was developed (Kung and Bakker, 2000):

$$CR = 3.2 \times 10^5 \times e^{\left(\frac{-15818}{1.987 \times T}\right)} \times (\text{H}_2\text{S})^{0.574} \times \frac{1}{(\%Cr + 10.5)^{1.234}} + 2.2$$

CR = Corrosion rate (mil/yr)

T = Metal temperature (K)

H₂S = H₂S concentration in flue gas in ppm

%Cr = wt% of chromium in steel

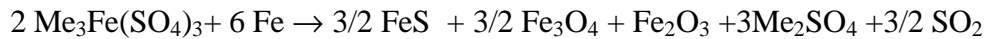
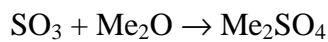
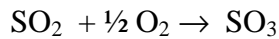
This correlation gave good results for coals with sulphur content between 0.9 and 1.2 %. However, it was noted that boilers have reported much higher corrosion rates than predicted using this correlation and it was concluded that the amount of H₂S in the flue gas is not the only or might not even be the major factor controlling waterwall corrosion in low NO_x boilers.

IHI, Japan (Kajigaya et al., d) developed an Improved Boundary Air System to improve the local furnace atmosphere near furnace wall and burner port where

extreme reducing conditions are present. The O₂ level is maintained at 0.2% at which no corrosive gases are formed thus reducing the corrosion rates.

4.2.2 Effect of alkali metals

IHI developed (Shigeta et al., e) a coal ash corrosivity index based on contents of acid soluble alkali and alkali earth metals in coal. A detailed study of ash deposit on test probe showed that the inner layer of the deposit contained higher amount of Na and K. The outer layers contained higher Ca and Mg. The corrosion promoting compounds are considered to be alkali iron sulfates such as Na₃Fe(SO₄)₃ and K₃Fe(SO₄)₃. The reaction mechanism is as follows.



where Me represents the alkali metals Na and K. Not all the alkali present in coal is associated with the formation of alkali iron sulfate. Only the fraction that is acid soluble or organically associated can be correlated to corrosion due to alkali iron sulfate. In addition, alkali earth elements like Ca and Mg are known to be anticorrosive which inhibit the formation of alkali iron sulfate. The corrosive index correlation is thus given by

$$W(\text{mg}/\text{cm}^2) = a \cdot b \cdot c \cdot d \cdot T \cdot f(\text{corr.})$$

where:

$f(\text{corr.})$ = weight loss (mg/cm²/hr) based on acid-soluble alkali content

a = f(K, Na) acid-soluble

b = f(CaO) acid-soluble

c = f(MgO) acid-soluble

d = f(SO₂)

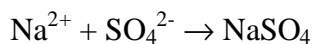
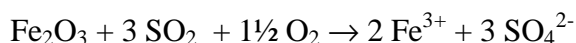
T = time (hrs)

The above equation was used to predict the corrosion rates for TP347h steel at 700°C and showed a good agreement. Corrosion index for various other alloys at different temperatures can be estimated by taking into account the relative corrosion resistance of each alloy.

4.2.3 Effect of chlorine

Another factor influencing the corrosion rate is the presence of chlorine in the coal. Corrosion from chlorine can be caused by either alkali chlorides in the deposit or by gaseous hydrogen chloride (HCl). The Central Electricity Generating Board (CEGB) in the United Kingdom has studied the effect of chlorine content on corrosion rate extensively and concluded that chlorine will indeed increase the corrosion rate, but

only at relatively high chlorine levels (> 0.2 %) and only in reducing conditions. A molten layer of alkali sulphates deposited on the metal dissolves the protective metal oxide layer via the following reaction (Cutler and Raask, 1981):



The relationship between the chlorine content and the corrosion rate was thought to be the result of the release of sodium from NaCl, depositing on the tubes and creating a molten sulphate layer which corrodes the metal as described above. They concluded that the effect of deposited alkali sulphates became apparent when the NaCl content was greater than 0.3 wt %. Another effect of chlorine can be attributed to the formation of a FeCl_2 layer under the protective scale. This only occurs when high heat fluxes are present (Kung and Bakker, 2000).

The effect of gaseous HCl on corrosion rate has been examined by (Salmenoja, Hupa et al., 1999). It was found that the oxidation of Fe, Cr and binary Fe-Cr alloys is enhanced by the presence of HCl in the flue gas. Significant corrosion of the high chromium alloys in the presence of HCl, in oxidising conditions, occurs when the metal temperature is above 600⁰C (Salmenoja, Hupa et al., 1999).

Most boiler manufacturers in the United States have used the maximum guidelines for Cl from 0.25-0.30 wt.% based on experience obtained in the United Kingdom. However, millions of tonnes of coal with much higher Cl levels have been burned for decades by other utilities without any adverse effect. Long-term experience burning Illinois Basin coals, with higher Cl levels, without corrosion attributable to Cl supports the contention that the Cl content of these coals is not a significant factor in high-temperature corrosion (Doane and Abbott, 1999). It should be noted, however, that papers suggesting little Cl impact have come from coal companies selling high Cl coals.

Unburned carbon deposited on the walls is also likely to promote corrosion rate. The carbon could locally increase the CO content in the flue gas near the waterwall. The reducing conditions created by the CO presence in this mechanism can increase the corrosion rate.

The research mentioned above together with experiences, indicate that S, Na, and Cl levels (and possibly K) in coal should influence corrosion. Some coal purchasers limit S-levels [McDonald, 1999 #13] and Cl-levels (e.g. to <0.25 – 0.30 wt %) for this reason. The use of a single element for this prediction is not expected to provide a good correlation due to the interaction indicated above.

4.3 Experimental Techniques Available

Reported corrosion rate studies at high temperatures can be divided in two types:

- Measurements of probe corrosion and deposit analysis in full scale boilers.

- Measurements of probe corrosion and deposit analysis in lab scale experiments.

The full-scale studies usually involve the use of probes at different locations throughout the boiler. In a study aimed at the influence of deposit on corrosion rates at a straw-fired boiler, deposits are collected on different probes. The deposits are examined and related to the probe metal corrosion at that location (Hansen, Nielsen et al., 2000). Collected deposits can be examined after short exposure periods (between 1-8 hrs) and longer exposure periods (~ one year), by examining deposits and corrosion on the waterwall after plant shut-down.

In laboratory scale experiments, the conditions under which corrosion rates are occurring can be more accurately defined, since all experimental parameters are determined. Different steel types can be covered by ash deposits and are exposed to gas mixtures for a certain amount of time.

An example of such an experimental set-up can be found in (Nielsen, Frandsen et al., 1999). In this study, two types of steel were covered with deposits and were exposed to synthetic flue gasses in electrically heated ovens. The samples were exposed at 550 °C for periods between 1 week and 5 months to determine their corrosion rate. The ash deposits varied in composition in order to view its effect on corrosion. Other lab-scale experiments have not used a deposit (Salmenoja, Hupa et al., 1999), so the effect of flue gas solely on corrosion can be investigated. In the lab-scale experiments, the corrosion rates are measured by determining their weight loss. The effect of different deposits and the corrosion mechanisms are investigated using SEM/EDX.

The present level of understanding concerning fireside corrosion mechanism prediction is substantial. It is now possible to predict the corrosion in supercritical and ultra supercritical boilers firing bituminous coals. However, prediction for high calcium coals is poor. Although power plants do not usually fire high calcium coals directly but in future high calcium coals may be used after blending with high rank and low sulphur coals like Australian coals. Therefore, there is a need to understand and develop correlations to predict corrosion rates due to high calcium coals.

5 Ash Deposit Formation and Corrosion

Ash deposits on waterwalls and superheaters has a dominant effect on corrosion rates. There are two factors that need to be considered for ash deposition related problems.

1. As the tube surface temperature increases, the temperature of the ash particles approaching the surface also increases. An increase in temperature of the ash particles increases the stickiness of the particles. Further, the sintering of the ash deposit also increases leading to strong deposits.
2. The increased surface temperature leads to increased corrosion due to S and Cl. A number of studies have been made at Denmark Technical University about this aspect of ash related problems (Hansen, Andersen et al., 1998; Michelsen, Frandsen et al., 1998).

A preliminary analysis of the impact of surface temperature alone on deposition was made on a number of coals using the CCSD Ash Effect Predictor. An increase in the surface temperature from 500 °C to 600 °C increased the deposition of ash by about 10%. The Predictor can therefore provide a tool for research in this area.

6 Biomass Co-Firing

In order to reduce CO₂ emissions, electric utilities use biomass for (co-) combustion. In supercritical boilers this practice may be associated with a change in corrosion rates. Biomass contains typically lower S and Cl levels than coal, but higher Na and K levels. It would appear that the co-firing of coal with biomass in supercritical units could be associated with corrosion problems.

Experience has been obtained in Denmark, where straw is used for co-firing in supercritical boilers. Straw is relatively high in potassium and chlorine and has posed the boilers with high corrosion and ash deposition propensities. A program of tests has been executed to examine the effects of straw co-combustion on different materials (Henriksen and Larsen, 1997). From these studies it was concluded that co-firing of straw in pulverised coal boilers was possible provided that the share of straw was limited. The maximum limit had not been established in that study. Another study on straw co-firing showed that high amounts of KCl were deposited, possibly increasing corrosion rates (Frandsen, Nielsen et al., 1998).

The effect of co-firing biomass with different fuels has been summarised by Hein (Hein, 2001). The results of these are shown in Table 6-1 and indicate that co-firing of coal with biomass in supercritical boilers is associated with corrosion problems.

Steam Temperature	450 – 520 °C	520 – 560 °C	560 – 600 °C	> 600 °C
Coal + wood	+	+	+	+
Coal + 10 – 20 % straw				?
Coal + > 20 % straw	0	-	-	-
Oil + wood	+	+	?	?

Table 6-1: Corrosion for Various Fuel Combinations Used in PF Boiler at Steam Temperatures from 450 – 600 °C. + acceptable corrosion rate, 0 may be acceptable or not, - unacceptable corrosion, ? to be verified. (Hein, 2001).

7 Acknowledgement

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