INFLUENCE OF DESIGN AND MATERIALS WITH CONSIDERATION TO THE ANNUAL MAINTENANCE WORKS IN RECOVERY BOILERS

by

Simon Praszkier

Diploma work No. 48/2011

at the Department of Materials and Manufacturing Technology CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden

Diploma work in the Master program Advanced Engineering Materials

Performed at:	Safe Control Boiler Service Tillgängligheten 1, 417 01 GÖTEBORG
Supervisor(s):	Lars Andersson, Safe Control Materialteknik Paul Praszkier, Safe Control Boiler Service Tillgängligheten 1, 417 01 GÖTEBORG
	Torbjörn Ylipää Department of Product and production development Chalmers University of Technology, SE - 412 96 Gothenburg
Examiner:	Mats Norell Department of Materials and Manufacturing Technology Chalmers University of Technology, SE - 412 96 Gothenburg

INFLUENCE OF DESIGN AND MATERIALS WITH CONSIDERATION TO THE ANNUAL MAINTENANCE WORKS IN RECOVERY BOILERS

Simon Praszkier

© Simon Praszkier, 2011.

Diploma work no 48/2011 Department of Materials and Manufacturing Technology Chalmers University of Technology SE-412 96 Gothenburg Sweden

Telephone + 46 (0)31-772 1000

INFLUENCE OF DESIGN AND MATERIALS WITH CONSIDERATION TO THE ANNUAL MAINTENANCE WORKS IN RECOVERY BOILERS

Simon Praszkier Department of Materials and Manufacturing Technology Chalmers University of Technology

SUMMARY

During the last decades there has been a strive for recovery boilers with high steam outlet temperature, high pressure and load capacity. One of the reasons for this has been the increased profit from producing and selling green energy as a by-product from the Kraft pulping process. While the boilers performance has increased, the design and materials used have much remained the same as before and thus many modern paper mills have had problems with expensive equipment wastage.

The annual maintenance outage is very costly for the mills when all the equipment must be inspected and, if needed, repaired. Each problem requires its specific personnel, time and spare parts which are all important resources. Furthermore security issues may require repairs to be queued and every hour is costly while production is stopped. Thus there is great value in reducing the risk of potential problems already in the design stage of the boiler.

This thesis investigates how the choice of design and materials affect the annual maintenance shut down and the associated costs. The study has focused on the temperature distribution inside the superheaters, how it depends on the design and how in turn this affects the superheater corrosion. Apart from reviewing the theory behind this matter, raw steam data was collected from the mills and analyzed. Furthermore three actual cases of superheaters corrosion were investigated to find the cause of the corrosion and possible solutions.

The studies revealed that many superheater corrosion problems could have been avoided using better materials and a design that reduces the temperature imbalances obtained with the conventional design.

Since the pulp and paper industry focuses on buying the cheapest possible design, the costs of some design related problems were investigated. In the cases of superheater corrosion and superheater ties, these costs were compared to those of a more robust initial design. In these cases, it was found that the costs of repair and production losses caused by inadequate designs were high and that the life cycle cost of the boiler could be lower using designs with higher initial costs.

Finally a design case where the maintenance perspective has been somewhat overlooked is described and followed by a suggested model for how the maintenance perspective could be included in new boiler project organizations.

Keywords: Recovery boiler, maintenance, corrosion, stainless steel.

Index

1	Intro	oducti	on	. 1
2	Shor	t over	rview of the kraft pulping process	. 2
	2.1	The o	chemicals used in the kraft pulping process	. 3
	2.2	The o	chemical recovery process	. 4
3	The	recov	ery boiler	. 6
	3.1	Step	through of the recovery boiler	. 8
4	Intro	oducti	on to superheaters	12
	4.1	Diffe	rent superheater designs	13
	4.1.1	L	Conventional design	13
	4.1.2	2	Wrap around superheater	13
	4.1.3	3	Integrated screen design	14
	4.1.4	1	Small superheater size design	15
5	Mate	erials	used in superheaters	16
	5.1	Carb	on steel and low alloyed steels	16
	5.2	Aust	enitic stainless steel	16
	5.3	Com	posite tubes	18
6	Tem	perati	ure imbalances in the superheaters	20
	6.1	Theo	bry	20
	6.2	Emp	irical analysis of the temperature imbalances	23
	6.3	Discu	ussion of consequences of imbalances	25
7	Theo	ory of	recovery boiler superheater corrosion	26
	7.1	Depo	osit melt corrosion	26
	7.2	Sulpl	hidation corrosion	30
	7.3	Chlo	rine induced corrosion	30
8	Anal	ysis o	f corrosion cases	32
	8.1	Case	1 – Nueva Aldea	33
	8.1.1	L	Examination of tube samples collected from the damaged superheater	33
	8.1.2	2	Temperature	37
	8.1.3	3	Ash composition	37
	8.1.4	1	Hardness measurements	38
	8.1.5	5	Sulphur print by Baumann method	39
	8.1.6	5	Discussion Nueva Aldea	40
	8.2	Case	2 - Burgo Ardennes (Belgium)	41
	8.2.1	L	SEM analysis	42
	8.2.2	2	Hardness measurements	43
	8.2.3	3	Sulphur print by Baumann method	44

	8.2.4	ļ	Temperature in the Burgo Ardennes superheaters	45
	8.2.5	5	Amounts of chlorine and potassium in Burgo	45
	8.2.6	5	Discussion	45
8	.3	Case	3 – Valdivia	46
	8.3.1	L	Introduction	46
	8.3.2	2	Location of damages	48
	8.3.3	3	Steam temperature trend and ash composition	50
	8.3.4	ļ	Hardness measurements	56
	8.3.5	5	Sulphur print by Baumann method	60
	8.3.6	5	Micro structural analysis of tube sample	60
	8.3.7	7	Discussion	63
8	.4	Supe	rheater corrosion & design discussion and findings	66
9	Econ	omy o	of boiler design	68
9	.1	Defir	nition of reliability and maintainability	68
	9.1.1	L	Reliability	68
	9.1.2	2	Maintainability	70
10	Er	npiric	al study of problems caused by the boiler design	71
1	0.1	Case	4 – Superheater corrosion	71
	10.1	.1	Costs of possible changes to the tertiary superheater:	72
1	0.2	Case	5 – Superheater ties	74
	10.2	.1	Life cycle analysis	79
1	0.3	Case	6 – Sootblower Wall boxes	83
	10.3	.1	Cost of the problem	85
1	0.4	Case	7 – Access	87
11	Tł	ne org	anization today	90
1	1.1	The o	different departments	90
1	1.2	The p	project organization	91
1	1.3	Discu	ussion	94
	11.3	.1	Problems with the organization today	94
	11.3	.2	Understanding and defining the project	95
12	Pr	ropose	ed organization	97
13	Co	onclus	ions	99
14	A	cknow	/ledgements1	.02
15	Re	eferen	nces	.03

1 Introduction

In modern paper mills it has become standard practice to elevate the steam outlet temperatures as much as possible in order to increase the electricity production. At the same time it is a quite common practise of the buying organizations, during a new boiler project, to take the cheapest offer available, as long as it fulfils the required performance regarding capacity and steam outlet temperature.

As a result several paper mills today experience expensive problems with the equipment in their facilities and a very common issue is severe superheater corrosion. It is common knowledge that many problems are inherited from the decisions made during the buying process of the boilers, which are generally delivered in a highly standardized and conventional design.

This thesis has two purposes: The first one is to investigate the mechanisms behind three cases of severe superheater corrosion and to analyze which parameters that affect the corrosion and in what way. Furthermore it is also the aim of the thesis to suggest how future corrosion can be avoided.

In order to investigate the superheater corrosion, various superheater designs were reviewed together with analysis of data regarding both temperature and chemical compositions of ashes. Material analyzes were then made on the corroded tubes in search of evidence for certain corrosion mechanisms.

The second purpose is to analyze how the buying organization's design decisions and organization during the buying process affect the maintenance costs of the recovery boiler.

In order to investigate how the buying organizations affect the maintenance costs of the recovery boiler some cases of problems caused by design were reviewed and their costs were calculated. Interviews were then held with personnel with experience of both boilers and boiler projects in order to get an understanding of how it is organized.

2 Short overview of the kraft pulping process

The paper manufacturing process begins with chipping wood and loading it into boiling vessels called digesters. The digesters can be of both batch and continuous type, but in modern plants continuous digesters are the most common.

In a continuous digester the chipped wood is introduced in an even stream through the top of the vessel, which has the shape of a circular tube. After loading the wood, white liquor (see Table 2 for reference) is added and the mixture is heated with steam. As the plug of liquor drenched wood is moved downwards, it is being cooked at the same time and in the bottom, finished and partially washed pulp is removed.

The average composition of wood can be found in Table 1 (Borg, 1986).

Table 1 – The average composition of wood

Wood	%
Cellulose	40
Hemicelluloses	30
Lignin	25
Extractives	5

The pulp consists of wood fibres, which are built up by cellulose. Thus the boiling process is about separating the cellulose from the lignin, which is the binder that holds the wooden fibres together.

As a rule of thumb about half of the amount of wood loaded into the digester, is turned into pulp in the process. The other half, which mainly consists of lignin, is found in the used cooking liquor, called black liquor.

After the separation of the fibres from the lignin, the pulp is washed in combinations of the following washing equipment:

- Pressure diffusers
- Atmospheric diffusers
- Vacuum drum washers
- Drum displacers
- Wash presses

The two main principles utilized in the washing process are diffusion and displacement. The idea is that the black liquor shall diffuse from the fibre out to the surrounding liquid, often with help of displacement. Displacement means that a purer liquid forcefully takes the place of the black liquor inside the fibre by pushing out the black liquor.

The reason for washing the pulp is that too much black liquor with the fibres will create problems with excessive foaming in the operation, high consumption of chemicals (in cooking and bleaching), toxic emissions and poor paper quality.

After the pulp has been washed it is bleached and further processed into paper or sold as market pulp. The black liquor created in the process is transported away for recycling.

2.1 The chemicals used in the kraft pulping process

White liquor

White liquor has a yellowish or green-yellowish colour and is an alkali solution containing various sodium compounds. Out of the various compounds in white liquor, only sodium hydroxide (NaOH) and sodium sulphide (Na₂S) can dissolve the lignin and they are therefore called the active components. Being an alkali solution, white liquor has a very high pH and is thus highly corrosive.

There are no exact values as to in which concentration the various compounds of the white liquor should be, since this varies a lot between different factories, depending on how the chemical recycling works. As a guideline, Table 2 below can be used.

Name	Formula	Conc. grams/litre
Sodium hydroxide	NaOH	100-120
Sodium sulphide	Na ₂ S	20-50
Sodium carbonate	Na_2CO_3	20-30
Sodium sulphate	Na_2SO_4	8-16
Sodium sulphite	Na_2SO_3	low conc.
Sodium thiosulphate	$Na_2S_2O_3$	11 11
Sodium chloride	NaCl	

Table 2 – Guideline to content of white liquor (Borg, 1986)

Black liquor

Black liquor is a black liquid consisting of the residue from the cooking operation, containing all the added chemicals (white liquor) and all organic substances dissolved from the wood during cooking.

Black liquor is however far from the same thing as white liquor since the alkali has changed into other kinds of sodium compounds. As seen in Table 3 below, the active sodium compounds (NaOH and Na₂S) from the white liquor have reacted with the lignin and bound to organic acids created from the lignin and hemicelluloses. Some sodium compounds remain as inorganic residues in the black liquor.

Table 3 – General composition of black liquor (Borg, 1986)

Substance	% of dry substance
Lignin compounds	31
Carbohydrates	31
Rosin	3
Inorganic chemicals	35
	100

2.2 The chemical recovery process

The recycling process of black liquor is concerned with transforming the black liquor back into white liquor so that it can be used again in the cooking process. Here a detailed description of the process will be given, but a flowchart of the process can be seen in Figure 1 on the next page.

As mentioned previously the black liquor consists of a very large amount of the original wood, which constitutes about 60 % of the dry substance of the black liquor. However the liquor that leaves the pulp washing process only contains about 13 - 16 % dissolved solids, which makes it incombustible. Thus the first step in the recovery process is the evaporation process where the dry content of the black liquor is increased to at least 60 % (Hough, 1992) via evaporation of water. This process takes place in a series of so called evaporator units, where the black liquor is heated with steam and the pressure is continuously reduced between each evaporator unit in order to lower the boiling temperature.

After the evaporation to about 60 % dry content, the black liquor contains (Borg, 1986): 40 % water 20 % inorganic, non combustible substances from the boiling chemicals 40 % organic, combustible substance from the wood

Note however, that in modern facilities the dry content is most commonly increased to about 72 %, which means that the content of water is only around 28 %. If the black liquor would be enriched to 80 % dry content or more, severe erosion of the piping can take place. If dry content of 80 % is to be used, the piping system has to be redesigned and other more erosion resistant materials must be used. Recommended materials include, for example, duplex stainless steel Avesta 22.05 or 25.07 (Metso Power AB).

Now the liquor is transported to the recovery boiler, where it is preheated in order to obtain the right viscosity and then injected into the furnace part of the recovery boiler. The viscosity is important because it greatly affects how the black liquor is distributed inside the boiler by the injection nozzle and splash plate.

In the furnace the organic content of the black liquor is burnt and the remaining water evaporated. In the process of burning the black liquor, sodium carbonate (Na_2CO_3) and sodium sulphate (Na_2SO_4) is formed. These chemicals are gathered in the bottom of the recovery boiler, where a deficit of oxygen creates a reducing environment in which the oxygen is forced out of the sulphate, reducing it to sodium sulphide (Na_2S) . Measured values of the heat in the furnace are often found to be about $1100^{\circ}C$ (Aracruz Cellulose S.A) and this intense heat melts the chemicals which then flow down to the dissolving tank via the smelt spouts.

In the dissolving tank the smelt is dissolved in hot water or weak black liquor (the black liquor received after washing of the pulp containing ≈15 % solid content). The colour becomes greenish and the solution is called green liquor.

The green liquor is then transported to the mixing tank, where it is mixed with burnt lime so that the sodium carbonate reacts with the lime and forms sodium hydroxide once more. This is called the causticizing process. After this final step the two active ingredients of the white liquor (Na₂S and NaOH) have been recovered and the chemicals can be used once more in the cooking process.



Figure 1 – The chemical recovery process

3 The recovery boiler

The recovery boiler is perhaps the most important unit of any cellulose factory since the black liquor from the evaporation process (strong black liquor) is burnt here. This is the primary function of the boiler because without the burning of the black liquor, no recycling can take place. A common misperception is that it is a primary function to generate steam, but this is incorrect. It is true that the energy from the steam produced in the recovery process is important for the economy of the facility, but it could be supplied from elsewhere. However, if the recovery process stops, the cellulose manufacturing stops as well. There are several reasons for this, the primary being that the large volumes of black liquor produced makes it difficult to store in wait for the boiler to start up again. Secondly, the white liquor is expensive so without recycling the cooking chemicals, it would be difficult to keep the production economy in order.

Thus we can define the functions of the recovery boiler as the following:

- Primary function Recycle the cooking chemicals
- Secondary function Generate steam and energy

In Figure 2, on the next page, the recovery boiler of Celulosa Arauco y Constitución, Nueva Aldea Mill in Chile is shown. This unit has a capacity of 4400 tds/day and produces 178 kg steam/s. Where tds is tons dry solids, which means that the quantity of water in the black liquor is not accounted for (i.e. black liquor with 100 % solid content). It is rarely the case that a recovery boiler is not used at its maximum capacity, so considering that Nueva Aldea burns the equivalent of 4400 tds/day and that the dry content of the actual black liquor is minimum 60 %, it would mean that this particular recovery unit processes about 7333 tons of thick black liquor/day. With this rough estimate it is easy to realize that not recycling the white liquor would be impossible from a processing point of view.



Figure 2 – The recovery boiler in Celulosa Arauco y Constitución, Nueva Aldea Mill in Chile (Courtesy of Metso Power)

3.1 Step through of the recovery boiler

Here the different parts and processes of the recovery boiler will be described. The description is based on interviews with Metso and Safe Control engineers as well as the books "Yrkesbok C III - Sulfatmassetillverkning (kokning, tvättning, återvinning)" by Olof F. Borg and "Chemical Recovery in the Alkaline Pulping Processes" by Hough, Robert P. Green & Gerald. Let us take the explanation of the recovery boiler in steps from the point when the black liquor enters the boiler (for reference, see Figure 2).

All recovery boilers are built out of tubes and flat bars called membranes. The tubes and membranes are welded together, as shown in Figure 3, to create boiler walls. There are around 120 to 180 tubes and membranes (made in carbon steel or stainless steel of various grades) in each wall, depending on the size of the boiler. Most frequently, 2 inch diameter tubes (63,5 mm) are used. The walls create the boiler furnace where the combustion takes place.



Figure 3 – The recovery boiler furnace wall

All recovery boilers are built up by tube walls containing pressurized water. Basically the boiler walls can be seen as welded together pressure vessels, in which water is heated by the burning of black liquor inside the furnace of the boiler. In the lower part of the boiler, where the temperatures are higher, composite tubes are often used. Composite tubes are basically carbon steel tubes with the outer side made of austenitic stainless steel (see Figure 4). The leading company manufacturing the composite tubes is Sandvik AB.



Figure 4 – Composite tubes with a membrane welded between the tubes, macro photo.

Higher up in the boiler, where the temperatures are lower, normal carbon steel is used. Circulation of boiler water through the furnace is by natural circulation caused by density differences. Water with higher density, at or below the saturation temperature, flows downwards from the steam drum through large-bore downcomers, to a series of headers that supply water to the furnace floor and

walls. Heat absorbed by the water walls causes steam to form in the boiler water and this lowers the density and causes the water to rise through the wall tubes.

The black liquor is introduced into the furnace via the liquor sprayers. Here the preheated liquor is shot through a nozzle onto a splash plate, which is designed to distribute the black liquor throughout the furnace as evenly as possible. This is very important since all of the water must evaporate before any of the high temperature processes of the recovery can occur and this happens more easily if the liquor droplets are small. If the droplets are too small, the dry content will combust before it reaches the bed and the ash will follow the gas stream and create problems with ash covering throughout the boiler (this is called black liquor carryover or just carryover in short). If the droplets are too coarse, the last of the evaporation will take place in the bed zone, which lowers the temperature of the bed and increases the amount of sulphur dioxide (SO_2) and total reduced sulphur (TRS) emissions.

In or close to the bed (bottom of the furnace), pyrolysis and gasification takes place. This degradation of the black liquor produces combustible gases and carbonaceous char. The char is a mixture of so-called fixed carbon and inorganic compounds such as Na₂CO₃, Na₂SO₄ and Na₂S.

The amount of oxygen available in the bed region is important since there must be so little air that the atmosphere is reducing in order for the recovery process to work. At the same time there must be enough oxygen available to allow combustion of volatiles and ensure a high enough char burning rate. This is controlled by the primary air which is found in the same level as the bed. The primary air controls the combustion, reduction, temperature and height (position) of the bed. Without control of the height, the bed would build up higher and higher and eventually collapse against the furnace wall, causing severe problems.

Above the bed, the secondary air is located. The secondary air governs the combustion of the volatiles released in the pyrolysis process as well as ensuring a suitable temperature for drying the black liquor sprayed out by the liquor sprayers.

The gas then continues upwards in the boiler to the oxidizing zone between the liquor sprayers and the tertiary air. Here the combustion process within the furnace is completed by oxidization of carbon monoxide and reduced sulphur gases into carbon dioxide and sulphur dioxide respectively.

In some facilities where the environmental demands are very high, quaternary air has been installed above the tertiary in order to further reduce NO_x emissions.

The secondary, tertiary and quaternary air are most often of interlace design, which means that they are displaced sideways relative to each other on two opposing walls (see Figure 5 below). The displacement helps to better distribute both the air and heat in the boiler.





Figure 5 – Interlace design of air systems

As the flue gas continues upwards, some of it hits the nose at the boiler's rear wall. This redirects the flue gas to hit the front wall and then turn towards the superheaters and the generating bank. In level with the nose the water screen is also located in some boilers (not all boilers have water screens). The water cooled screen lowers the temperature of the flue gases before they reach the superheaters. This is not so much for the sake of the superheaters as for the generating section since the "stickiness" of the ash is temperature dependant and the closely spaced tubes of the generating section makes them susceptible to rapid ash fouling. The screen also provides some coverage of the leading edges of the superheater, which helps reduce metal wastage rates. Water circulation of the screen works in the same way as in the water walls.

As the water rises in the water walls of the boiler, it is subsequently heated all the way and as such the amount of steam in the water increases. Apart from burning black liquor in order to recycle the chemicals, the idea behind the recovery boiler is also to use the energy released in the process to generate steam and electricity. This can be done with the help of a steam turbine and so the steam inside the water walls needs to be separated from the water. This takes place in the steam drum

which is located on top of the boiler. When the steam-saturated water enters the drum, it basically allows the steam to exit through the roof of the drum. Meanwhile gravity forces the water to the downcomers which returns it to the boiler.

From the steam drum the steam enters the superheaters which consist of a series of intermeshed tubes as shown in Figure 6. As the steam flows though the loops of the superheaters, the temperature of the steam increases to around 400-500°C (486°C in Nueva Aldea) before it exits to the turbine. The increase in useful energy of the steam allows for more efficient generation of electricity by the turbines. As heat is absorbed by the superheaters the temperature of the flue gases is decreased further.

Beyond the superheaters is the generating section. In addition to the waterwalls, the generating section, which is connected to the screen, helps generating steam. Both the generating section itself and especially the screen are more efficient surfaces for heat absorption



Figure 6 – Bottom part of a tertiary superheater panel in Nueva Aldea

than the waterwalls, since the flue gases hit them straight on. In much the same way as the furnace waterwalls, the generating section is fed by downcomers from the steam drum. The water enters in the bottom of the generating section and flows upwards by natural circulation. When it reaches the top, it exits through the outlet headers and continues to the steam drum. Unlike the furnace and superheaters, which rely mostly on radiant heat transfer, the generating section relies on convective heat transfer. This demands the generating section to be arranged on fairly close centers in order to develop sufficient flue gas velocity for efficient heat transfer. At the same time it makes the generating section susceptible to gas side ash fouling.

The last section reached by the flue gases is the economizer. Strictly spoken, the economizer is not actually part of the recovery boiler, but rather an auxiliary system driven by pumps. Water is pumped to the economizers and through them to the steam drum by the feed water pumps. The water heated in the economizers is called feed water and it must be fed into the boiler to compensate for the steam taken from the boiler to the turbines. The reason for pumping the feed water through the economizers is to preheat it in order to avoid the risk of damage when it enters the hot steam drum and of course in order to increase the thermal efficiency of the boiler. The economizer consists of vertical tubes connected to headers in both top and bottom. The feed water usually enters the economizer through the lower headers and exits through the upper ones. In order to maximize the heat transfer surface of the economizer, the tubes are generally finned here.

4 Introduction to superheaters

The main purpose of the superheaters is to overheat the steam, meaning raising the temperature over the saturation point. In the past there were many steam boilers that did not contain any superheaters since not all boilers produced steam to the turbine and thus higher steam temperatures were not needed or desired in the pulp paper production process. Today all recovery boilers contain superheaters and due to the power costs and "Green Energy" benefits, the steam temperature and pressure tend to rise.

The older Kraft Recovery Boilers contained superheaters that produced steam with 420-450°C and the pressure was often limited to 50-75 BAR. In the nineties the temperature was raised to 480°C and the pressure increased to 75-100 BAR. 480°C was for a long time considered to be the absolute limit for recovery boilers, with consideration to corrosion.

Today we know that higher steam temperatures can be produced in a recovery boiler, but the operating margins become smaller. That is to say that the margin between normal operating conditions and conditions where severe corrosion can occur become small. Strict control of the chemical composition of the ash and strict control of the operational variables are necessary in order to avoid severe material loss in the superheaters.

Japan was early with fabrication of boilers with high steam performance and they must still be considered to be world leading when discussing superheater design. Götaverken made good progress in the field of high temperature design of superheaters, but after being incorporated into Kvaerner, no new boiler designs are made in Sweden. The dominating manufacturers, Metso (who bought Kvaerner) and Andritz continue to deliver all their boilers with conventional superheater design, even for new high pressure, high temperature steam boilers. The result of this is that the operating margins are lower (see the section "Temperature imbalances in the superheaters") and that several mills with both high pressure and temperature have problems with severe superheater corrosion as seen in plants like Burgo Ardennes in Belgium, Botnia in Urugay, Aracruz C in Brazil and Valdivia in Chile.

So what is the difference between a modern superheater design and the classical one and how does the design affect superheater corrosion? To answer these questions we must have a look at the different designs and how they affect important parameters of superheater corrosion.

4.1 Different superheater designs

Here the different superheater designs will be described and some pros and cons with each design will be explained.

4.1.1 Conventional design

The conventional design, as seen in Figure 7, is a very simple one where tubes are connected to an inlet header and go down and up several times in a wave pattern inside the boiler, before finally exiting through the outlet header. In the conventional design every tube maintain its original position, with respect to each other, throughout the entire run through the boiler. Because of this the outer tubes will be longer than the inner tubes and as such they will absorb more heat than the inner ones. Furthermore the inner tubes are protected from hot gases and radiation by the outer ones, which will be exposed to a higher heat flux.

Advantages:

- Easy to fabricate (cheap)
- Allows continues line fabrication

Disadvantages:

- The outer tube will always be directly exposed to hot gases and radiation whereas the inner tubes are always protected by the outer one
- The outer tube is longer than the adjacent tubes
- The hottest tube (outer tube) is not protected

Result:

 The outmost tube will be hotter than the inner, protected tubes and thus the temperature difference (ΔT) between the tubes can be significant. The superheater "imbalance" may be very large

4.1.2 Wrap around superheater

"Wrap around" is a simple and inexpensive way to eliminate some of the disadvantages with the conventional superheater. By the use of a protective wrap around the outmost tube, it gets shortened. In this way the outmost tube will pick up less heat and thus it will stay cooler than in the conventional design. A "wrap around" superheater panel is shown in Figure 8.

The general idea with the "wrap around" design was to imbed the superheater panel with cooler tubes to protect the hotter tubes by having them inside the panel. This design was often used in the 1970's and 1980's by both B&W and Götaverken. Götaverken boilers had a steam screen wrapping around the entire secondary superheater. One boiler of this kind, which is still in service, is the Göteverken boiler in Alto Parana, Argentina.



Figure 7 – Conventional superheater design, shortened two sections (courtesy of Metso Power)



Figure 8 –Wrap around superheater design, shortened two sections (courtesy of Metso Power)

4.1.3 Integrated screen design

The integrated screen design, where the hottest tubes run inside the panels, was introduced by B&W Canada a long time ago. When it started it was not aimed at being the bridge into higher steam performance, only additional protection of the tubes.

Götaverken developed the integrated screen design to state of the art technology before high steam data boilers where commonly fabricated, expecting the demands around 10 years before they actually occurred.

As seen in Figure 9, the hottest tubes are running inside the screen, in the integrated screen design, making them completely protected. Furthermore, all tubes with similar steam temperature are welded together with a $\frac{1}{2}$ inch membrane. This design minimizes the ΔT within a screen.

Advantages:

- The hottest tubes run inside the screen, resulting in a smoother temperature profile around and across the screen
- There are no tubes that always meet the hot gases straight on or receive full radiation i.e. the ΔT is lower inside the screen
- The ΔT between adjacent tubes is limited (except at the loop turning)
- Less amount of ties needed

Disadvantages:

- Can be more expensive to manufacture
- Require flexible manufacturing facilities
- Larger ΔT at the loop turn requiring larger expansion allowance
- Lower thermal efficiency in membrane panels.



Figure 9 –Integrated screen superheater design, shortened two sections (courtesy of Metso Power)

4.1.4 Small superheater size design

The idea behind the design with small superheaters is the fact that the higher the amount of tubes from an inlet header, the lower the steam velocity through a panel. The more loops the tubes make, the longer are the tubes and the steam retention time in the tubes. Both factors contribute to making the temperature imbalances larger.

Japanese manufacturers like Hitachi and Mitsubishi were early in introducing much thinner superheaters (fewer amounts of loops) in the recovery boilers with high steam temperatures. It was mainly the final superheaters that were much shorter and therefore the steam was mixed more often. Instead of one large tertiary superheater the boilers could contain two tertiary superheaters or even one tertiary and one quaternary superheater with attemperation in between them.

As previously mentioned, above 480°C steam temperature the operating margins against severe corrosion are not very large. Above 480°C the temperature is very close to temperatures where most of the aggressive corrosion mechanisms are present. By making the final superheater smaller and mixing the steam more often, the imbalances are reduced significantly. This allows for reaching higher average steam temperature without locally increasing individual tube temperatures.

An example of a smaller superheater is shown in Figure 10 below.

Advantages:

- The steam is mixed more often and so the imbalances (all of them) are significantly reduced.
- The average steam temperature better reflects the highest tube temperature.

Disadvantages:

• More expensive to manufacture since it requires at least two more headers and cross over piping if same amount of tubes is maintained.



Figure 10 – An example of a smaller superheater with only two loops and a wrap around

5 Materials used in superheaters

The materials for the chemical recovery boiler superheaters can be divided into three main groups: carbon steel and low alloyed steels, austenitic stainless steels and composite tubes containing both these groups. In the following text high strength at elevated temperatures does not only refer to the yield strength of the material but also its resistance to creep. For reference to material strengths and alloying elements, please see Figure 11 and Table 5 at the end of the chapter.

5.1 Carbon steel and low alloyed steels

Carbon steel is only used in the coldest part of the superheaters i.e. the primary superheater I. The main reason for this is the extremely low strength at elevated temperatures and their low scaling temperature. From an engineering point of view these materials should not be used in superheaters, but because of their low cost they are frequently used in the "cold" primary superheater. Low alloyed steels for the superheaters are typically designated by a certain amount of chromium and molybdenum. The two most typical low alloyed steels that are used worldwide by all boiler manufacturers are the 1,25% Cr + 0,5% Mo, such as SA213T11/T12 or 13CrMo44 and the 2,25% Cr + 1% Mo such as SA213T22 or 10CrMo910. These are characterized by significantly increased strength at elevated temperatures and elevated scaling temperature. However, the corrosion resistance against deposit melting or sulphidation corrosion is quite limited. The price of these steels is still quite low, the weldability is good and the material is generally easy to attain on the market. These factors have made the material the most commonly used material in superheaters today.

Adding more chromium and molybdenum creates alloyed steels which are characterized by high strengths at elevated temperatures at a cost of reduced weldability (Almar-Naess, 1983). The higher the chromium content, the more self-hardening is the steel at welding operations. The limit is passed around 3% Cr. Thereafter the welding properties decline rapidly.

This causes severe maintenance problems by requiring complicated welding procedures and post weld heat treatment at all thicknesses as for SA213T91 (9% Cr + 1% Mo). The operations are not impossible but they are expensive and time consuming. During an ordinary shut down of a recovery boiler it may result in expensive production losses due to prolonged shut down.

Despite these additions, the materials corrosion resistance is still limited and only slightly better than SA213T11 or SA213T22. SA213T91 is commonly used in superheaters with very high pressure and design temperature due to the fact that the ordinary low alloyed steels such as SA213T12 or T22 would require too thick tube wall thickness. In general, wall thicknesses above 8 mm are not desired in the superheaters and one of the reasons for this is the reduced heat transfer.

5.2 Austenitic stainless steel

In order to find a material with sufficiently high resistance against deposit melting corrosion and sulphidation, austenitic stainless steels have been tested. There is a large range of different alloys designated for superheater materials. The simplest ones are the most common austenitic stainless steels containing 18% Cr + 9% Ni, for example SS2333 or AISI304 and they are then often stabilized with Ti as for the alloy AISI347. The most common and classic austenitic stainless steels for

superheaters are SS2361 and AISI310 containing 25% Cr + 20% Ni. There are several special alloys, very similar to the AISI310, slightly modified and sold under different trade names.

AISI310 has very good strength at elevated temperatures and rather good corrosion resistance against the most common corrosion types. The weldability of austenitic steel is also good, as long as the welding is done "in cold", so as to avoid sensibilization.

However, austenitic stainless steels with low amounts of nickel are very sensitive for stress corrosion. Low bending radius, high residual and high operational stresses combined with salts may result in stress corrosion cracking. Sodium hydroxide (NaOH) and chlorine contamination of the steam are common causes of stress corrosion cracking (SCC) and several cases of SCC in bent areas have been reported over the years (Götaverken Energy, 1989).

The risks are not that high, if the mill has good control of its operating procedures, but the consequences are severe. If stress corrosion cracking takes place, a leakage will normally not just occur in one bend, but in several bends at the same time, resulting in a very long down time of the boiler.

Another problem with the austenitic stainless steels is their thermal expansion which is approximately 30% higher than that of ferritic steels (Gale & Totemeier, 2006). This may cause problems if austenitic and ferritic steels are used together. The differences could result in tube deformations, tie cracking or both.

Yet another drawback with austenitic steel is its lower heat transfer rates (Gale & Totemeier, 2006) which give a few degrees higher surface metal temperature. However, this last drawback is generally considered as a non critical problem for these steels (Götaverken Energy, 1989).

The homogenous austenitic stainless steel tubes would be a good possible solution to the superheater corrosion problems if not for the SCC sensibility. Examples of plants that have experienced this problem are Riu Andallan in Indonesia and Pacifico in Chile.

In Table 4 below, the creep resistance of two ferritic and two austenitic steels are shown. As seen in the Table, the creep resistance of austenitic steels is higher than that of ferritic steels.

Table 4 - Load required to cause creep fracture in 100 000 hours at 500°C and 600°C. Based on values from (Götaverken Energy, 1989)

Maximum load for creep fracture	e time of 100 000 hours (MPa)
---------------------------------	-------------------------------

Steel	%Cr	%Ni	%Mo	Other	Classification	500°C	600°C
T22	2,25	0	1	-	Ferritic	69 Mpa	34 Mpa
T91	9	0	1	-	Ferritic	93 Mpa	37 Mpa
TP304	18	8	0	-	Austenitic	115 Mpa	74 Mpa
TP321	17	10	0	1% Ti	Austenitic	-	106 Mpa

5.3 Composite tubes

In order to escape from the SCC risks, composite tubes have since long been introduced. The composite tubes combine a good strength at elevated temperatures and high resistance against stress corrosion with very good corrosion resistance. Basically the composite tubes consist of two parts (see Figure 4 on page 8). The inner pressure retaining part is made of normal low alloyed steel, which is resistant against stress corrosion cracking. Around the inner, pressure retaining part, an outer protective layer is wrapped, giving the composite tubes very good outer corrosion resistance as well.

The leading supplier of composite tubes is Sandvik AB and the two most common composite tube materials for recovery boiler superheaters are AISI310/SA213T22 and the newer Sanicro28/SA213T91. The first one is a classic tube that has been used since the beginning of 1990'ties. The second one is a new combination that saw usage after year 2000 and was designed for boilers with higher steam temperature and pressure. The experiences of composite tubes in the superheaters are excellent and looking from a technical point of view they are a good solution to the problem. The largest disadvantage of the tubes is the high price (see Table 19 on page 72) which has limited the use of these tubes in the superheaters. Today composite tubes are most commonly found in the outer lower bends and along the hottest, outmost steam outlet tube of superheaters that have experienced corrosion problems in these areas.



Figure 11 – Material strength as a function of temperature (Based on values from ASME Boiler and Pressure Vessel Code, Section II – Materials 2007)

Table 5 – Chemical composition and classification of alloys commonly used in recovery boilers (Based on values from ASME Boiler & Pressure Vessel Code, Section II – Materials 2007)

Material name	Classification	Alloying element (%)						
		Cr	Ni	Мо	Mn	Other		
SA213T91	Ferritic	9	-	1	-	V		
SA213T22	Ferritic	2,25	-	1	0,6	-		
SA213T12	Ferritic	1	-	0,5	0,6	-		
SA209T1	Ferritic	-	-	0,5	0,6	С		
SA210A1	Ferritic	-	-	-		-		
SA178A	Ferritic	-	-	-		-		
SA213TP310S	Austenitic	25	20	-	-	-		
SA213TP304H	Austenitic	18	8	-	-	-		
SA213TP316L	Austenitic	16	12	2	-	-		
AISI304	Austenitic	18	9	0	0-1	-		
AISI316	Austenitic	18	9	2,5-3	0-1	-		
AISI347	Austenitic	17	12	2-2,5	0-2	Ti		
AISI310	Austenitic	25	20	0	0-2	-		
Sanicro28	Austenitic	27	31	4	-	Cu		

6 Temperature imbalances in the superheaters

6.1 Theory

The standard way of measuring the temperature of the superheaters is to measure the temperature of the outlet steam from each superheater prior to and after attemperation. This means that we are measuring the steam temperature after the outlet header, but before the inlet header to the next superheater. The temperature measured is the temperature of the steam from all the panels, mixed together in the outlet header (see Figure 12).

The temperature measurements represent an average steam temperature in the particular superheater, but do not say anything about the lowest or highest temperature in each part of the superheater. It is impossible, or at least very difficult, to measure the metal temperature at the bends or straight tubes in the gas affected area.

In order to get some information about the local temperature, measurements are usually also taken on the outlet tubes up in the penthouse of the boiler, which is to say above the roof of the boiler. This means that the measurements are taken in colder environment not affected by the flue gas. Furthermore the boiler roof holds no more than 300°C and as the superheater tubes pass through the roof this should have a cooling effect on the tubes. The measurements are taken using thermocouples attached to the tubes. With perfect temperature balance this would suffice for controlling the process, but in reality there can never be a perfect balance. There are some parts of the tubes that will reach much higher metal temperatures than others. In areas where the radiation or gas velocities are higher than average, it simply follows that the same goes for the local tube temperature.



Figure 12 – Attemperation and measurement location between superheater panels (arrows show steam direction)

To complicate matters further, different tubes in the panels can have different lengths which then cause a temperature difference and thus an imbalance in each panel. The outmost superheater tubes, if not protected, will absorb more heat than the tubes hidden inside the panel. In a perfect design and perfect operational condition the unbalances would be limited to the above mentioned variables/factors:

- 1. Tube length
- 2. Tube position

This is unfortunately not the case, which means that we have further variables creating temperature differences between the panels and tubes.

One of the most common disturbances is the "chimney – effect". It has its origin in the location of the bed, which is placed in the centre of the boiler. This in turn centres the flue gases and thus the heat in the middle of the boiler. If the secondary, tertiary and possible also quaternary air systems (today most often of interlace design) do not succeed in cutting the central gas concentration and redistribute it evenly across the entire furnace, the central panels will be more heat affected than the panels located closer to the sidewalls.

The panels located adjacent to the sidewalls will also be further cooled by the sidewalls which are only heated to the saturation point (often < 300 C).

This provided that the inlet and outlet headers are of correctly designed size. If not, this is another source of the temperature imbalance. As the steam enters the inlet header it begins flowing down into the superheater panels, lowering the overall pressure in the header the further towards the middle the steam reaches. Since the speed for passing from one header to the other (i.e. to flow through a superheater panel) depends on the pressure, the speed is lower in the middle than at the ends (see Figure 13 below). This increases the retention time of the steam in the middle panels, which increases the steam temperature, which in turn gives less cooling to the tubes of those panels.

A well trained designer has this in account even though it affects prices, so it should not be a problem in a normal case. However, it may still affect the imbalance somewhat.



Figure 13 – Steam velocity differences in panels between inlet and outlet headers

In summary we have tube temperature imbalances within each panel depending on:

- 1. Tube length
- 2. Tube position

Furthermore we have panel temperature imbalances depending on:

- 1. How well the secondary, tertiary and possibly quaternary air skews of the central heat pillar (Chimney-effect)
- 2. Design of inlet and outlet headers in the superheaters

In the worst case, these individual imbalances may together lead to the consequence that the operator sees the temperature as adequate, judging from the average data, whereas in reality some panels and/or tubes are overheating while others are cooler than intended. In turn this may cause serious damage in the superheaters, as seen in Case 3: Valdivia in this thesis.

6.2 Empirical analysis of the temperature imbalances

In order to quantify the imbalances, raw data from Celulosa Arauco y Constitución S.A. was analyzed as part of this thesis work. Note that the imbalances here are only the imbalances between panel positions and between panels and outlet steam. It does not reveal anything about the imbalances within each screen. In Table 6 below, a set of momentary values of temperature imbalances are given. This is however only an instantaneous observation.

 Table 6 - An example of a set of data from the superheaters in Nueva Aldea showing the temperature difference

 between the hottest and coldest panel in each superheater

Superheater Metal Temperature (°C)								
Panel	l Primary 1 Primary 2 Seconda		Secondary	Tertiary				
1	327,60	357,86	391,44	452,17				
2	330,70	363,63	152,78	464,69				
3	330,55	360,54	446,04	471,47				
4	332,11	369,47	432,94	468,09				
5	330,86	365,97	463,49	479,10				
6	338,40	372,49	441,75	473,69				
7	332,44	368,84	478,13	478,83				
8	340,77	376,08	444,60	477,52				
9	334,99	371,55	471,35	488,05				
10	340,26	383,95	464,38	488,47				
11	336,89	375,31	481,72	494,09				
12	338,56	377,05	449,89	482,04				
13	333,66	367,42	467,78	480,62				
14	336,66	375,01	432,31	476,73				
15	328,78	364,70	446,12	483,37				
16	334,33	367,53	421,41	474,34				
17	328,10	359,17	433,39	465,43				
18	316,02	358,75	396,85	454,07				

	Superheater Metal Temperature (°C)							
	Primary 1 Primary 2 Secondary Tertiary							
Mean:	332,87	368,63	444,92	475,15				
Hottest:	340,77	383,95	481,72	494,09				
Coldest:	316,02	357,86	391,44	452,17				
Diff:	24,75	26,09	90,28	41,92				

Based on data from 345 observations, received from the Nueva Aldea mill, a more general value can be given to these imbalances. The average difference between the two hottest and coldest panels (measured on the outlet tube of each panel up in the penthouse) is as follows:

Tertiary superheater: average difference of 31,81°C Secondary superheater: average difference of 80,21°C

As can be seen the average values differ quite a lot from the momentary values in Table 6. The difference can be explained by the fact that the temperature is not an easily set variable in the process, but rather it varies during operation depending on other operational parameters such as the amount of attemperation.

What is of more interest is the difference between the hottest outgoing tube and the outlet steam temperature. This data is presented in Table 7. The term "Maximum outlet tube metal temperature" in Table 7 can be confusing and is in need of an explanation. For the outlet steam temperature, only one value per day was received (supposedly an average value), but for the penthouse metal temperatures (the panels), several values per day was received. As such an average value had to be calculated from the highest panel temperatures. This was then designated as "Maximum outlet tube metal temperature".

Date	Outlet temperature tertiary L1	Maximum outlet tube metal temperature, panels 1-9	Difference: steam/max. tube metal temperature	Outlet temperature tertiary L2	Maximum outlet tube metal temperature, panels 10-18	Difference: steam/max. tube metal temperature
2010-09-18	485,01	491,04	6,03	485,34	488,68	3,35
2010-09-19	484,81	491,04	6,22	484,89	491,29	6,40
2010-09-20	485,07	489,69	4,63	485,20	490,44	5,24
2010-09-21	485,09	491,02	5,92	485,15	492,04	6,89
2010-09-22	485,59	491,47	5,88	484,61	491,36	6,76
2010-09-23	484,89	490,36	5,47	485,63	491,09	5,46
2010-09-24	485,01	490,75	5,74	485,16	489,31	4,16
2010-09-25	485,03	490,15	5,12	484,70	489,06	4,36
2010-09-26	485,01	489,95	4,95	485,09	488,57	3,48
2010-09-27	485,09	490,78	5,69	485,04	490,79	5,75
2010-09-28	485,29	490,09	4,80	485,22	490,41	5,20
2010-09-29	484,84	491,65	6,81	484,80	491,29	6,48
2010-09-30	484,88	491,19	6,31	485,34	490,33	4,99
2010-10-01	484,78	491,86	7,07	484,96	488,96	4,00
2010-10-02	485,20	491,63	6,43	484,91	489,41	4,50

Table 7	7 - Comparison o	of tomporature	differences	hotwoon	hottest su	norheater	nanel and	d outlet steam	temnerature
I able /	/ - Comparison C	n temperature	unierences	between	nottest su	perneater	panel and	u outlet steam	temperature

What Table 7 above shows, is that the temperature of the outlet steam, that is to say the mixed steam from all the superheater panels, is colder than the outgoing tube of the hottest panel when measured up in the penthouse. This is off course logical since the mixed steam contains steam from all panels, while the given metal temperature here is the average of the extreme values (the hottest panel only). However, it shows that the imbalances exist throughout the entire boiler even in very friendly environments.

A difference of on average 5,47°C may seem very small, but as stated previously, this is in the penthouse. The surrounding temperature here is approximately 300°C and as such, it has a cooling effect on the tubes, meaning that the steam inside these tubes is actually some degrees warmer than the measured metal temperatures. This is in sharp contrast with the situation inside the boiler where the tubes are exposed to very hot flue gases ($\approx 1000°C$) and the steam needs to act as a coolant. So what the above data indicates, from an analytical point of view, is that the outlet steam temperature can be far from the actual metal temperature inside the boiler, where corrosion damages often occur.

6.3 Discussion of consequences of imbalances

Outlet steam data is not optimal for evaluating the tube surface temperature since this is the final steam temperature when the steam from all panels has been mixed together and as has been shown, there are always temperature imbalances between the different panels. Furthermore the gas-side tube surface will always be hotter than the cooling medium (the steam), but how much hotter is difficult to predict.

The thermocouples used for measuring metal temperatures in the penthouse are also not really reliable since they are not exposed to heat radiation or hot flue gases as is the case inside the boiler.

The difference between the steam inside a tube and the surface temperature of the tube is dependent on the heat transfer rate through the tube wall and it is affected by for example tube thickness, gas-side deposits, steam-side deposits, radiation from other parts of the boiler etcetera.

To give an example it has been seen that bends exposed to direct radiation from the smelt bed (i.e. bends in secondary superheater) can experience 100° C higher material temperatures than non exposed areas. This has been verified by metallographic examinations where exposed areas have shown affected microstructures and oxide layers with a thickness of 150 µm on the steam side. Non exposed areas from the same tube samples have shown considerably thinner oxide layers of only 20-30 µm and no heat affected microstructure (Eilersson, Lejonberg, & Praszkier, 1995).

As a general value the difference between steam and metal surface temperature of tubes inside the boiler is assumed to be around 50° C when the boilers are designed (Haaga, 2004).

7 Theory of recovery boiler superheater corrosion

In high temperature environments metals tend to oxidize. The goal of protecting the metal is not to have it create a passive film as in standard wet corrosion, but rather to have it create a cohesive oxide that does not allow oxygen or metal ions to diffuse through it. During oxidation the metal reacts with oxygen according to:

 $2M(s) + O_2(g) \to 2MO(s)$

One factor that affects whether or not, the formed oxide is protective is the Pilling-Bedworth ratio, which is the volume ratio between metal consumed and oxide formed. A protective oxide will have a ratio of close to one since this implies a non porous oxide with good coverage of the metal surface. If the ratio is low (< 1), the oxide coating is broken and the metal surface exposed. As such no protection will take place (Khanna, 2002). A high ratio means that the oxide will cover the entire surface of the metal, but it may also be porous and as such oxygen will easily penetrate it. Thus new oxygen will reach the metal surface and the oxidation will continue. A high ratio may also imply that the oxide is poorly adhesive and that it will spall off and expose new surfaces to the oxygen. Alternatively the oxide can have good adhesion initially, but as it grows in volume, high stresses are introduced in the oxide, causing it to crack.

Mechanisms of high temperature corrosion are those that disturb the formation of a protective oxide or that breaks the protective oxide once it has been formed. There are numerous such processes, but in this thesis only three mechanisms which are readily associated with recovery boiler superheater corrosion will be discussed.

7.1 Deposit melt corrosion

One possible cause of severe corrosion in superheaters is associated with salt deposits on the metal (Khanna, 2002). In general terms this is called hot corrosion and there are two types.

Type I occurs at temperatures higher than the melting temperature of the salt deposits and is very rapid.

Type II begins at a slow pace at temperatures lower than the melting temperatures of the salt deposits. As the corrosion slowly oxidizes the metal, the oxidation product reacts with the salt deposits and form complex mixtures of salts which have lower melting temperatures than the original one. Once the salts melt they immediately dissolve protective oxide layers and the corrosion rate increases notably.

When the deposits have melted they immediately begin to dissolve the oxide layer of the metal and the mechanism for material loss can simply be described as washing away of the corrosion products or as a dissolving of the metal into the molten compound. This will in turn often give a characteristic appearance where there are no visible corrosion products (Eilersson, Lejonberg, & Praszkier, 1995).

One possible explanation to the increased corrosion after melting can be due to faster kinetics of chemical reactions in the liquid phase and due to increased speed of ion transportation through the liquid electrolyte than is possible in a solid state (Folkeson, 2010).

In an ideal state in the boiler, no carryover should take place and the salt deposits should only consist of a blend of sodium carbonate and sodium sulphate (Bruno, 1995). However, carryover of unburned

or half burned black liquor is often present and this causes a reduction of sulphate into sulphide, which in turn causes a reduction of the melting temperature of the deposits.

There have been several studies made on the topic of melting of alkali deposits and it is generally agreed upon that chlorides and potassium can cause severe drops in the first melting temperature of the deposits. The first melting temperature of the deposits is generally called the T_0 . It has been shown that potassium lowers the first melting temperature while chlorine increases the corrosion rates by increasing the amount of melt when the T_0 is reached (Salmenoja, 2001).

A more recent and extensive study was carried out by B.-J. Skrifvars et al in 2007 where synthetic alkali salts were manufactured in order to study their melting behaviour and corrosiveness on various steels. An important result from this study was that chlorine and potassium must be present at the same time in order to obtain a low T_0 and high corrosion rates. The interaction between chlorine and potassium can be seen in terms of corrosion rate and T_0 for some different alkali salts and metals in Figure 14 on the next page.



Figure 14 – The mean corrosion layer thickness as a function of temperature with steel type as parameter and different salts covering the steel test specimen. Time:168 hours. (Skrifvars, Hupa, Salmenoja, Backman, & Vakkilainen, 2008) License given by ELSIVIER.

The synthetic salts in the study were based on sodium sulphate with varying amounts of chlorine and potassium and the following peroxidised steels were tested:

Steel 1 – 10CrMo9-10 Steel 2 – T91 (\approx 9.5Cr-0.4Ni-1.05Mo) Steel 3 – Esshete 1250 (\approx 16Cr-11Ni-1.2Mo) Steel 4 – Sanicro28 (\approx 28Cr-32Ni-4Mo) Steel 5 – HR11N (\approx 30Cr-42Ni-1.5Mo) Steel 6 – Sanicro63 (Nickel based with \approx Ni-21Cr-8.5Mo-3.4Nb-3Fe) In the case of Kraft recovery boilers, steel number 1 is of most interest since this is the most common material used in superheaters. What is of particular interest to notice is the interaction between potassium and chlorine that both lowers the melting temperature and increases the corrosiveness of the alkali salts. In Figure 14 on the previous page, the addition of only 0,3 % chlorine to a salt containing 10 % potassium, lowers the T_0 with 308°C and also greatly increases the corrosion rate (compare salt #2 and salt #4). Another important observation to keep in mind is that pre-melting corrosion takes place although at lower rates than post-melting corrosion.

In this study a melting temperature of as low as 522° C was reached, but it is important to note that this study was carried out in a normal atmosphere and that the atmosphere in the boiler is very different. Also note that the alkali salts in this study were based on only sulphate and that in a normal recovery boiler other elements such as carbonate are often present. It is the belief of several boiler experts that if the T₀ of a deposit can come down to temperatures as low as 520° C, deposit melting can occur for very low temperatures of mixed steam due to the temperature imbalances and high local heat flux in the superheaters (Eilersson, Lejonberg, & Praszkier, 1995).

The connection between first melting temperature and content of chlorine and potassium can be found in Figure 15 below.



Figure 15 – Effect of chlorine and potassium rates on first melting temperature T₀ (Salmenoja, 2001). Courtesy of Keijo Salmenoja

7.2 Sulphidation corrosion

In most high temperature alloys the resistance towards sulphidation relies on the formation of chromium oxide scales and in oxidizing environments these scales form easily due to high oxygen activity. That is to say that oxidation dominates the corrosion reaction (Lai, 2007).

A normal condition in the superheater section of a recovery boiler is an excess of oxygen in order to oxidize residual SO_x gases originated from the burning of black liquor. In such a condition the standard 10CrMo9-10 steel should be resistant to corrosion up to temperatures of 575°C.

If the environment has low oxygen potential however, the corrosion reaction becomes a competition between oxidation and sulphidation. Thus if the surrounding atmosphere becomes reducing the sulphidation will become the dominant corrosion reaction (Lai, 2007). Sulphidation is thus controlled by both sulphur and oxygen activities.

Carryover of unburned, glowing black liquor droplets depositing on the tube can create a locally reducing and sulphur rich atmosphere. If this occurs, the corrosion mechanism will be a conversion of the steel into a sulphide scale instead of an oxide scale, following the reaction below. Fe + S \rightarrow FeS

The sulphide scale is generally less protective and has lower adherence to the underlying steel than an oxide scale (Eilersson, Lejonberg, & Praszkier, 1995).

Also the sulphides provide paths for rapid outward diffusion of metal ions, such as for example chromium and iron, resulting in rapid corrosion (Lai, 2007).

A typical appearance when carryover has caused sulpihidation corrosion is a rough surface with large pits on the windward side and a distinct transition zone with no or little corrosion towards the leeward side. The resulting corrosion product (sulphide scale) is thin in relation to the amount of material that has corroded away. As a result of deposition of glowing black liquor particles, which contain carbon, carburization usually takes place on the surface. This may increase the hardness towards the gas-side of the tubes with more than 100 HV (Eilersson, Lejonberg, & Praszkier, 1995).

Since the scale formed is a sulphur compound FeS, instead of an iron oxide, an imprint by the Bauman method will reveal if the tube has been exposed to a sulphur rich atmosphere.

It is generally considered that the sulphidation resistance of Fe-Cr alloys increases with increased chromium content and slight to moderate additions (8-40 %) of nickel (Lai, 2007). Greater additions of nickel decrease the resistance because of formation of nickel/sulphur compounds that melt at low temperatures and attack the grain boundaries of the steel (Götaverken Energy, 1989).

7.3 Chlorine induced corrosion

Compounds containing chlorine is generally considered to be the most corrosive elements in the fireside environment of any boiler and this is why most mills actively try to reduce the chlorine content in the ash. When corrosion is caused by chlorine, no passivation by a protective oxide layer occurs and the process is called active corrosion.

There are various ways active corrosion can take place. What many theories have in common is that the first step is the formation of $Cl_2(g)$ which then reacts with the metal to form metal chlorides (Salmenoja, 2001). One example of such a reaction is:
$2NaCl(g) + Fe_2O_3 + \frac{1}{2}O_2(g) \rightarrow Na_2Fe_2O_4 + Cl_2(g)$ $Cl_2(g) + Fe \rightarrow FeCl_2(s)$

At the high temperatures of the superheater tubes the metal chlorides have considerable vapour pressures and are expected to evaporate and the following reaction will thus be:

$$\frac{3}{2}O_2(g) + 2FeCl_2(g) \rightarrow Fe_2O_3(s) + 2Cl_2(g)$$

The newly formed chlorine gas would then again react with the metal and so on. The limiting mechanism suggested by Grabke et al. would then be the outward diffusion of $FeCl_2(g)$.

At the scale-metal interface the gradient of the oxygen partial pressure would suggest that no evaporation will take place there due to the reducing environment at the interface. This is supported by findings of metal chloride layers at the interface (Folkeson, 2010).

The result would be a rapid, linear corrosion and corrosion products with a blistered nonadherent morphology. The main corrosion product would be unprotective (porous) Fe_2O_3 (Salmenoja, 2001).

One important driving force of chlorine induced active corrosion is the sulphation of alkali chlorides by $SO_2(g)$. This process can occur for alkali chlorides in both gas phase and condensed state but it is much faster in gas phase than in molten (condensed) phase (Salmenoja, 2001).

The overall sulphation can be written as:

$$2KCl(s/g) + SO_2(g) + \frac{1}{2}O_2(g) + H_2O(g) \to K_2SO_4(s/g) + 2HCl(g)$$

With a following reaction as

$$2HCl(g) + \frac{1}{2}O_2(g) \to Cl_2(g) + H_2O(g)$$

According to Grabke et al, the sulphation process mainly takes place near the surface and as a result most of the chlorine released should be lost into the flue gases (Salmenoja, 2001). A small portion may however, still diffuse towards the metal surface. As seen in the reactions above the amount of KCl decreases if HCl is produced.

Presence of sulphur in the flue gas causes the alkali chlorides to convert into their corresponding sulphates which do not react with the chromium rich oxides that keep the steel protected. KCl on the other hand, reacts with chromium oxide to form non-protecting chromates which destroy the protecting properties of the oxide through chromium depletion (Pettersson, 2008).

Deposits of KCl on Fe-2,25Cr-1Mo steel (standard superheater material in pulp industry) accelerate corrosion already at 400°C, with a significant mass gain within the first 24 hours. At 500°C the difference between corrosion rates with and without presence of KCl is reduced, although still significant (Folkeson, 2010).

In waste fired boilers and biomass fired boilers field experiments have shown that addition of sulphur to the fuel reduces the corrosion rate of low alloyed materials by 50 % due to the elimination of alkali chlorides (Folkeson, 2010).

8 Analysis of corrosion cases

Three separate cases off superheater corrosion will be examined in search of the cause of the problems experienced by the plant in question. The first case is from the Nueva Aldea plant and regards intermediate corrosion damages on the secondary superheater, while case two concerns severe corrosion of the tertiary superheater in the plant Burgo Ardennes. Case three is from Valdiva and also concerns severe corrosion of the tertiary superheater. Burgo Ardennes is owned by the company Burgo while both the Valdivia and Nueva Aldea plants are owned by Celulosa Arauco y Constitución S.A.

The main focus of the investigation is a search for indications of the three corrosion types previously described i.e. hot corrosion, sulphidation corrosion and chlorine induced corrosion. This will in turn be based on reviewing the temperature in the superheaters, the chemical composition of the ash and lab reports from investigated tube samples.

8.1 Case 1 – Nueva Aldea

8.1.1 Examination of tube samples collected from the damaged superheater

Two tube samples of SA213T12 steel from panel 16 in the secondary superheater (i.e. close to the middle) were investigated by Safe Control Materialteknik the 21st of May 2010.

The ocular inspection revealed areas with material loss and a thick deposit on the gas-side of the tubes. The deposits had a red-brown and dark grey appearance as seen on the tube sample is shown in Figure 16.



Figure 16 – Tube sample from Nueva Aldea with the deposit clearly visible in gray/blue

Towards the gas-side the minimum wall thickness on one of the tubes was measured to be 6 mm in the areas of material loss. Maximum wall thickness, on macro section was measured to be 8,35 mm. On the other tube sample, minimum wall thickness was measured to 5,9 mm and the maximum was measured to 8,4 mm. The thickness of the gas side oxide layer was found to be up to 1,5 mm (Andersson, 2010).

Gas-side tube surface revealed intergranular corrosion, but no changes to base material structure which consisted of ferrite and pearlite.



Figure 17 – Microstructure in tube sample from Nueva Aldea

In the areas close to the base material and suffering from intergranular corrosion, energy-dispersive x-ray spectroscopy (EDS) revealed high content of chlorides, oxygen and carbon. The results are presented in Figure 18.



Figure 18 – Chemical composition by spot analysis at point shown by arrow

In the deposit about two thirds towards the gas-side EDS analysis of a light coloured part of the deposit revealed high content of sulphur and carbon. The results of the analysis are presented in Figure 19.



Figure 19 – Area analysis of deposit about 2/3 towards the gas side

EDS was also performed on a chipped flake of the deposit from the tubes gas-side surface and the area analysis of the flake demonstrated high amounts of iron, sulphur and oxygen. Spot analysis in one part of the investigated area showed high amounts of potassium, chlorine and oxygen. A second spot was found to contain high amounts of iron and oxygen (iron oxide) but also elevated amounts of carbon. A fourth spot within the analysed area revealed high amounts of sodium and chlorides, but also quite large amounts of sulphur and carbon. The flake and the results from the area analysis are shown in Figures 20 and 21 respectively.



Figure 20 – The flake taken from the deposit





Figure 21 – Area analysis of the flake as shown in the Figure

8.1.2 Temperature

As was seen in Figure 14, metal temperatures of at least 522°C should be reached in order to proclaim that according to laboratory tests (assuming a viable chemical composition of the deposits), deposit melting can have occurred. As previously mentioned the environment inside the recovery boiler is very different from the one in which laboratory testing has taken place. From laboratory testing, a gas-side surface temperature below 520°C is considered to be safe. Since the environments are so different, this may not be true and a safe temperature may be considerably lower or higher in the real case. However, since there exists no reliable data from the real environment in a boiler, 520°C will be used as a simplification.

In this evaluation the difference between the steam outlet temperature and the gas-side metal surface of the outlet tube, below the boiler roof, will be assumed to be around 50°C, since this is generally the interval used by boiler designers.

The data here is not the historical data from before the damage was discovered, but no process changes have been reported since the damage was discovered. As so, the data from 2010 which is used should be representative for the past as well. The outlet stem temperatures seem normal with a mean of about 443°C and only 27 out of 334 measurements showing temperatures above 450°C. The global maximum during the period was a measurement of 457°C.

Looking at the metal temperatures in the penthouse, 22 out of 333 measurements showed temperatures of 490°C or more. These temperatures can be regarded to be within high risk if the chemical ash composition is unfavourable. The three highest encountered temperatures were found to be 505, 501 and 499°C. The remaining 19 top notations were all below 497°C.

8.1.3 Ash composition

When ash samples are collected for examination they are usually collected from the electro filters of the facility. This means that the quantities of potassium and chlorine in the ash samples are not necessarily equal to the quantities found in the ash in contact with the superheaters. It is common that the amounts of potassium and chlorine are slightly higher in the electro filter due to accumulation.

The chemical composition of the ash in Nueva Aldea looks very good, going back as far as the beginning of 2008. The weight percentage of potassium has never been above 6,65 % (2008-03-31) and for most part in the period of 2008-01-01 to 2008-04-21 the potassium level has been kept around 5 wt%. From 2008-04-21 to 2008-05-31 the potassium levels have always been less than 5 wt% and from 2008-05-31 they have been kept below 4 wt%.

The chloride levels were between 1 and 2 wt% during the period 2008-01-01 and 2008-05-12, with a maximum of 2,12 wt%. From 2008-05-12 and to the present, the chloride levels have been kept close to 1 wt%.

8.1.4 Hardness measurements

The hardness of the damaged tube from Nueva Aldea was tested with the Vickers method, using a load of 1 kg for the indentation. Measurements were first made in a line going from the outmost part of the tube wall (as close as possible to

the oxide) towards the centre of the tube wall as shown in Figure 22. The distance between each measurement was kept at 0,3 mm in order to ensure that they did not affect each other. All measurements were kept at the metal that is to say that no measurements were made in oxidized areas. The results of the measurements are presented in Tables 8 and 9.



Figure 22 – Hardness measurements method on the tube sample from Nueva Aldea

Table 8 – Hardness measurements of Nueva Aldea tube sample. First series

Indentation nr.	d ₁ (μm) horizontally	d₂ (µm) vertically	HV 1	Area
1	105	102	173	Edge of oxide
2	110	108	156	+0,3 mm towards centre
3	113	112	146	+0,6 mm towards centre
4	115	113	143	+0,9 mm towards centre
5	112	112	148	Centre

As seen in Table 8, the tube had hardened towards the oxide layer. Five more measurements at other parts of the oxide border were also made, in order to verify the results. Also one more measurement was taken in the centre of the tube wall to confirm the base hardness of the steel.

Table 9 - Hardness	s measurements	of Nueva	Aldea tub	e sample.	Second	series
--------------------	----------------	----------	-----------	-----------	--------	--------

Indentation nr.	d_1 (µm) horizontally	d_2 (µm) vertically	HV 1	Area
6	110	110	168	Edge of oxide
7	100	100	185	Edge of oxide
8	107	103	168	Edge of oxide
9	108	108	159	Edge of oxide
10	108	106	162	Edge of oxide
11	114	112	145	Centre

The measurements presented in Table 9 reveal a local increase in hardness at the outer edge of the tube wall. The mean hardness at the edge was calculated to be approximately 169,2 HV, which can be compared with a mean hardness of about 145,5 HV in what appears to be unaffected areas of the tube wall.

8.1.5 Sulphur print by Baumann method

The EDS analysis of the tube sample from Nueva Aldea revealed high contents of sulphur in the oxide layers of the tube. In order to confirm these findings a sulphur print was done, using the Baumann method. The procedure is a very simple and gives fast results qualitative results. Photographic paper is (in a dark room) soaked in weak acid and placed on a flat surface. The tube sample is placed on top of the photographic paper and left there for ten seconds, before it is removed. If there is any sulphur in the sample an imprint will be seen and the darker the area of the imprint, the more sulphur at that location. Care must be taken to remove the tube sample straight up as to avoid smearing the sulphur on the photographic paper.



As seen in the print presented in Figure 23, the Baumann test revealed what looks like high concentrations of sulphur in some parts of the tube. Please note that the tube was cut in half before the test was made and that is why there appears to be sulphur-free areas in the middle of the tube.

Figure 23 – Baumann sulphur imprint made with tube sample from Nueva Aldea

8.1.6 Discussion Nueva Aldea

The temperature of parts of the secondary superheater seems to be very high occasionally. If the outlet tube of the warmest panel is around 490 degrees in the penthouse, then it is possible that the same tube reaches a minimum of 540 degrees down in the superheater. However, due to the excellent control of potassium and chloride in the boiler, it is unlikely that corrosion due to deposit melting has been a major issue. Following Figure 15 and the data of the chemical composition in the boiler, a first melting temperature of around 555 degrees can be assumed to be quite representative. This assumption is based on an average composition of 5% K and 1% Cl. In reality the amount of potassium has more often been below 5% than above it and less potassium means higher T_0 of the ash. Even though first melting may have occurred during smaller time periods, the amount of melt in the ash at such an occasion can be assumed as limited due to the low amount of chlorine.

Also, since no damage had occurred in the tertiary superheater, which is hotter than the secondary, ash melting is very unlikely to have caused any larger problems.

There are indications that imply that carryover has taken place during operation. The high amounts of sulphur observed in the oxide as seen in the EDS analysis and the following sulphur print is one such sign. If sulphur is to be deposited on the tubes, it is necessary for it to arrive at the superheaters in a high concentration. With that in mind, the only way this can occur is if the sulphur comes in contact with the superheater tubes as part of the black liquor. Another similar indicator of carryover is the fact that EDS revealed carbon inside the deposit and at the deposit/base material interface. Carbon can only accumulate on the tubes if it is brought by black liquor. This finding also goes hand in hand with the next sign of carryover, which is the increase in hardness that was encountered. It is quite typical for tubes exposed to carryover to harden as a result of shallow carburization of the surface layers of the metal.

It is difficult to give a correct estimation of the amount of carryover that has occurred, but based on some observations it is estimated to have been small. First of all, the damages were very local with only some seriously corroded areas and the damages were only found on some tubes in the centre panels of the boiler. Secondly, a heavy carryover should have resulted in damages also in the tertiary superheater, but no such damages were found. Also a heavier carryover is likely to cause more hardening of the steel, since the carburization process is dependent of glowing black liquor particles.

Following the findings in the different tests and investigations, it is very likely that sulphidation has been a major cause of the damages. What may have happened is that carryover into the secondary superheater caused a locally reducing and sulphur rich atmosphere which allowed sulphidation to occur. Since these sulphide scales have bad adhesion to the tube surface and tend to easily spall off, it may explain the local material loss, especially if the tube samples were taken from a level in close proximity to a soothblower. Furthermore the sulphide scales are permeable and allow new sulphur and other reactants to easier reach the tube metal. Because the atmosphere turned reducing, the partial oxygen pressure became lower, allowing for accumulation of chloride on the tube surface causing chlorine-induced corrosion to also take place. This is confirmed by high findings of chlorides in the metal-oxide interface, in this case 19,88 wt% which is in sharp contrast with the average of 1 wt% chlorine content in the ash.

8.2 Case 2 - Burgo Ardennes (Belgium)

During the inspection of 2010 in the Burgo Ardennes plant in Belgium, damages with similar appearance to those in Nueva Aldea were encountered. The Burgo plant utilizes the same kind of superheater design as Nueva Aldea, but the boiler is a lot smaller.

In the Burgo plant the damages were found in the tertiary superheater and not in the secondary superheater. Furthermore the damages appeared to be more severe than in Nueva Aldea. The damages typically began about one meter below the boiler roof and reached approximately three meters downwards. All tubes except for the tubes closest to the boiler sidewalls were affected and the tubes are all made in SA213T22 steel. The tubes, shown in Figure 24, had an appearance of a moon landscape with thick and poorly adhesive scales of corrosion products and deposits. The worst damages were found to be very local. Differences in thickness of up to 2 mm were found at a distance of only a few mm from the local damage.



What is interesting with the damages found in the Burgo plant is that the general steam temperatures are so low, that no serious damage to the superheater tubes should occur at all.

8.2.1 SEM analysis

Scanning electron microscope (SEM) analyses of a thick scale from the tube sample revealed layers with high contents of sulphur, sodium and potassium as well as high contents of chlorine closest to the tube surface. Notable was that the sulphur and sodium layers follow each other tightly. The result of a line analysis is showed in Figure 25 below.



Figure 25 – Line analysis of the corrosion layer. The aluminium comes from the sample holder. High chlorine is observed closest to the tube surface.

As seen in Figure 26, high concentrations of chlorine was only encountered close to the tube surface. Sulphur and sodium concentrations seem to follow each other neatly.



Figure 26 – Concentration of the elements Cl, K, S and Na. Bright colours such as white and pink represent high concentrations whereas dark colours represent low concentrations.

In the SEM pictures, the tube surface is located to the far left, in line with where the chlorine is observed. Beyond that the sample holder is seen in the pictures.

8.2.2 Hardness measurements

i

Hardness measurement on the Burgo tube sample revealed a great increase in hardness close to the tube surface. The measurements were done with the same method as for Nueva Aldea on different locations of the tube sample. Typically one indentation was done at the oxide/base material interface and then indentations were done moving towards the centre. Each Table represents a series made at a specific location. The measured data can be found in the Tables 10 - 13 below.

i.

Indentation nr.	d_1 (µm) horizontally	d_2 (µm) vertically	HV 1	Area
1	92	87	229,5	Edge of oxide
2	96	96	201	+0,3 mm towards centre
3	104	100	178	+0,6 mm towards centre
4	105	103	171	+0,9 mm towards centre
5	105	105	168	+1,2 mm towards centre
6	113	113	145	Centre
7	113	112	146,5	Centre
8	114	111	146,5	Centre

Table 10 – Hardness measurements of Burgo Ardennes tube sample. First series

i.

	1			1
Indentation nr.	d_1 (µm) horizontally	d_2 (µm) vertically	HV 1	Area
9	86	86	245	Edge of oxide
10	94	94	210	+0,3 mm towards centre
11	97	97	195	+0,6 mm towards centre
12	103	103	179,5	+0,9 mm towards centre
13	104	104	171	+1,2 mm towards centre

Table 11 – Hardness measurements of Burgo Ardennes tube sample. Second series

Table 12 - Hardness measurements of Burgo Ardennes tube sample. Third series

Indentation nr.	d_1 (µm) horizontally	d_2 (µm) vertically	HV 1	Area
14	89	86	242,5	Edge of oxide
15	90	88	234	Edge of oxide
16	114	112	145,5	Centre

Table 13 – Hardness measurements of Burgo Ardennes tube sample. Fourth series

Indentation nr.	d_1 (µm) horizontally	d_2 (µm) vertically	HV 1	Area
17	95	90	217	Edge of oxide
18	94	92	214,5	Edge of oxide
19	112	114	145,5	Centre

As seen in the Tables, the hardness in some locations had increased with almost 100 Vickers. This should be interpreted as a sign of heavy carryover since the carburization is dependent on the amount of glowing black liquor the steel comes in contact with.

8.2.3 Sulphur print by Baumann method



To confirm the finding and suspicions, a Baumann print was also done for the tube sample. As seen in Figure 27 to the left, the print revealed high quantities of sulphur in most parts of the tube.

Figure 27 – Baumann sulphur print made with the tube sample from Burgo Ardennes

8.2.4 Temperature in the Burgo Ardennes superheaters

The temperature analysis was conducted in the same way as for the case "Nueva Aldea" (see section 10.1.2).

The average penthouse metal temperatures for the secondary superheater are 393,7°C, with the absolutely warmest panel reaching almost 422°C. This should correspond to an average metal surface temperature of 443,7°C for the outlet tubes below the boiler roof (following the rule of thumb to add 50°C). In the case of the hottest panel this temperature would reach as high as 472°C. This would give the interval 443,7-472°C.

In the tertiary, the penthouse metal temperatures are typically around 440°C with the occasional panel reaching up to 457°C, which should correspond to a metal surface temperature of in between 490-517°C.

8.2.5 Amounts of chlorine and potassium in Burgo

From the Burgo Ardennes mill there is unfortunately no data collected regarding the content of these elements in the ashes. Instead they have occasionally analyzed their virgin black liquor. From the black liquor an estimation of the content in the ash can be calculated, using an empirical formula. The values obtained with help of the formula should not be regarded as exact, but rather as an estimation of the true value.

Potassium %: $\frac{K_{BL}}{20} \times 1,5 = \frac{K_{Ash}}{30}$

Chlorine %: $\frac{Cl_{BL}}{20} \times 3,0 = \frac{Cl_{Ash}}{30}$

Using the formulas above, the table below was obtained. To the left in Table 14, the potassium and chlorine content of the black liquor is showed and to the right the calculated content in the ash is seen.

Black liquor			Ash (calculated	from BL)		
Date	K wt%	Cl wt%	Date	K wt%	Cl wt%	
19-05-2010	3,84	0,43	19-05-2010	8,64	1,94	
07-01-2010	3,83	0,34	07-01-2010	8,62	1,53	
20-10-2009	4,42	0,34	20-10-2009	9,95	1,53	
29-06-2009	4,3	0,5	29-06-2009	9,68	2,25	
16-04-2009	5,3	0,53	16-04-2009	11,93	2,39	
05-11-2008	5,2	0,53	05-11-2008	11,70	2,39	
02-10-2007	5,7	0,57	02-10-2007	12,83	2,57	

Table 14 – Content of K and Cl in black liquor and calculated content in ash in Burgo Ardennes

8.2.6 Discussion

Both the hardness increase, sulphur print and the carbon finding in the tube oxide point toward carryover taking place and that the mechanism of corrosion should be sulphidation. The fact that the tube sample is scaly and that the scales have poor adhesion also point in that direction.

But if carryover can cause sulphidation in the tertiary superheater one can ask why there were no damages found in the secondary superheater in the Burgo Ardennes plant? The most likely

explanation to this is that the temperature in the Burgo facility is very low for a boiler and because of this the temperature in the secondary superheater is not high enough. It would seem that up to 470°C is just too low to initiate the sulphidation process, since no damage to the secondary superheater was encountered, whereas 490°C seems to be enough for low alloyed 2,25% Cr + 1% Mo steel.

Even though most data points towards sulphidation, there is also another possibility, namely deposit pre-melt corrosion. According to Skrifvars et al and following Figure 14, alkali deposits can actually accelerate corrosion even before they melt if they contain high amounts of both chlorine and potassium. As seen in Table 12 the calculated content of both chlorine and potassium is enough to give deposit pre-melting corrosion. Taking the average temperature in the tertiary in consideration and making a comparison to Figure 14, a corrosion rate of 60-80 μ m/week should be received. However one must have in mind that Skrifvars et al did their study on specimens that were only pre-oxidized 24 hours in 200°C. In comparison with the superheater tubes, those specimens must be considered to have been very clean.

The question is what happens with deposit pre-melting corrosion as the oxide layer starts to build up? Following the reported corrosion rates by Skrifvars et al of 60-80 μ m/week, the superheater would have already failed since the black liquor records show that this mechanism should have been active for at least three years. That would give a total material loss of 9,36-12,48 mm which is more than the initial tube thickness! It may well be that these rates were reached when the superheater was new, but it is likely that the rates decrease with the time of service. It may have been active at lower rates or it may have stopped entirely. Something that suggests that the mechanism is very slow or even inactive on unclean surfaces is the lack of damages to the secondary superheater. According to Figure 14, a surface temperature of 470°C should be sufficient to cause a quite high corrosion rate. This is the case of the secondary superheater, but still it has not suffered any serious corrosion damage.

As such the conclusion here is that sulphidation has been the mayor contributor to corrosion and that deposit –pre-melting corrosion has played a smaller secondary roll to the total damage.

8.3 Case 3 – Valdivia

8.3.1 Introduction

During the annual maintenance inspection in August 2009, severe corrosion in the tertiary superheater was encountered. As a result panels 5-31 required tube replacements of 12 m each, during the maintenance shut down in 2010. The tertiary superheater is manufactured in SA213T22 steel and the cost of repairing the damages is estimated to be:

Material Cost	178'143 USD
Fabrication cost + Installation cost during the shutdown	317'078 USD
Inspection cost in both stages	41'316 USD
Steam blowing equipment (for cleaning of the superheater)	523'557 USD
Total cost	1'060'094 USD

If however the plant fails to finish these repairs on time, the cost will quickly increase as the cost for lost production hours start to build up. The cost of these can be estimated to be approximately

1'000'000 USD per day for a unit with the size of the Valdivia plant (Celulosa Arauco y Constitución S.A.).

During the maintenance inspection in 2008, what visually appeared to be some minor corrosion was encountered. It is customary to use non destructive testing (NDT) for thickness measurements in such cases to ensure that significant material loss has not occurred and so thickness measurements were done in 2008. These measurements showed that significant material loss had actually occurred, but the material loss was only reported by the responsible NDT-company after the outage and thus no actions were taken to prevent future corrosion.

In 2009 a full thickness measurement was recommended to be done and eventually measurements were carried out at the two highest sootblowers. However, once again the responsible NDT-company was slow to communicate the results, even though the minimum wall thickness was found to be 4,1 mm which is far below the minimum requirement of 5,82 mm following the ASME code (Safe Control Boiler Service, 2009). Despite the recommendation of a full thickness measurement in the superheater, no measurements were taken below the level of the two highest sootblowers. During the outage in 2010, tube samples from the outlet tube on panel 14 were taken and analyzed. The results are presented further on in this case description. The appearance of one of the tubes with severe corrosion can be seen in Figure 28.



Figure 28 – Photo of tertiary superheater tube close to the boiler roof (courtesy of Safe Control Boiler Service)

8.3.2 Location of damages

Med.

Min.

7,36

6,60

6,26

4,90

5,91

4,60

-1,10

-2,30

-0,35

-1,00

7,02

5,80

As seen in the Table 15, the panels toward the middle of the boiler seem to have sustained the largest loss of material, whereas the panels toward the boiler walls seem to have suffered comparatively little corrosion damage.

Table 15 – Thickness measurements of superheater tubes at sootblower levels 329-334 (Celulosa Arauco y Constitución S.A.) In the Figure, the tubes below minimal required wall thickness are marked with yellow and material losses above 1 mm/year are marked with blue.

Celu	osa Arau	co Y Cons	titucion S.A	A - Valdivia						Material:			SA 213 T22	
TERT	IARY SUP	PERHEATE	R							Dimensions:			60.3	mm
Locat	on of the m	neasured n	oints							Nom thickney	ss (mm)·		7 20	mm
Sooth	ow er line 32	0-330 / 330-3	240							Min thicknes	s recom (n	nm).	6.00	mm
COOLDI		0 000 / 000 0	0+0							Min thicknes	e calc (mm	<i>.</i>	5.82	mm
										with. thicknes	s calc.(IIIII	ı).	3,02	
	TERT	IARYS	SUPERI	HEATER	- GAS (DUTLE		Ξ						
			SB 329-330					SB 331-332	•			SB 333-334	<u>1</u>	
N⁰														N⁰
Panel	2008 April	2009 April	2010 March	Dif. 2009-2008	Dif. 2010-2009	2008 April	2009 April	2010 March	Dif. 2009-2008	Dif. 2010-2009	2008 April	2010 March	Dif. 2010-2008	3 Pane
1	7,7	7,0	6,0	-0,7	-1,0	6,3	7,4	6,4	1,1	-1,0	8,0	7,0	-1,0	1
2	7,8	7,2	6,2	-0,6	-1,0	7,7	7,6	7,3	-0,1	-0,3	7,3	7,0	-0,3	2
3	7,4	6,6	6,4	-0,8	-0,2	7,7	6,6	6,5	-1,1	-0,1	7,3	6,4	-0,9	3
4	7,4	6,4	6,3	-1,0	-0,1	7,5	6,4	6,2	-1,1	-0,2	7,2	6,9	-0,3	4
5	7,6	6,7	6,5	-0,9	-0,2	6,4	5,3	5,0	-1,1	-0,3	7,0	6,6	-0,4	5
6	7,2	6,8	6,4	-0,4	-0,4	7,3	6,5	6,3	-0,8	-0,2	6,7	6,5	-0,2	6
7	7,7	6,1	5,7	-1,6	-0,4	7,4	5,3	5,0	-2,1	-0,3	7,2	6,5	-0,7	7
8	7,4	5,4	5,4	-2,0	0,0	7,4	6,7	6,5	-0,7	-0,2	6,9	6,3	-0,6	8
9	7,4	5,7	5,4	-1,7	-0,3	5,8	4,3	3,9	-1,5	-0,4	7,1	6,0	-1,1	9
10	7,2	4,9	4,6	-2,3	-0,3	7,0	5,5	5,3	-1,5	-0,2	7,2	6,0	-1,2	10
11	6,8	5,5	5,2	-1,3	-0,3	6,7	5,0	4,8	-1,7	-0,2	6,7	6,0	-0,7	11
12	7,9	6,2	5,6	-1,7	-0,6	7,0	4,4	4,0	-2,6	-0,4	7,0	6,2	-0,8	12
13	7,6	5,8	5,4	-1,8	-0,4	7,0	4,4	4,2	-2,6	-0,2	7,0	6,4	-0,6	13
14	6,6	6,4	6,0	-0,2	-0,4	6,4	4,6	4,4	-1,8	-0,2	6,9	6,5	-0,4	14
15	7,1	5,8	5,4	-1,3	-0,4	6,8	4,1	3,7	-2,7	-0,4	7,1	6,6	-0,5	15
16	7,9	6,9	6,7	-1,0	-0,2	7,6	6,4	5,8	-1,2	-0,6	7,1	6,7	-0,4	16
17	7,9	6,7	6,2	-1,2	-0,5	7,0	4,9	4,8	-2,1	-0,1	6,9	6,4	-0,5	17
18	6,9	5,4	5,2	-1,5	-0,2	6,9	6,4	6,0	-0,5	-0,4	7,0	6,4	-0,6	18
19	7,4	6,2	6,0	-1,2	-0,2	6,9	5,2	5,0	-1,7	-0,2	7,1	6,6	-0,5	19
20	7,3	6,3	6,0	-1,0	-0,3	7,1	5,3	5,0	-1,8	-0,3	7,1	6,7	-0,4	20
21	7,0	5,2	5,0	-1,8	-0,2	6,9	5,0	4,7	-1,9	-0,3	7,5	6,9	-0,6	21
22	6,8	5,1	4,9	-1,7	-0,2	6,4	4,4	3,9	-2,0	-0,5	6,7	5,9	-0,8	22
23	7,1	5,8	5,6	-1,3	-0,2	7,0	5,1	4,7	-1,9	-0,4	7,7	6,9	-0,8	23
24	7,0	6,1	5,9	-0,9	-0,2	6,7	5,0	3,9	-1,7	-1,1	7,2	6,8	-0,4	24
25	7,4	6,1	6,0	-1,3	-0,1	6,3	4,3	4,7	-2,0	0,4	7,1	6,9	-0,2	25
26	7,2	5,6	5,5	-1,6	-0,1	6,7	4,9	4,6	-1,8	-0,3	7,4	6,8	-0,6	26
27	7,1	5,3	5,0	-1,8	-0,3	6,9	4,4	4,2	-2,5	-0,2	7,2	6,8	-0,4	27
28	7,1	5,8	5,6	-1,3	-0,2	7,1	5,2	4,9	-1,9	-0,3	7,4	7,2	-0,2	28
29	7,2	6,9	6,1	-0,3	-0,8	6,7	5,9	5,6	-0,8	-0,3	7,6	7,2	-0,4	29
30	7,3	6,9	6,5	-0,4	-0,4	7,8	6,5	6,2	-1,3	-0,3	7,0	6,8	-0,2	30
31	7,8	7,3	6,6	-0,5	-0,7	7,3	5,8	5,6	-1,5	-0,2	7,4	7,0	-0,4	31
32	7,6	7,3	6,9	-0,3	-0,4	7,7	6,7	6,6	-1,0	-0,1	7,4	6,5	-0,9	32
33	7,7	7,9	7,5	0,2	-0,4	7,7	7,0	6,8	-0,7	-0,2	7,4	6,3	-1,1	33
34	7.8	7.7	7.3	-0.1	-0.4	7.7	7.7	7.4	0.0	-0.3	7.5	6.8	-0.7	34

From Table 15 it becomes clear that most corrosion damage has occurred high up on the tubes since the lowest measurement level (i.e. SB 333-334) has suffered a lot less damage than levels 331-332 and 329-330 (close to the roof). Please see Figure 29 on the next page for level references.

5,59

4,10

5,29

3,70

-1,43

-2,70

-0,30

-1,10

7,19

6,70

6,60

5,90

-0,58

-1,20

Med.

Min.



Figure 29– Superheater panels in the Valdivia plant. Tertiary panel in red with sootblower levels marked (Safe Control Boiler Service, 2009) (Courtesy of Metso Power)

Furthermore it was noted during the inspection that the severe corrosion was almost exclusively found high up on the outmost tube at the gas outlet side in each of the affected panels. The tubes further into the panel had sustained less and less corrosion damage as seen in Figure 30.



Figure 30 – Photo from tertiary superheaters in Valdivia showing severe corrosion on the outmost tube and diminishing corrosion damages on the tubes further inward the panel (picture courtesy of Safe Control Boiler Service)

8.3.3 Steam temperature trend and ash composition

The data regarding the steam temperature and chemical composition of the ash for the period 2008 - 2010 have been weighed together and will be presented in Figures 31-34 underneath this headline. Since it is not possible, nor useful to present all of the data, only important aspects and findings will be presented here. Just as in the case of Nueva Aldea, the ash samples were all taken from the electro filter.

2008-2009:

As seen in Figure 31 below, the steam temperature has continuously been close to and often above 495°C in the period of November 2007 to April 2009. Add to that the expected difference between steam and surface temperature (50°C) and we can draw the conclusion that metal surface temperature has been at least 545°C during a substantial part of the period. During the same period, the mean composition of the ash has been 1,08 % chlorine and 8,79 % potassium.

From Figures 31 and 32 below, a selection of periods of high temperature and content of Cl or K during 2008-2009 have been marked with boxes and important ash compositions and dates have been given in accompanying Tables. Above each box in Figure 31 and 32 the estimated maximum steam temperature peak is given for that interval.



Date

Figure 31 – Steam temperature and date in tertiary superheater in Valdivia with top interval notation above each box (Celulosa Arauco y Constitución S.A.)

Α	Date	Chlorine %	Potassium %
	2008-01-14	0,53	9,33
	2008-01-17	0,66	9,14
	2008-01-21	0,54	9,45
	2008-01-24	0,76	9,19
	2008-01-28	0,56	9,05
	2008-01-31	0,71	10,24
	2008-02-04	0,23	9,31
	2008-02-07	0,64	9,13
	2008-02-11	0,87	9,55
	2008-02-14	0,66	9,14
	2008-02-18	0,83	9,23
	2008-02-21	0,68	9,25
	2008-02-24	0,29	9,35
	2008-02-25	0,7	9,1

	Potassium %	Chlorine %	Date
	18.58	0,9	2008-04-24
L	19,53	0,87	2008-04-28
	17,32	0,82	2008-05-01
	9,76	0,06	2008-05-08
	9 <mark>,</mark> 36	0,39	2008-05-12
	9,16	0,06	2008-05-15
	<mark>9,42</mark>	0,15	2008-05-19
	9,12	0,59	2008-05-29
	9,42	0,99	2008-06-02
	9,01	0,93	2008-06-05
	9,12	0,77	2008-06-12
	9,26	0,88	2008-06-19
	9, <mark>1</mark> 8	0,39	2008-07-10
	8,2	0,74	2008-07-14
	8,8	0,34	2008-07-17
	9,05	0,5	2008-07-21
	9,17	0,35	2008-07-24
	9,61	0,53	2008-07-28
1	9,4	0,33	2008-08-04
	9,57	0,38	2008-08-07

T⁰C



Date

Figure 32 – Steam temperature and date in tertiary superheater in Valdivia (Celulosa Arauco y Constitución S.A.)

С

Date	Chlorine %	Potassium %			
2008-10-01	1,99	9,31			
2008-10-03	2,03	9,52			
2008-10-05	2,03	7,42			
2008-10-13	1,8	8,02			
2008-10-14	1,76	7,31			
2008-10-15	1,66	8,4			
2008-10-29	2,17	8,03			
2008-10-30	2,57	7,39			
2008-10-31	2,04	8,37			
2008-11-04	2,43	8,06			
2008-11-05	2,37	8,26			
2008-11-06	2,43	8,04			
2008-11-07	1,86	9,33			
2008-11-16	0,96	9,24			
2008-11-19	1,39	10,24			
2008-11-22	1,12	9,12			
2008-11-24	1,45	9,85			
2008-11-30	1,66	9,72			
2008-12-03	0,92	9,15			
2008-12-06	1,09	8,09			

Date	Chlorine %	Potassium %	D
2008-12-25	1,09	8,01	
2008-12-31	1,17	8,54	
2009-01-01	0,9	8,14	
2009-01-06	1,01	8,6	
2009-01-07	0,05	8,71	
2009-01-11	1,01	8,4	
2009-01-12	1,55	9,67	
2009-01-13	1,08	9,5	
2009-01-19	0,43	9,03	
2009-01-20	1,27	8,06	
2009-01-21	1,51	8,2	
2009-01-27	1,68	8,59	
2009-01-28	1,66	8,62	
2009-01-29	1,58	8,14	
2009-02-05	1,52	8,29	
2009-02-06	1,29	8,26	
2009-02-13	1,2	8,1	
2009-02-15	1,2	8,24	
2009-02-22	1,05	8,01	
2009-02-28	1,14	7,87	

NoTable for the period between 2008 and early 2009 are very high temperatures and high levels of potassium (mean 8,79 %). Until about the 8th of September 2008, chlorine levels were kept low (mean value of 0,47 %). In September 2008, the chlorine levels rapidly increased to quite high levels (mean value of 1,47 %) and remained there until late Mars 2009. This while temperatures were still very high and while potassium levels remained quite high.

2009

In the end of April 2009 discussions regarding the corrosion damages were held. As a result temperatures were lowered and changes in the process were made in order to achieve a better chemical composition of the ash.

In Figure 33 and 34 below, a selection of periods of important temperature and composition interactions during 2009, have been marked with boxes and important ash compositions and dates have been given in accompanying Tables. Above each box in Figure 33 and 34 the estimated maximum steam temperature peak is given for that interval.

The early parts of 2009, until May, can be said to consist of medium-high levels of potassium, quite low levels of chlorine and a quite sTable steam temperature of about 480-490°C. From May to August the potassium levels generally lie between 6-7 % and the chlorine levels are kept around 1 % while the temperature remains unchanged. However in August 2009 something changes and the chlorine levels go up to over 2 % (high amount), while potassium levels are still kept around 7 %. Mostly the situation remains the same throughout September with the exception of a serious spike in potassium the 13th of September.

In October something happens and chlorine levels go up to very high amounts, passing 3 % for a period of about two weeks (late October/early November) with levels above 2,5 % for an even longer period. During this time the outlet steam temperature stays at about 480°C. The chlorine levels remain high until late December when they fall to a medium level below 2 %. NoTable for the period of high chlorine levels is a slight decrease in potassium.

The mean values for the period of August-December 2009 was 2,26 % chlorine and 6,5 % potassium.



Date

Figure 33 – Steam temperature and date in tertiary superheater in Valdivia (Celulosa Arauco y Constitución S.A.)

E	Date	Chlorine %	Potassium %	Date	Chlorine %	Potassium %
	2009-08-06	0,87	6,98	2009-09-01	2,19	6,91
	2009-08-08	0,73	7,37	2009-09-03	2,03	6,96
	2009-08-10	1,71	7,19	2009-09-05	1,67	6,59
	2009-08-12	2,22	6,74	2009-09-07	1,86	6,73
	2009-08-14	2,31	7,8	2009-09-09	2,13	7,19
	2009-08-16	2,03	6,99	2009-09-11	1,8	6,69
	2009-08-18	2,51	7,33	2009-09-13	2,31	9,63
	2009-08-19	2,52	8,14	2009-09-15	2,43	6,55
	2009-08-20	2,47	7,26	2009-09-17	2,52	6,91
	2009-08-22	2,25	7,24	2009-09-19	2,48	6,94
	2009-08-24	2,42	7,13	2009-09-21	2,51	6,48
	2009-08-26	2,28	7,38	2009-09-23	2,44	6,36
	2009-08-28	2,13	7,24	2009-09-25	2,49	4,53
	2009-08-30	2,21	7,68	2009-09-27	1,97	6,61
	2009-08-31	2,14	6,68	2009-09-29	2,34	6,8



Date

Figure 34 – Steam temperature and date in tertiary superheater in Valdivia (Celulosa Arauco y Constitución S.A.)

G

Chlorine % Potassium % Chlorine % Potassium % Date Date Н 6,44 2009-10-01 2,37 6,39 2009-11-01 2009-10-04 7,18 2009-11-02 6,04 2,16 2009-10-08 2,19 6,7 2009-11-03 5,75 2009-10-14 2,45 5,86 2009-11-04 2,79 5,98 2009-10-17 6,28 2009-11-07 2,5 5,93 2,81 2009-10-19 6,04 2009-11-10 2,34 5,63 2009-10-20 6,34 2009-11-13 2,28 5,62 2009-10-21 3,41 6,32 2009-11-16 2,02 5,92 2009-10-22 6,76 2009-11-19 2,04 5,71 2009-10-25 7,04 2009-11-22 2,21 5,86 2,87 2009-10-26 6,83 2009-11-25 2,73 6,36 2009-10-27 6,9 2009-11-27 6,81 2009-11-28 2009-10-28 6,45 6,68 2009-11-29 2009-10-29 6,96 2,82 6,1 2009-11-30 2009-10-30 6,36 4,11 2009-10-31 2009-12-02 6,24 6,33

8.3.4 Hardness measurements

Tube samples were taken from two different levels of the outlet tube of panel 14 in tertiary superheater. The first sample was taken high up on the outlet tube at sootblower level 329-330 (see Figure 29 for reference) and the second one was taken about two meter below the first sample. Hardness measurements were made on both samples, using Vickers method with a load of 5 kg for the indentation. The measurements of each series were taken in a straight line with 1 mm between each indentation, beginning at the gas-side surface (at the edge of the oxide layer) and moving inwards toward the steam-side. The distance between indentations was selected according to the indentation standard in order to avoid deformation hardening between the indentations.

8.3.4.1 Upper sample:

The location of each series of measurements on the upper sample is presented in Figure 35 and the results from each series are presented in Table 16.



Figure 35 – Tube sample from sootblower level 329-330, showing where hardness measurement series were made

Table 16 – Hardness measurements of the tube sample in Figure 35 displaying the hardness in Vickers. The measurements were made with 5 kg load for the indentations.

Series	Edge of oxide	+1 mm	+2 mm	+3 mm	+4 mm	+5 mm	+6 mm
1	193,5	161	153	149,5	149,5	-	-
2	192	167	150,8	147,1	148,3	144,9	141,5
3	212	168	153,2	148,3	146	147,1	140,4
4	182	153,2	149,5	-	-	-	-
5	172	158,3	153,2	-	-	-	-

Sootblower level 329-330 (HV 5)

The measurements revealed increased hardness in the outer part of the tube at all locations measured. Series 4 and 5 show a smaller increase in hardness than the other series, but there is still a significant increase. The smaller increase may be explained by the location of the measurements, which is on the leeward side of the tube. The generally increased hardness should be interpreted as a sign of carryover.

8.3.4.2 Lower sample:

The location of each series of measurements on the lower sample is presented in Figure 36 and the results from each series are presented in Table 17.



Figure 36 - Tube sample from 2 meters below sootblower level 329-330, showing where hardness measurement series were made

Table 17 - Hardness measurements of the tube sample in Figure 36 displaying the hardness in Vickers. The measurements were made with 5 kg load for the indentations.

Series	Edge of oxide	+1 mm	+2 mm	+3 mm	+4 mm	+5 mm	+6 mm
1	165	152	142	150,8	140	-	-
2	167	161	148,3	143	145	142	140
3	206	167,5	149,5	144,3	142,6	139,8	137,7
4	174	154,5	140,4	141,5	142,6	-	-

2 meters below sootblower level 329-330 (HV 5)

The measurements taken on the second sample confirms the findings on the first sample. The hardness has increased in the outer layer of the tube at all locations measured. Series 2 and 4 show a smaller increase in hardness, which may be explained by the measurement locations being on the leeward side of the tube.

8.3.4.3 Micro hardness measurements

Since an increased hardness in the tube sample would be caused by carburization, micro hardness measurements were done in order to confirm the findings of the macro hardness tests. In the micro hardness tests a load of 50 g (HV 0,05) was used to find the hardness of specific grains in the microstructure and the results are presented in Table 18 on the next page. The locations of the measurements on the sample can be seen in Figure 37. Although the data is presented with the values going from the highest to the lowest for each zone, they were all taken at the same location. That is to say that unlike the previous hardness measurements these measurements do not move from the gas-side towards the steam-side. NoTable in Table 18 below is that the hardness appears higher in the micro tests than in the macro tests. This is caused by the plastic deformation zone around the indentation which is negligible for the macro indentations but not for the micro indentations.



Figure 37 – Some of the measurement locations used for the micro hardness measurements. The measurement points can be seen as black dots within the marked rectangles.

Table 18 – Hardness of specific grains within the given zones given in Vickers. It can be seen that both the ferrite and pearlite closest to the gas-side is harder than their respective phases in the centre or towards the steam-side of the sample

_				HV 0,05	5				
Grain nr:	1	2	3	4	5	6	Mean		
Gas-side (15 μm from gas-side edge)									
Pearlite:	302	300	299	291	278	270	290		
Ferrite:	230	215	210	210	206	200	212		
Centre (2 m	nm from s	team side (edge)				Mean		
Pearlite:	258	243	240	232	-	-	243		
Ferrite:	184	183	175	164	-	-	177		
Close to decarburized zone (0,6 mm from steam-side edge)							Mean		
Pearlite:	251	241	220	218	-	-	233		
Ferrite:	170	163	158	155	-	-	162		
Decarburized zone (70µm from steam-side edge)							Mean		
Ferrite:	191	189	183	160	-	-	181		

The micro hardness test was consistent with the macro hardness test and showed an increased hardness in both the pearlite and ferrite towards the gas-side of the sample.

8.3.5 Sulphur print by Baumann method

In order to search for more indications of carryover a sulphur print was made for each sample, using the Baumann method and as seen in Figure 38, the imprints revealed high quantities of sulphur in both samples.



Figure 38 – Baumann sulphur print made with the tube samples from Valdivia. The upper sample is to the right in the picture and the lower sample is to the left.

8.3.6 Micro structural analysis of tube sample

A micro structural analysis was done on the upper tube sample from sootblower level 329-330 and the microstructure is shown in Figure 39. The microstructure of the sample consisted of fine grained ferrite and pearlite with an average grain size of 8,5-9 using ASTM standard (\approx 10 µm). On the steam-side of the sample a decarburized zone consisting only of ferrite was encountered. The decarburized zone had a thickness of 150 µm and can be seen as an entirely white zone in Figure 40.



Figure 39 – The microstructure of the analyzed tube showing a fine grained structure consisting of ferrite (bright) and pearlite (dark)



Figure 40 – The steam-side of the sample showing a decarburized zone in areas closest to the steam side. The decarburized zone consists of only ferrite (bright grains in the picture)

On the steam-side of the sample, the magnetite (oxide) layer was found to have thicknesses of up to $85 \mu m$. The oxide layer can thus be considered to be thick. On the gas-side surface of the sample, intergranular corrosion was found. This is shown in Figure 41 below.



Figure 41 – The metal/oxide interface on the gas-side of the sample showing intergranular corrosion

After etching the sample a closer examination of the microstructure was conducted. It was found that the pearlite in the entire sample had been spheroidized. In comparison with the microstructure in the centre of the sample (Figure 43), the pearlite appears to be a lot denser closer to the gas-side surface (Figure 42). This is consistent with carburization.



Figure 42 – A close up on the microstructure towards the gas-side of the sample consisting of spheroidized pearlite and ferrite.



Figure 43 – A close up on the microstructure in the centre of the sample consisting of spheroidized pearlite and ferrite.

8.3.7 Discussion

Summary of findings

It has been seen that the outlet steam temperatures in the tertiary superheater have continuously been very high during the entire year of 2008 and the first quarter of 2009. During the same period the potassium levels have been high whereas the chlorine levels have been low to medium. From Table 15 it is clear that it is also during this time that the worst material losses have occurred.

During the rest of 2009, the steam outlet temperatures were kept considerably lower, usually around 480°C, with temperatures rarely surpassing the limit of what is considered to be safe, with regards to corrosion. From a chemical perspective the last three quarters of 2009 can be considered to have had low amounts of potassium but medium-high to very high amounts of chlorine. The material loss in this period has been a lot smaller than during 2008, but the amount of material loss has still been significant in some locations (see Table 15).

The tube samples from Valdivia showed a significant increase in hardness in the gas-side parts of the samples. Both the pearlite and ferrite was harder towards the gas side when compared to the values obtained in mid section or steam side part of the sample. Together with the Baumann prints, that shows high amounts of sulphur in the samples, it is likely that carryover has taken place. It suggests that suplphidation corrosion has taken place.

Why the pearlite in the sample has speroidized is difficult to say. The most likely explanation is that the steel was heat treated before delivery, but spheroidization can also occur slowly with time if the temperatures are high enough.

The thick oxide on the steam-side of the sample suggests that the tube has been very hot during an extended time in service. The superheater in Valdivia has been in operation for six years giving a total of about 51'000 hours. Following a study made by Montgomery and Karlsson that was presented in the article "Bericht über das oxidation von neun Sthaltypen in dampfseitigen verhältnissen" and the report "Pannrevisioner" from Studsvik (Falk, 1986) the 85 µm oxide suggests an average steam temperature of about 500-510°C in the outlet tube during the six years in service.

Corrosion mechanism 2008

The high rate of material loss, high temperatures and high amounts of potassium suggest that deposit melting has been a likely cause of the problem. Following Figures 14 and 15 we can see that:

- 10 % K 1,3 % Cl gives a T_0 of 522°C and at that point a corrosion rate of 0,1 mm/week
- 10 % K 0,3 % Cl gives a T_0 of 526°C and at that point a corrosion rate of 0,05 mm/week
- 10 % K 0 % Cl gives a T₀ of 834°C and at 525°C a corrosion rate of about 0,01 mm/week
- 8 % K –3 % Cl gives a T_0 of about 537°C, corrosion rate at T_0 unknown
- 5 % K 8 % Cl gives a T_0 of 550°C, corrosion rate at T_0 unknown

An example about what consequences this gives:

During the period of May-August 2008, the mean composition was 9,58 % K and 0,48 % Cl while outlet steam temperatures were far above 500° C, with a peak value of about 527° C. Using the values above, a T₀ for this composition could be estimated to be close to $526-530^{\circ}$ C.

This actually means that the temperature of the tubes coolant has, on at least one occasion, been only a few degrees below the expected T_0 of the mean composition during the same period of time. With an expected temperature difference of at about 50°C between outlet steam and tube metal surface, deposit melting has certainly occurred and in reference to Figure 14, corrosion rates of above 0,05 mm/week can be expected to have been the case during this period of time. One should still keep in mind though, the difference between the theoretical short time corrosion rates of Figure 14 and the reality in which the tubes have built up oxide layers which may impede the corrosion rates.

Over the year 2008 the range in both potassium and chlorine: Potassium – Highest: 20 % ; Lowest: 5,84 % Chlorine – Highest: 2,57 % ; Lowest: 0,02 %

The implication of the above variance is that in some periods deposit melting has been able to occur at quite low temperatures while at other occasions, very high temperatures would have been required to cause the mechanism to become active. However ash compositions of 8-10 % K together with 0,3-1,5 % Cl have not been uncommon and thus leading to the conclusion that deposit melting has likely been a major contributor to the material losses experienced during 2008 and the first quarter of 2009.

Since the analysis of the tube samples point towards the presence of sulphidation corrosion, this mechanism may also have occurred during this period in combination with the deposit melting corrosion. If the two mechanisms have occurred simultaneously it would explain the small amount of scales on the tubes since sulphidation corrosion normally causes a great amount of scaling.

Corrosion mechanism 2009

Considering the low outlet steam temperatures and potassium levels during the last three quarters of 2009, deposit melting is unlikely to have been a major contributor to the corrosion damages experienced. However, it is difficult to say if the material losses during the period 2009-2010 have occurred mainly during the first quarter through deposit melting, or if another slower mechanism has been the main contributor over a larger period of time. Even though both the ash composition and temperatures were improved in May of 2009, high heat fluxes may still have caused occasional deposit melt corrosion, but it would then have been a lot less aggressive and frequent due to the lower amounts of potassium.

In reference to Table 14, one thing that suggests a different mechanism during 2009 is the corrosion distribution, which is no longer focused on the central panels as was the case in 2008. Since there are several typical signs of sulphidation corrosion, it has most likely contributed to the continued corrosion. However, it is difficult to say if the sulphidation corrosion has been aggressive or not. The large hardness increase and high amounts of sulphur would suggest that it has, but the absence of large quantities of scaling speaks against it. Also the secondary superheater only shows signs of light corrosion and a heavier carryover (which is required for aggressive sulphidation corrosion) would most likely have affected the secondary as well.

Indeed the high levels of chlorine during 2009 and especially during the period 17-10-2009 to 02-12-2009 also makes chlorine induced corrosion a possible contributor to the material losses during that year.

Yet another possibility is that we have some discrepancies of the measurements. Keeping in mind how the tube surface appears, the measurements depend a lot on how the surface is prepared before measurements are taken. Furthermore the measurements only give a spot value and thus differences between the values may also be caused by operator technique, operator skill and equipment used. Since there have been several issues with the thickness measurements earlier, the measurement values should not be considered as exact values, only as guidelines.

Conclusions

The strong indices of both deposit melting corrosion, as well as sulphidation corrosion in the tertiary superheater makes it most likely that a combination of these two mechanisms are responsible for the damages. Deposit melting corrosion has likely been the more aggressive mechanism of the two.

If some other mechanism than sulphidation has been active as well is difficult to say and will thus be left unsaid. Deposit melting corrosion has been most active during 2008 and early 2009, but when the sulphidation corrosion has been active is more difficult to predict. The same goes for the quantity of the sulphidation corrosion.

8.4 Superheater corrosion & design discussion and findings

The main factor determining if severe superheater corrosion occurs is temperature. In a recovery boiler the temperature control is normally based on the outlet steam temperature, which is the mixed steam from all the panels in the tertiary superheater. This is a highly inaccurate variable to use when controlling the operation of the boiler. The reason is that there exist several factors which are difficult to estimate, for example temperature imbalances between superheater panels, flue gas velocities, heat radiation from other parts of the boiler etc. All the various factors discussed in this thesis (as well as others) can have strong local effects on the superheater tubes, which makes it difficult for the operator to foresee the actual temperature inside the superheater section. At best this inaccuracy lowers the safety margin of what the materials can withstand, whereas at worst the inaccuracy brings about severe corrosion attacks. Furthermore some possibly dangerous occurrences in the boiler are undetectable during operation, such as for example carryover.

Now days the mills use more and more thermocouples on the hottest outlet tubes of the superheater panels inside the penthouse in order to get a more accurate picture of local temperatures. As we have seen in the presented cases, this is still not enough. Still the operator cannot be certain of tube metal surface temperatures below the boiler roof, which is the determining factor behind corrosion. There exists a rule of thumb to add approximately 50°C to the measurements in the penthouse in order to get an estimate of the tube metal surface temperature. However this is just an estimate and local conditions can render this rule useless. Another part is estimation of the imbalance between the tubes and the panels. At least some panels should have thermo-couples attached to all of the tubes, not only the outmost one. If installed to a few panels, covering the panels at the sidewalls and at the furnace centre, a much better control of the process would be achieved. Since this would enable measurements of the coldest and hottest temperature, it would be useful for estimations of the corrosion and it would help in avoiding condensation of the steam in the coldest tubes at boiler trips or "Chill & Blow" operations.

Another important variable when discussing superheater corrosion is the amounts of chlorine and potassium in the black liquor. Although not discussed in this thesis, more and more mills are investing in various ash-leeching facilities and ash-purging procedures in order to better control the amounts of these substances. As seen in the case of Nueva Aldea, this can be highly effective.

Apart from the problem with inaccuracy in the variables chosen to control the boiler, it is also often the case that the cheapest possible materials and design are used in the superheaters. The standard material is, as previously mentioned, steels containing 1,25% Cr + 0,5% Mo or 2,5% Cr + 1% Mo and the cheapest design is the conventional design. Using the conventional design, adds to the inaccuracy of temperature control, by having rather large temperature differences between the tubes. At the same time, using the cheapest materials helps decrease the safety margin. There are designs that can balance the temperature distribution better, thereby increasing the safety margin. For materials there are several more alloyed steels that resist corrosion better, as clearly seen in Figure 14. In many boilers that have experienced severe problems with corrosion, composite tubes have replaced cheaper materials and solved the problems.

Would a different superheater design and use of other materials have prevented the damages investigated in this thesis?
Is it possible, from a superheater point of view, to achieve higher steam temperatures while still maintaining a low rate of wear/corrosion?

Case 1 – Nueva Aldea

Since only the absolutely hottest tubes in the warmest panels were locally damaged, a different design with better temperature balance would be likely to at least have reduced the problems. This is probable because a better temperature distribution in the panels is likely to reduce the temperature of the warmest tube, while still maintaining the outlet steam temperature at the same level as was the case here. Using higher grade steel such as composite tubes would probably have eliminated this problem completely.

Case 2 – Burgo Ardennes

The conclusions must be similar in the Burgo Ardennes case. Since it is only the hottest, outmost tubes in the warmest superheater which are affected, any design protecting these tubes or lowering their temperatures would decrease the damages. How much is depending on how effective the design improvement would be. All improvements lowering the imbalances would decrease the corrosion rate. A change into stainless steel or composite tubes would probably have eliminated or significantly decreased the material loss experienced. Since sulphidation is the likely cause of the majority of the material loss, more resistant steel is likely to have a better effect than just lowering the temperatures unless these are lowered so much as to go below the required temperature for sulphidation to become active.

Case 3 – Valdivia

Also in the Valdivia case it can be concluded that an improved design would have decreased the material losses or even eliminated them.

The question is how much it is worth? Several of the design changes are very expensive, even if implemented at the start of the project. The high steam pressure and temperature result in some profits. The profits must then be compared to the costs for larger margins against this kind of corrosion.

It can never be assumed that the conditions will be monitored and controlled to 100%. Thus the safety margins should ensure that minor deviations do not automatically result in severe tube damages.

A new boiler project of Valdivia size should either have a lower steam temperature or a design with higher margins against corrosion.

Changing into composite tubes in the lower bends and high up along the outmost outlet tubes would be the priority, since it has a largest impact on the corrosion rates. This is based on experience that suggests that these are the parts that most commonly suffer from severe corrosion attacks. It has been experienced that composite tubes are very corrosion resistant in general.

Another future improvement would be cost effective design changes that effectively equalize the temperature differences along the tubes in the panels. It is worth to note that the Valdivia plant actually has a wrap around design in the tertiary superheater and that they still received severe corrosion on the outlet tubes. This says a lot about how much heat the outmost tube actually absorbs during each loop.

9 Economy of boiler design

Depending on the project organization, its knowledge and will, the design of the recovery boiler can be more or less optimized. In this thesis, the optimization of the boiler is regarded with consideration to the performance of the boiler during operation, as well as the amount and costs of maintenance works. During the recent years, it seems like the cost and performance of each new project has been the main focus of the buying organizations, whereas the maintenance aspects have been more or less disregarded.

As just said, the focus of the buying organization lies mostly in the process aspect, that is to say performance of the boiler with regards to black liquor combustion (capacity) and steam (electricity) production. This focus on price versus performance has led to a lack of maintenance thinking in the project organizations. The idea seems to be that as long as the initial price is low, any defects and problems can be eliminated during the maintenance shut downs, once the boiler is in operation.

Another result of this cost focus is that hardly any vendor of recovery boilers today (if any at all), seeks to produce and deliver an optimized design, but rather a design that is cheaper than the competitors. A consequence is often that boilers with predestined problems and breakdowns are delivered to customer specifications.

Interviewing senior engineers from one boiler manufacturer makes it clear that the last two decades of development in the industry has been focused on making the boilers cheaper and not so much better.

The aim of this part of the thesis is to investigate how the lack of the maintenance aspect and expertise within a buying organization can affect future costs. These costs do not only derive from the costs of solving acute problems as they occur, but also from the extra outage time that the boiler may suffer as a result of the problems. The cost of extra outage time depends a lot on the pulp prices at the time of the outage, but for a boiler size of 4 000 tds/day the production losses can be estimated to be approximately 1'000'000 USD/day (calculated with a pulp price of 900 USD/ton).

With some simple cases this thesis intends to show some problems that followed because of less successful choices of design from the part of the buying organizations. These are problems that an experienced maintenance engineer might have predicted, had that particular aspect been seen as important during the initial stages of the project planning. Finally the thesis aims to propose how a buying organization should be organized and what such an organization should keep in mind.

9.1 Definition of reliability and maintainability

Here the concepts of reliability and maintainability will be defined. These are important concepts when discussing the economy of a recovery boiler design, since they are the essence of what is required to minimize the outage time of the boiler.

9.1.1 Reliability

Reliability can be defined as the probability that a system will perform its task in a satisfactory manner for a given period of time in predetermined operating conditions (Blanchard & Fabrycky, 1997). In other words reliability is a measure of the probability of failure-free operation during a given time interval. Within this definition there are four critical elements namely probability, satisfactory performance, time and specified operating conditions. A good definition of failure when

discussing reliability is to define a failure as any time the system is not functioning properly. The failures themselves can be classified as inherent failures or dependent failures (Barringer, 1997).

Inherent failures deal with failures built into the system and are largely dependent on the components that make up the system. Dependant failures are failures that can be traced back to certain events for example operator-induced failures, wear out, maintenance-induced failures etc.

When discussing the reliability of the recovery boiler, one must perhaps deviate a bit from the standard definitions of inherent and dependent reliability because for some components of the boiler these two go hand in hand. In many production systems the parameters and operating conditions can be largely set to and kept at a certain predefined state with few deviations. That is at least true for some automated systems. In the case of the recovery boiler it is if not impossible, then at least very difficult to eliminate variations of critical factors such as temperature throughout parts of the system. As a result the probability of failure for a certain component may not just depend on the component itself but also on changes to the operating conditions, the operator's ability to recognize dangerous deviations and the operator's ability to control them.

It may then be better to define the inherent reliability in terms of how large deviations from the predetermined operating conditions the component can withstand without a failure occurring.

A good example of this is the superheaters. In sections 6 and 8 various superheater designs and temperature imbalances were discussed. In these sections it was concluded that some designs were more able to have an even temperature distribution throughout the superheater than others, which is to say that the operating margins are larger in some designs than in others.

For example in the conventional superheater design the outmost tube will always be hotter than the inner tubes (see section 6,1) which means that even though the system is in balance the outmost tube may very well be close to a temperature when failure would occur. In this case failure would be defined as unaccepTable corrosion attack.

In the case of an integrated screen design or a wrap around design the difference in temperature between the outmost tube and the rest of the tubes in a superheater screen is smaller and a temperature deviation is thus likely to have less effect in those cases.

Following the suggested definition of inherent reliability would then mean that an integrated screen design or a wrap around design has larger inherent reliability than a conventional design because they have larger operating margins against corrosion attacks.

In chapter 5 it was concluded that some materials are more resistant to corrosion attacks than others and the use of more corrosion resistant materials would also increase the operating margins.

Increasing the operating margins is thus the same thing as increasing the inherent reliability of the superheaters and thus safeguarding against failures.

Continuing with the superheater example the dependant reliability would be increased with increased possibility of controlling the process and making sure that critical variables are kept at safe levels. This in turn translates into several things such as control equipment, procedures, staff education and so on.

To give some examples; installing more thermo couples would give the operators the ability to overview the temperature in a more local manner than before and make it easier to detect when a deviation becomes close to causing problems. Frequent measurements of chlorine and alkali in the ash, combined with procedures of transmitting the information to the operators as well as educating the operators in at which conditions certain amounts are accepTable or not, would also increase the dependant reliability.

To have high inherent and dependant reliability is important since the recovery boiler is only accessible during the outage and every hour of a shutdown is expensive. Apart from possibly costly repairs a non catastrophic failure that has occurred during the year in operation can cause a prolonged outage which translates into high costs of production losses or it may require the boiler to tune down during the following year which would cause costs in terms of lower capacity and losses in steam (electricity) production.

9.1.2 Maintainability

In section 9.1.1 it was pointed out that reliability is important due to the possibility that a breakdown can cause prolonged outages and other costly problems. When a failure of some kind has occurred it is important to rapidly be able to correct the problem and return to operation. Maintenance is a series of actions that are executed in order to keep a system component or installation in an effective operational state. In the case of the recovery boiler it is always the goal of a maintenance shutdown to be as quick, safe and cost effective as possible due to the high costs of production losses during the shutdown.

The key to reaching a state where maintenance is quick and cost effective is to think in terms of maintainability. Maintainability is the ability of an item to be maintained in an effective operational state and it is largely dependent on the design (Blanchard & Fabrycky, 1997). The dependence of the design is inherited from the fact that the design sets maintenance procedures and repair times (Barringer, 1997). It simply refers to the measures taken during the design, development and manufacturing of an installation in order to reduce the required maintenance, repair skill level and costs needed to ensure that the installation meets the requirements for its intended use (Stapelberg, 2009).

Implementing the concepts of maintainability is thus an effective way to increase the availability of an installation and to decrease production losses. These considerations must however be made during the conceptual, schematic and detail design phases, it is not something that can be easily implemented after the installation has been manufactured since it would require extensive reengineering and modifications.

10 Empirical study of problems caused by the boiler design

Here four cases of designs, where the maintenance aspect has been somewhat omitted, will be explained together with the problems and costs caused by the designs. Some of the cases are older and resolved whereas others are ongoing. The study is based mainly on old inspection reports and interviews with maintenance personnel involved in the annual outages of the plants. For the cases "Superheater corrosion" and "Superheater ties", a price comparison will be made between the actual design and a proposed design which would be better from a maintenance point of view. This while still keeping the performance of the boiler at the same level as with the actual design. In the case of "Superheater ties", a life cycle cost will be made for both the actual and proposed designs in order to investigate if a more expensive initial design really is more expensive in the long run.

10.1 Case 4 – Superheater corrosion

With the analyzed superheater corrosion in the Valdivia and Nueva Aldea cases, the most important variables of the superheater corrosion and the different design aspects were reviewed. It was seen that the design is not the absolutely best that can be achieved today in terms of corrosion resistance. The question is if the design is optimized only for the sale or if it is also optimized with regards to the life cycle of the boiler?

There are no doubts that the industry has the "know-how" to build completely optimized superheaters, which would withstand the corrosion environment in the chemical recovery boilers in an optimal way. The question is if they would be able to sell it?

The answer to this question is not that simple. It very much depends on the end clients project organization and previous experiences of the people in that organization. Another important factor is also who has the authority to make decisions within the project organization. The price for more corrosion resistant superheaters would be higher than design used today and therefore the pressure from competitors would be much higher as well.

What would be the difference?

- 1. The primary superheaters would probably not need any changes because of the low temperatures they experience and there are seldom any serious damages to them.
- 2. The secondary superheater, which is hanging first in the gas direction and directly above the char bed, resulting in high heat flux and full radiation, would perhaps be 1/3 less wide with two loops instead of three. The superheater would also probably contain some kind of wrap around, shortening the first inlet tube somewhat or be made as an "integrated screen" with the hottest tubes protected in the middle of the panels. The outer loops of the secondary superheater are the parts that receive most heat and as such they would probably be manufactured in compound, AISI 310, Sanicro 28 or some other high grade austenitic stainless steel.
- 3. The tertiary superheater does not experience the high heat flux from the bed, but instead the steam temperatures inside the tertiary are very high. High steam temperatures mean less cooling to the tubes and as such they would need better protection. As such they would probably be made with a wrap around or integrated screen as well. Since the outlet tubes are the warmest they would have been fabricated in composite tubes with an outer layer

made in AISI 310 or Sanicro 28. Alternatively they would be manufactured in high grade austenitic stainless steel.

- 4. Another alternative for the tertiary superheater would perhaps be to have it divided into two separate superheaters with attemperation or at least a mixing header in between in order to mix the steam more often and to possibly have one more station for regulation of the final outlet steam temperature. This change is motivated since the lesser amount of loops in a superheater panel, the smaller are the temperature imbalances in each panel. If the final steam temperature is between 480°C and 510°C, each 5°C of stability significantly increases the safety margins.
- 5. The instrumentation (measurement devices) would probably be extended, allowing monitoring of all panels and all tubes in some of the panels.

10.1.1 Costs of possible changes to the tertiary superheater:

A design change into an integrated screen, if manufactured in Sweden, turns out to actually be estimated to cost about the same as a conventional superheater. That is to say approximately 5'000'000 USD (35'000'000 SEK) (Metso Power AB). The cost may however differ much between different manufacturing facilities, depending on their configuration (some are strictly focused on producing conventional designed superheaters). Integrated screen is likely to be somewhat more expensive due to fabrication procedures etc, but the difference can be assumed to be small.

The Valdivia superheaters are approximately 20 meters long (length varies over the bull nose in the boiler). Making the outer tube in Sanicro28/SA213T22 (composite) instead of SA213T22 would cost approximately 440 USD/meter, making a total of 8'800 USD per panel.

The Valdivia plant has 34 panels in the tertiary superheater, making the total cost 299'200 USD for using composite material consisting of Sanicro28/SA213T22 instead of only SA213T22.

The material prices, presented in Table 19, are as given by Arauco Constitución, Sandvik and Metso. The prices do however depend a lot on tube dimensions and the quantity of material bought. The dimension used for the comparison is 63,5 x 7 mm. That is to say tubes with a diameter of 63,5 mm and a thickness of 7 mm.

Material	Price
Carbon steel	23 USD/m
SA213T12	32 USD/m
SA213T22	40 USD/m
SA213T91	110 USD/m
AISI310	265 USD/m
Compound: SA213T91/Sanicro28	440 USD/m

Table 19 - Costs of tubes with dimension 63,5x5 mm for different materials (Based on prices from Arauco Constitución, Sandvik and Metso)

The cost of dividing the tertiary superheater into two separate superheaters (tertiary and quaternary) is very difficult to estimate since it has never been done by western manufacturers. What can be said however is that it would be very expensive due to the need of additional headers, additional cross over piping and most likely design changes to the boiler. The material cost for a header can be roughly estimated to be in the range of tens of thousands USD. Add to that the labour costs and it starts to clear just how expensive it would be.

The changes in the instrumentation would not improve the resistance against the corrosion, but it may prevent some damages caused by operator error due to more efficient monitoring. The cost for one thermo-couple is 555-677 USD (3'885-4'740 SEK) (Celulosa Arauco y Constitución S.A.). Estimated price for additional 50-60 thermo-couples is 27'750-33'850 USD.

So to sum up the costs to improve the design of the tertiary superheater and to improve the instrumentation would be:

Integrated screen design	≈0 USD
Better material in the outlet tubes	299'200 USD
More instrumentation	27'750 - 33'850 USD
Total	326'950 – 330'050 USD

Considering the high prices for the additional benefits and additional corrosion resistance, is it motivated? The question needs to be put in perspective to the situation from the opposite side, that is to say, how much does it cost to repair the present superheater in Valdivia?

For the moment they need to replace all the tubes in the superheater from the boiler roof and half the distance down to the bends. The lowest part will also need to be changed in the future.

With the superheater being 20 m long, the distance to be replaced now is approximately 12 meters per damaged panel with total cost of 1'060'094 USD. The cost for each step is specified here below.

Material Cost	178'143 USD
Fabrication cost + Installation cost during the shutdown	317'078 USD
Inspection cost in both stages	41'316 USD
Steam blowing equipment (for cleaning of the superheater)	523'557 USD
Total cost	1'060'094 USD

Normally this work would require around seven days to accomplish, which is two days more than an ordinary shut down. For a boiler with the same size as in Valdivia (4 000 tds/24h boiler), this corresponds to production losses of about 1'000'000 USD/day (estimated with a pulp price of 900 USD/ton). Thus two extra days give a total of 2'000'000 USD for this particular damage and a total cost of 3'060'094 USD.

During this particular outage however, there are no direct production losses to be added to the costs of replacing the superheater tubes due to the fact that the prolonged outage was caused by repairs of other components that were damaged by the earthquake February 27-2010.

Unfortunately, the reparation of the superheater is probably not a final repair. The composite tubes will only protect the hottest part which corroded 2008-2010 and there are no guarantees that further replacements will not be required. If it is assumed that also the lowest section will need to be replaced, including the lower bends, the final costs for this modification will be very expensive as well.

As seen in the cases of Burgo and Nueva Aldea, severe corrosion damages can occur as a result of carryover and this is a rather unpredictable occurrence since there are no systems that can readily alert the operators to its presence. However, material with better corrosion resistance, limited temperature imbalances, tube protection and thorough temperature control would be likely to reduce or eliminate these damages.

10.2 Case 5 - Superheater ties

Apart from the actual design of the superheaters (conventional, wrap around or integrated screen) another factor that affects the cost of the superheater is the tube spacing. In order to reach a certain steam temperature, the superheaters need a certain effective area. As the tube spacing increases, the effective area of each tube increases and thus fewer tubes are needed to achieve the required effective area. The phenomenon has to do with how the flue gases pass through the superheater panels and how the panels absorb heat. The more tube spacing there is, the more contact area there is between each tube and the flue gas, as demonstrated in Figure 44.



Figure 44 – Tube spacing and heat efficiency of superheaters

The increased contact is caused by the flue gas being able to better enter the area in between the tubes as the tube spacing increases. Depending on the material selected for the superheater tubes, the cost reduction achieved by increased tube spacing and reducing the number of tubes can be substantial. However, the increased tube spacing comes at a cost, which is the cooling of the

superheater ties. Since the superheater panels oscillate during operation there are ties holding the tubes together and preventing them from moving too much relative to each other. These ties are cooled by the tubes and the cooling is a function off:

- Heat transition area (size of the weld between the tie and the tube)
- Distance from the tie end to the tube
- Steam and metal temperature of the tube
- Heat flux

Therefore increased tube spacing will result in less cooling of the tubes.

The distance between the tubes can vary as much as from close to 0 mm (tangent design) and up to 60 mm. Both these designs are troublesome. The tangent design does not allow for any simple tube replacement and too large tube spacing most often results in tie problems.

The large superheaters can contain up to 5 000 ties per superheater. If a tie problem occurs, it may suddenly be a major problem for the mill. During an ordinary shut down there are limitations to how many ties that can be repaired or replaced.

The high amount of ties in a superheater often causes the ties to be optimized with respect to fabrication costs, rather than with respect to the lifetime costs or maintenance issues. There are rather many design types, but they can be divided into few groups presented in Figures 45-50:

"Fish tail tie"

Gliding tie - "Fish tail tie" (Götaverken)



Figure 45 – Gliding tie by Götaverken design

Gliding tie – Plate tie (Tampella)



Figure 46 – Gliding plate tie by Tampella design

"Plate tie"

Another classic tie, introduced largely by the Finish Tampella. Good tie for primary superheaters. Commonly used by Tampella and Götaverken in the past. Today it is still used by Metso (ex Tampella and Götaverken). Fabricated in various heat resisting materials.

A classic casted tie, commonly used by Götaverken and B&W in the past. It hs been fabricated with various spacing ranging from ½ inch to 2 inches in various materials such as A217C5 (5%Cr+1Mo), AISI 310 (25%Cr+20%Ni) or IN 657 (50%Cr+50%Ni).

Gliding tie – "Packman" (Andritz)



"Packman tie" Tie used by Andritz in the tangent design superheaters.

Fabricated in AISI 310.

Figure 47 – Gliding "packman" tie by Andritz design

Gliding tie – Hinge tie (Götaverken / B&W)



Figure 48 – Gliding hinge tie by Götaverken design

Fix tie



"Fix tie"

Tie used by SMV, Götaverken, CE etc. Used in the past in everything from tangent design to ½ inch spacing. Fabricated in ferritic heat resisting steels like 13CrMo44 or 10CrMo910. The fix ties were only used where temperature difference between adjacent tubes was not significant i.e. between parallel tubes.

Figure 49 – Fixed tied

Membrane tie





"Membrane tie"

Membrane was used in the past by Götaverken to weld the first tube in the gas direction with the second one in order to equalize the material temperature.

Götaverken began to use membrane superheaters in the 1990ties, where parallel tubes were provided with continuous membranes. It has been shown that membrane superheaters have less heat exchange compared to large spacing conventional superheaters. Tube replacements are also more troublesome, but unbalances are minimized.

Figure 50 – Membrane tie

Mill X – Brazil - South America

The production has been significantly increased, following increased gas flow and gas velocities through the superheaters. Increased fouling on the upper sections of the superheaters probably results in a further increase in gas velocities due to preferential gas flow channeling. Extreme wastage of ties began in 2007/2008 and in 2010 the failures created a situation where large production losses are foreseen due to the necessity of significant repairs.

Furthermore, continuation of tie failures may force the mill to an extremely long and cost intensive outage.





The deterioration of these ties has been analyzed by the mill and by Safe Control Boiler Service AB.

The conclusion has been that the ties require significantly better cooling in order to survive in the present environment. Presently, the tie material temperatures simply become so high that the material loses much of its strength. This is why the ties deform plastically and open up or fail at the

slots as seen in Figure 51 above. The main failure is thus caused by overheating due to lack of sufficient cooling. For this particular case what would be desired is either colder cooling media (colder steam), lower heat input (lower heat load) or much shorter distance to the tube surface (lower tube spacing or other design of the tie). The path of the heat transfer is showed in Figure 52.



Figure 52 – Heat flow in a tie. The red arrows show the way the heat travels through the tie in order to dissipate

During 2010, approximately 400 ties were replaced and in 2011 around 500 ties will be replaced. As the problems do not have any permanent solution, it is predicted that about 500 ties need to be replaced annually.

Estimated cost of one tie: 40,7 USD (Celulosa Arauco y Constitución S.A.)

Estimated cost for installation of one tie: 150-200 USD (Carlson, 2010) depending the country and labor costs. In this case a mean value of 175 USD/tie will be used.

Estimated costs per outage: 500 x (175 + 40,7) = 107'850 USD

With the present situation it is foreseen by representatives from Safe Control Boiler Service AB and Metso Power AB that additional down time will be required, in order to bring the situation under control i.e. to be able to replace all broken ties. A minimum of two additional days is estimated to be required:

Estimated cost for additional down time: 1'000'000 USD/day x 2 days = 2'000'000 USD (Based on estimates for the Valdivia plant).

Could these failures have been foreseen and avoided at the purchase and planning stages? The answer to this question is without a doubt yes.

This boiler had the option of upgrading to higher loads and higher loads mean more heat input. Thus boiler superheater corrosion and ties should have been studied with respects to maintenance for original MCR loads and predicted future loading. A rapid check of the blueprints reveals weaknesses in both aspects. The boiler superheaters are not sufficiently protected from the corrosion point of

view or from the mechanical side with regards to the ties. The secondary and tertiary superheaters contain too large spacing for the used tie design. A better tie design should have been used and it still would not guarantee a trouble free operation.

In order to guarantee a successful and maintenance free operation, shorter tube spacing is required in combination with optimization of the superheater tie, seen from the maintenance point of view.

10.2.1 Life cycle analysis

Today the superheater panels consist of 24 tubes with 60,3 mm in diameter, the distance between each tube is 34 mm. The tubes are manufactured in SA213T22 steel which costs 40 USD/m (see Table 19 for reference).

The total amount of ties in each level of the panel is 23. Thus the total width of each panel is equal to $24 \times 60,3 = 1447,2$ mm for the tubes plus $23 \times 34 = 782$ mm for the clips (spacing in between the tubes).

As such, the total width of each panel is 1447,2 + 782 = 2230 mm.

If the width is to be maintained, in order to maintain the performance of the boiler, but the distance between the tubes is to be shortened to 20 mm, four more tubes are required. As a result of having more tubes in each panel, four additional ties would be required at each tie level.

There are eight tie levels which give $8 \times 4 = 32$ extra ties. Each tie costs approximately 40,7 USD (Celulosa Arauco y Constitución S.A.).

The extra cost would be: 4 tubes extra \implies 4 x 20 m x 40 USD = 3600 USD/panel 32 ties extra \implies 32 x 40,7 USD \approx 1302 USD

There is also an extra installation cost of the ties which is hard to estimate. During an outage the cost of changing a tie is 150-200 USD (Carlson, 2010), but the cost is considerably lower during manufacturing. In order to not underestimate the cost, it will be set to 100 USD/tie here, which is still most likely an overestimation.

Installation costs for 32 extra ties \implies 32 x 100 USD = 3200 USD

Thus the total extra cost per panel would be 3600 + 1302 + 3200 = 8102 USD/panel

With 34 panels the extra cost for the entire superheater would be 8102 x 34 = 275'468 USD

With a distance of 20 mm between the tubes, generally no more than 5 ties need to be replaced each year.

As seen above, the yearly costs for the now used design is 107'850 USD/year (outages take place only once per year) with an extra cost of 2'000'000 USD for the additional outage time required. In this case the estimated, required extra outage time already makes the initially cheaper design more costly, but since pulp prices may vary, the outage time will not be accounted for in the life cycle analysis. The method "Net present value" will now be used to compare the net present cost of the alternatives for some different rates of interest.

The formula for calculating the net present value is (Skärvad & Olsson, 2005):

NPV = (a x C) - G + (s x B) where
a = yearly cost saves (in this case yearly costs)
C = net present value factor
G = initial investment
s = scrap value
B = net present factor for single payment

Although there is a scrap value for the superheater once decommissioned it is somewhat difficult to estimate and of less importance. Thus it will not be considered here even though the scrap value for the more expensive alternative should be larger since it contains more tubes.

The net present value factor C is calculated as: $\frac{1-(1+r)^{-n}}{r}$ where r is the interest and n is the number of years.

The results of the calculations that will follow are summarized in Tables 20 and 21 on page 82.

Cheaper alternative:

G = 5'000'000 USD a = -107'850 USD n = 30 years

<u>r = 10 %</u>

$$C = \frac{1 - (1 + 0, 10)^{-30}}{0, 10} = 9,43$$

NPV = -5'000'000 + (-107'850 * 9,43) = -6'017'025 USD

<u>r = 15 %</u>

 $\mathsf{C} = \frac{1 - (1 + 0.15)^{-30}}{0.15} = 6,56$

NPV = -5'000'000 + (-107'850 * 6,56) = -5'707'496 USD

<u>r = 20 %</u>

 $\mathsf{C} = \frac{1 - (1 + 0.20)^{-30}}{0.20} = 4,98$

NPV = -5'000'000 + (-107'850 * 4,98) = -5'537'093 USD

<u>r = 30 %</u>

 $\mathsf{C} = \frac{1 - (1 + 0,30)^{-30}}{0,30} = 3,33$

NPV = -5'000'000 + (-107'850 * 3,33) = -5'359'140 USD

<u>r = 38 %</u>

$$C = \frac{1 - (1 + 0.38)^{-30}}{0.38} = 2,63$$

NPV = -5'000'000 + (-107'850 * 2,63) = -5'283'798 USD

<u>r = 39 %</u>

 $\mathsf{C} = \frac{1 - (1 + 0.39)^{-30}}{0.39} = 2,56$

NPV = -5'000'000 + (-107'850 * 2,56) = -5'276'524 USD

More expensive alternative:

G = 5'275'468 USD a = -5 x 175 = 875 USD n = 30 years

<u>r = 10 %</u>

C = 9,43 NPV = -5'275'468+ (-875 * 9,43) =- 5'283'719 USD

<u>r = 15 %</u>

C = 6,56 NPV = -5'275'468+ (-875 * 6,56) = -5'281'208 USD

<u>r = 20 %</u>

C = 4,98 NPV = -5'275'468+ (-875 * 4,98) = -5'279'825 USD

<u>r = 30 %</u>

C = 3,33 NPV = -5'275'468+ (-875 * 3,33) = -5'278'382 USD

<u>r = 38 %</u>

C = 3,33 NPV = -5'275'468+ (-875 * 2,63) = -5'277'770 USD

<u>r = 39 %</u>

C = 3,33 NPV = -5'275'468+ (-875 * 2,56) = -5'277'711 USD

Cheaper alternative:

r (%)	С	NPV (USD)
10	9,43	-6 017 025
15	6,56	-5 707 496
20	4,98	-5 537 093
30	3,33	-5 359 140
38	2,63	-5 283 798
39	2,56	-5 276 524

Table 20 - Net present value of the cheaper alternative as a function of the internal rent

More expensive alternative:

Table 21 - Net present value of the more expensive alternative as a function of the internal rent

r (%)	С	NPV (USD)
10	9,43	-5 283 719
15	6,56	-5 281 208
20	4,98	-5 279 825
30	3,33	-5 278 382
38	2,63	-5 277 770
39	2,56	-5 277 711

The interests used to calculate the NPV here are just a randomly taken numbers, since the true internal interest of a company is very difficult to estimate. Only when the internal rent becomes >38 % does the cheaper alternative begin to be cheaper throughout the lifetime of the boiler when the cost of the extra outage time is excluded. However, if the production losses from the extra outage time are taken into account the cheaper alternative, with the massive replacements of ties, becomes much more expensive even at interest rates >100 %.

10.3 Case 6 - Sootblower Wall boxes

In order to avoid that the superheaters become too clogged during operation and finally loose too much of the efficiency, they are cleaned during operation by sootblowers. A sootblower is a machine connected to hot steam, some centigrades above the saturation point. When started, the sootblower wagon starts to move towards the boiler, introducing a lance into the sootblower lane, located between the panels of the superheaters, generating bank or economizers. When the lance is free inside the boiler, approximately 200-300 mm from the boiler wall, a valve (poppet valve) opens and the steam blows between the panels. The lance typically contains two nozzles that are turning during the entire cleaning operation. In modern chemical recovery boilers there are two sootblowers in the same lane at the same elevation. Both operate at the same time, but one of them is slightly delayed in order to avoid contact at the centre of the boiler. After reaching the centre, the sootblowers retract home, still blowing the steam. In similarity to the start, they stop blowing steam some 200-300 mm prior the furnace wall centreline.

There are several sootblower designs used. The most common ones today are the Diamont Power and Bergeman sootblowers. There are also several different designs of the sootblower wall box which is the part that connects the sootblowers to the boiler. The wall box can be described as a port with a hole through which the sootblower lance enters the boiler. The wall box also protects the boiler against condensate pouring from the lance into the boiler and seals the opening via an air seal system. The latter is to prevent flue gases from escaping through the sootblower openings.



In one of the Andritz fabricated recovery boilers, in South America, the sootblower wall boxes were built as shown in Figure 53 below:

Figure 53 – Sootblower wall box with welded seal plate

This particular boiler contains 84 sootblowers in the pressure part section and 20 in the economizers where the design does not result in any water leakage risks.

At a very early stage, the wide sealing plates began to reveal thermal cracking as seen in Figure 54. The problem was addressed to the manufacturer who suggested installation of an additional sleeve inside the wall box i.e. a sleeve inside the already existing sleeve.

The problem with this particular design was that condensate drops down onto the wide and hot seal plate. This locally cools the plate, causing a local decrease in volume which creates a very large thermal stress that in turn causes the plate to crack. The general problem with this particular design is not that condensate drips down onto the seal plate, which is inevitable, but rather that the seal plates lack sufficient cooling resulting in severe thermal chocks. Since thermal stress depends on temperature difference, the higher the initial material temperature, the higher the stress once it locally comes in contact with the condensate. As such they are very prone to cracking. Since the seal plates were continuously welded into the boiler tubes, the welds provided a "bridge" for the cracks developed in non-pressure retaining parts into the main boiler pressure parts. The plates cracked and the thermal fatigue cracks propagated via the seal welds into the opening tubes. This is a very serious damage that puts the entire boiler at risk.



Figure 54 – Sootblower wall box with severe cracks

As the suggested design change did not help, the thermal cracking in the sootblowers began to dominate the shut down activities after a few years. Safe Control Boiler Service was then contacted.

During the first subsequent outage, all sootblower opening were dye penetrant tested and all cracks were identified. The quantity of cracks in the sootblowers was almost out of control. The only temporary solution to the problem was to manually grind out each one of the detected cracks and test the opening again. Doing this thoroughly required a large amount of skilled inspectors and mechanics.

As a permanent solution to the problem, it was suggested a replacement of the openings during several subsequent shut downs and the new design can be seen in Figure 55. The work began in 2007 and during each year between 5 and 15 openings were completely replaced by the new design created by Safe Control Boiler Service AB. The design consisted of a large refractory box from the outside and a simple, replaceable sleeve on the inside.



Figure 55 – Improved design of sootblower wall box

The design has shown to be satisfactorily. No new defects have occurred.

During the replacement work in 2008 – 2010 at least three tubes with deep cracks were detected and repaired. In all three cases it was shown that the defects were not detectable with the common NDT methods used from the inside. This means that at least three cases could have resulted in an unplanned shut down.

10.3.1 Cost of the problem

The cost of this simple design flaw can be estimated as follows:

Costs of the annual shut down activities in order to reexamine and remove all detected cracks:

The cost of NDT personnel stated here is based on Swedish prices NDT operator cost: 100 USD/hour Hours of NDT detection work: 40 hours Hours to grind out cracks: 10 - 40 hours

This would result in a total annual cost of approximately 5'000-10'000 USD.

Replacement of sootblower openings to an adequate design:

The cost for replacement of one opening: ≈10'000 USD

The cost to replace all openings with an adequate design: 84 x 10'000 = 840'000 USD.

Fortunately, the mill did not experience any unplanned shut downs, but it came very close to that at several occasions. In a new similar boiler in another South American country, the mill suffered a tube

leakage in this position, detected during a hydrostatic test after the shut down. The leak resulted in the loss of one production day.

If such a leakage occurs during operation, four days would be required to repair the damages in this position. That would correspond to approximately 4'000'000 USD (for a boiler size of 4000 tds/24h).

The extra time involved in an unplanned shut down during operation includes time to allow the boiler to cool, reparation of the damage and the start up. Furthermore the location is likely to require some kind of scaffold for access, which can take quite some time to prepare as well.

Why was this problem not considered already during the design overview? There may be several explanations, but they should all come down to the following three possibilities;

- 1. The wall boxes and the sealing were not reviewed at all.
- 2. The project organization did not include personnel from the maintenance department.
- 3. The maintenance department lacked the expertise to foresee this problem.

10.4 Case 7 - Access

It is extremely rare to evaluate necessary access in all of the recovery boiler parts during the project. From the maintenance point of view it is of course not acceptable and rather unprofessional. A life time of a recovery boiler is estimated to be between 30 and 40 years. Lack of access to any part of the boiler will result in either repair difficulties, or even the necessity to replace the part entirely even at limited damages.

This kind of policy is very common in power boilers or small package boilers, but there is a huge difference in the size of the components and huge difference in the replacement costs when comparing a power boiler to a recovery boiler. In the recovery boiler the components are both larger and more expensive than in a power boiler.

One of the best examples for such an occurrence is the economizers.





The latest designs of the economizers do not allow any access to the economizer sootblower lanes (see Figure 56 for reference). Since the gas inlet and outlet sides are to a large extent closed off by baffle walls, there is no access to the 22-26 meters long economizers that often contain more than 100 panels each. Many simple problems in the economizers now require difficult, expensive and often ineffective repair methods and procedures. If there was full access to the sootblower lane, a majority of the problems would be easy to resolve and repair effectively to low costs.

There are many examples of problems in the economizers which are not easily solved due to lack of access or very limited access.

The typical problems in the economizers which would be easily solved if there had been access to the sootblower lanes are;

- Stabilization of panels in order to avoid too large side movements. (Severe problems in Veracel and Skoghall, desired in Valdivia and Nueva Aldea)
- Stabilization of the baffle wall
- Inspection of the sootblowers, casing and panels inside the package.

The main question is why this can occur?

The answer is rather easy to explain. The sootblower lane is already rather wide from the beginning, due to the safety margins for the sootblower operation. Making the space wider would result in loss of thermal efficiency. As seen in Figure 56, the flue gas always tries to take the easiest way, which is through the open space between the economizer panels. The gas velocity in this open space would increase and a too large quantity of the flue gas would by-pass the economizer heat exchanging surfaces.

The projects are very often dominated by the process engineers and the economy departments on the client side and the process engineers and the sale department on the other side. In those discussions, access and maintenance are often secondary questions if not tertiary. Since there is no larger pressure on the designers, the access questions are often not properly evaluated and the design is not optimized with consideration to the maintenance aspects. The requests are easily dismissed.

It is absolutely true that the wider the sootblower opening is, the less efficient is the economizer. This is at least the case for the present design. The design can however be easily modified in order to not lose the efficiency but still provide full access.

Andritz are bending the tubes, creating a full access to all sootblowers. This design is optimized with consideration to the process and the maintenance problems. The solution is rather expensive and not fully optimal from the maintenance point of view.

Another design is to increase the present space by removal of the outer membranes. This helps only if the original space is close to what is required. In case Valdivia and Nueva Aldea this would have been sufficient. In both cases access could have been obtained by either cutting the fins after welding or welding in much smaller fins (5 mm) from the beginning. It must be pointed out that at membrane welding it is necessary to weld on both sides if severe tube deformation shall be avoided (weld shrinkage).

If a spacing of 450 mm is created, the thermal losses can still be reduced by installation of "Chinese hats" (division plates) in the soothblower lane that force the gases into the heat exchanging surfaces. If this is done frequently, for example at every two meters, the losses would be reduced and the maintenance completely satisfied. This solution is shown in Figure 57.



Figure 57 - Economizer with "Chinese hats" installed

11 The organization today

This section of the thesis will describe how the buying organizations may be organized in terms of influence, authority and decision making. The study is based on interviews with mainly maintenance personnel from six different South American mills, but also staff that has been involved in projects both from the customers and suppliers side.

11.1 The different departments

Process

The process department charged with handling and controlling the process of the boiler so that it goes smoothly and stays within preset parameters. The main parameters concerned are the capacity of combustion which means the amount of black liquor burned per day and the outlet steam temperature. As explained previously in the section "The chemical recovery process", the steam is used as a heat source in the digesters and evaporators, but also to generate electricity with the help of a turbine. It is the job of the process department to ensure that these processes work properly and that a sufficient amount of white liquor is recovered from the black liquor. The department is also responsible for controlling other important aspects of the process such as the chemistry of elements inside the boiler (for example black liquor, ash etc).

The main competences within the department are thus the chemistry of the recovery boiler and process control. As a physical unit the department is usually located in close proximity to the boilers' control room.

Maintenance

As the name implies the maintenance department is focused on maintaining the boiler functionality. They are responsible for the annual shut down and the preventive maintenance of equipment inside the boiler during this time. During the rest of the year they are responsible for maintenance of accessible equipment outside the boiler e.g. sootblowers, air systems, motors etc.

The main competences of the maintenance department is equipment understanding, equipment evaluation and maintenance planning (what needs to be done when, how and what parts are needed in storage). The location of the department is often in close proximity to the work shop, some distance away from the boiler.

Purchasing department

The purchasing department is part of the economy department and tasked with economical aspects of all the things the mill buys. Their main competence regards contracts, payments and negotiations.

As a unit they are normally placed in the main office building.

Engineering department

The engineering department is responsible for installation and equipment and future development of the boiler (e.g. upgrades). Their know-how is mostly concerned with how to construct for functionality within given sets of parameters.

The unit is located at the workshops, but separated from the maintenance department.

11.2 The project organization

As said before the main focus of many clients today is price and performance, while the maintenance aspect is perceived as being less important for the initial buy. Based on the outcome of many boiler projects and interaction with various agents of different companies and departments, the organizational model in Figure 58 comes to mind. In the Figure, the arrows show the flow of information. A dotted arrow means less information. The model is more of an overall outline of the entire project, whereas in reality the degree of involvement of different departments changes over time.



Figure 58 – Model over the buying organization and influences

In this simplified model the main actors are the sales department and project organization of the supplier, together with the purchasing department and project organization of the customer. The project organizations are independent of the other departments within both the selling and buying organizations. In theory they consist of contracted people with knowledge within these areas and are supposedly well familiar with the different needs, but they largely act independent of the standard departments. On the buyer's side, the project organization generally consists of personnel from the engineering department, with support from the process department.

In the venders case the goal of the sales department is to get the highest possible price while still having a lower price than the competitors. It is then the task of the venders' project organization to take the price given by sales and make sure that the project makes a profit. What occurs after the project has ended and the boiler is taken into operation is not their primary concern as long as the boiler is capable of meeting the set warranty time (which is generally quite short). The technical line organization is then assigned to construct a boiler that accomplishes the requested process parameters while keeping the costs within a set budget. Their influence is practically limited to support the project organization if consulted and to follow their boiler specifications to the lowest possible cost. Even though the technical line organization most likely has the know-how to construct a technically superior boiler they are forced to cheaper designs due to budget.

The customer's project organization has a budget for the new project (boiler) and with the help of the process department they are tasked with handling the requested parameters of the boiler. They are also responsible for evaluating the technical aspects of the suppliers' proposal. Based on the specifications from the project organization, the purchasing department is assigned to handle the offers from the various suppliers. Their main goal is to negotiate the lowest possible price. The role of the maintenance department is often quite limited. Even though they may be consulted regarding some issues, their influence is fairly limited.

The involvement of the maintenance department in the actual way the buying organization works is a bit more complex. Explained by a senior maintenance manager, a new boiler project is carried out in six steps which are explained in short here below. Basically the maintenance department becomes more and more involved the further the project proceeds, while being involved very little in the initial phases.

The six phases are as follows:

Conceptual engineering:

In this first step the overall concept is determined with regards to size, performance (load capacity, steam temperatures etc), costs and the future of the boiler. The future of the boiler is concerned with for example possible upgrades later on. The process and engineering departments are mainly involved during this step, whereas the maintenance has no involvement.

Definition of purchase:

What is defined here is the large overall parts and designs that are going to be bought for the boiler. Superheaters, air systems, drums, economizers etc are examples of what is defined for the project here. Once defined the order of these parts is placed with the manufacturer. During this step the maintenance department is still not involved even though they may be consulted if the project organization has any questions. However, the maintenance has little influence over the decisions even when they are consulted.

Detail planning:

The detail planning is concerned with the small details of the boiler, such as electrical motors etc, for the large parts that have already been ordered. During the detail planning the maintenance departments becomes involved in the project with the task of optimizing the life cycle costs of the detailed plan.

Construction phase:

As the name implies this phase begins when all of the boiler parts have been bought and it is time to put together the project. This is generally done under supervision of the supplier, but with the buyer's workforce. The maintenance department is responsible for verification of technical aspects such as quality control during this phase.

Commissioning:

The commissioning is the process of reviewing the installation of the equipment to ensure that is functional and installed according to the technical specification of the project. The commissioning phase consists of two parts: inspection of the now ready plant and flushing of the equipment. Flushing is a general term used for cleaning of the equipment in order to ensure that no residues from the construction reside within the equipment. The maintenance department is responsible for the inspection during this part of the project.

Handover:

Completion of the project. The supplier trims in the boiler and hands it over to the customer's personnel.



Figure 59 – The six steps of the buying process with the involvement of the maintenance department showed by the big arrow. Maintenance becomes more and more involved later on in the process, while being little involved in the beginning

After the project has been finished, it has many times been the case that the project personnel have been moved on to new projects at other facilities instead of being put back in their original positions in the mill. When this has been the case it has mainly been due to the fact that their original positions have been filled with new staff during the time in which the project has been going on.

11.3 Discussion

In this section some important organizational aspects of boiler projects will be discussed.

11.3.1 Problems with the organization today

Inherent reliability and performance:

The six-step procedure of commissioning a new boiler may appear adequate in theory but there is one serious problem with it. The maintenance department first becomes involved in depth during the detail planning phase, but by that time all the major components have already been bought and cannot be changed easily. The problem is that in the case of boilers, the major components are what define the inherent reliability. As seen in the cases described earlier, the costs have mainly arisen as a result of the inherent reliability built in already at the purchase of the overall larger components.

The inherent reliability and performance of the overall larger components inside the boiler have a very large impact on the maintenance costs. Since these components cannot be accessed during the year in operation it is difficult if not impossible to evaluate their status during operation. As a result any divergences between process parameters and the components performance may cause them to deteriorate rapidly without anyone knowing it.

It is then easy to realize that even if the smaller details are a perfect selection it does not help the maintenance aspect if the major components are flawed.

By the time of the involvement of maintenance personnel, all these factors are already set. To change these components later on in the project is then much more costly than before. The rule of thumb is that a change that costs 1 USD during the planning phase, costs 10 USD during the construction phase, 100 USD during the production phase and 1000 USD when in operation (Hagberg & Henriksson, 1994). Another important aspect is that the supplier is often unwilling do any changes, once the contract has been signed. As a result it is likely to reside an unwillingness to change the overall parts later on in the project.

As seen in the cases described earlier in this thesis this can in turn lead to the customer experiencing expensive problems during the lifetime of the boiler. Higher involvement of experts in boiler technology on both the buying and selling side earlier in the project is likely to improve on predicting and resolving these kinds of problems already in the initial stages of the project planning.

Understanding between the departments:

Since the departments are physically separated there is most likely very little everyday contact between the staff of the different departments. As a result there is no daily informal exchange of information between these workers.

A consequence is that there is a gap in knowledge of how different decisions affect the work of the other departments. The main gap lies between maintenance and the process departments since process and engineering usually are the influential departments in the project organization.

One may argue that managers can bridge this gap via meetings and conferences, but this does not give the natural understanding of the opposing parts daily job. Especially as there often exists a rivalry between the departments.

Loss of accumulated knowledge:

When people involved in a project have been moved on to new facilities or projects, any experiences gained during the first project is lost from the departments of the original plant. The same goes for the departments understanding of each other's work and the cause and effect between them. Furthermore the relations between the staff that have been involved in the project are also lost together with the informal information flow between them.

11.3.2 Understanding and defining the project

According to Slack et al, a project can be viewed as consisting of five stages that are relevant for the success of the project (Nigel Slack, 2007):

- 1. Understanding the project environment
- 2. Defining the project
- 3. Project planning
- 4. Technical execution
- 5. Project control

In this thesis, key elements in stages 1 and 2 will be discussed from the customers' point of view.

The project environment:

Regarding recovery boilers, senior management often consider them to be auxiliary equipment that does not have any effect on competitive factors, as opposed to the production facilities where the paper pulp is processed. It is therefore important to keep in mind that stake holders who are not commonly involved in the boiler, once it has been taken into service, often focus on initial costs and performance. It often happens that they fail to realize that if reliability and maintenance are not carefully considered, it will translate into high costs later on.

The project organization responsible for the new boiler project is disbanded once the boiler becomes operational. Many of the people involved are then moved to positions in the standard departments such as process or maintenance. Thus their post project responsibility is limited. The issue is that it may take years before problems with the boiler begin to show and when that happens, the main part of people responsible for the project are no longer involved in the boiler. This makes it difficult for the organization to learn from their experiences.

Different departments have different opinions about what should be prioritized in the project and competition between them is to be expected since their interests may conflict.

One reason for the common lack of interest and knowledge in maintenance by senior management is that they are often recruited from the production or economy departments within most companies. As such they are often production-oriented with the opinion that production gives the income to the company (Ljungberg, 1997). A consequence of the lack of knowledge that follows is that it is seen as certain that the maintenance is always possible.

Defining the project

According to Slack et al, defining a project involves defining its:

- Objectives The end state that project management is trying to achieve
- Its scope Define the dividing line between what each part of the project will and will not do
- Its strategy How project management is going to meet its objectives

The scope and strategy of the project are more of management issues and they will not be discussed here. What is more relevant to this thesis is the definition of the objectives of each project.

Today they seem very short-term where mainly the investment budget, time plan and process parameters are considered. That is to say:

- Did we finish the project within budget?
- Did we finish the project within time?
- Are the process parameters the desired ones?

Often the final evaluation of the project is done within the first three years of the boilers existence with the result that the long-term perspective is then missing completely. The objectives ought to be long term objectives which define not only the time and budget for the project, but also future objectives. These should be considered with future costs and reliability in mind. Had the objectives of many boiler projects been more long term, it is very likely that they would be considered to be failed projects. It is understandable that someone who is only involved in the boiler during its planning and construction is focused on the objectives most important to this phase, but it covers only a small part of the time span that should be considered.

When defining a boiler project, the lifetime of the boiler must be taken into serious account. The standard lifetime is approximately 30 years and thus there will be secondary costs in this period of time. Secondary costs are all costs that occur after the boiler is taken into operation. Examples of what this includes are operational costs, maintenance costs, costs of production loss, exchange of components, upgrades etc.

As such it must be carefully investigated whether there should be a large initial investment with lower secondary costs during the lifetime of the boiler, or if a smaller initial investment should be made with expected higher secondary costs. It is important to acknowledge that there is a strong correlation between initial and secondary costs.

There can be various strategies where, for example the initial investment is smaller and the boiler is upgraded little by little towards a more expensive alternative.

There is off course no right or wrong strategy as long as the pros and cons are evaluated and the consequences of the chosen strategy are known and budgeted for in the future. Important to keep in mind is that the chosen strategy will have a big impact on the inherent reliability.

12 Proposed organization

When it is decided that a new boiler is to be constructed, management must be certain about what they require from the boiler and how much they are willing to pay for it. That is to say that the strategic value of the boiler must be clearly defined. They must also realize that there are limitations to what can be achieved with a certain budget and then choose what is to be the main focus. That is to define the objectives of the new boiler in terms of performance, reliability, maintainability and costs.

For example they may want to focus on steam temperatures to generate electricity, high capacity of black liquor burning, low future costs etc. The problem is often that the buying organization believes that they can get all in one and for a low price.

When they have decided upon their needs, the long term objectives should be defined. The idea is to have a plan for the boiler throughout its lifetime which also includes the maintenance aspect.

It may sound like what is proposed here, are projects dominated by technical experts in boiler technology, but this is not the case. A technical perfection is not necessarily economically optimal. What is suggested here is more balance in between the costs, performance and technical aspects of the boiler as seen in Figure 60 below.



Figure 60 – Model over the proposed way to work in a buying organization

In the proposed model for the overall project, the customers' project organization is one physical organization containing all the necessary competences for the new project.

Instead of having a project organization separated from the other departments and with its own personnel, it should consist of representatives from all departments. The various departments then influence each other in order to reach the best possible trade off between costs, performance and technical aspects of the boiler. Using in-house personnel borrowed from the standard departments of the customers' organization, the communication between the project organization and the departments should improve and flow more naturally. As such the understanding between the departments should increase and no aspects of the evaluation of the suppliers' proposal are forgotten or less prioritized. Also it may be easier for persons of interest to criticize or propose improvements to the concept and proposed design.

External consultants should not be entirely relied upon for the project, but rather they should be used in specific issues where the customers' own organization either lack in competence or want a second opinion. This since experts often have a very high expertise in one particular area such as maintenance, process etc, while having limited knowledge of other areas.

When the first phase of the project has ended, that is to say when the boiler is operational, it is vital that the people from the project organization are returned to their original positions within the mill's organization.

13 Conclusions

The increased demand for green energy over the last years has created a strive for elevating the steam outlet temperatures of the recovery boilers, in order to produce more electricity. As the steam temperatures, pressure and capacity of the boilers have increased, the design and choice of materials have not been focused on facilitating these increases from a maintenance perspective, but rather they have been focused on keeping the initial costs down.

As a result many modern mills have had serious problems with wastages of boiler components, resulting in high maintenance costs and a quite common problem has been aggressive superheater corrosion.

The reason being that as a crucial factor, such as the steam temperature increases, the safe operating margins decreases and thus it becomes more difficult to keep the operation parameters inside the safe zone. Temperature is not the only vital factor when considering superheater corrosion. The amount of potassium and chlorine in the ash can also decrease the safe operating margins by lowering the melting point of the deposits and giving way for deposit melt corrosion at temperatures that would normally be considered safe.

One factor that explains the difficulty in controlling the temperature is the temperature imbalances in a superheater, which can create a significant difference between the global and local temperatures within a superheater. The imbalance has two parts; between panels and inside panels.

Steam data analysis showed that the general temperature difference between the hottest and the coldest panels in the tertiary superheaters was 31,81°C. In the secondary superheater the difference was higher and amounted to 80,21°C.

When comparing the average temperature of hottest outlet tubes (in the penthouse) with the average steam outlet temperature the difference was found to be $3,35 - 7,07^{\circ}$ C.

The imbalance inside the panels is much affected by the design and the conventional design is the design that gives the largest temperature imbalance. As seen in cases 1-3, the corrosion attacks are often highly localized and often found on the outlet tubes of the central superheater panels. This suggests that the temperature imbalance is of high significance for the corrosion attacks by causing locally elevated temperatures. Unfortunately there was no way of investigating the quantity of the imbalances inside the panels in this thesis since thermo couples are usually only installed on the hottest outlet tubes.

In the Valdivia mill, where evidence of deposit melt corrosion was encountered it had mainly affected the outmost outlet tubes of the center panels, suggesting that the temperature imbalances had a large part in the corrosion occurrence.

Control of the combustion of black liquor is another important factor to consider. Even though the temperature and ash composition are controlled, the combustion can in itself cause corrosion attacks via carryover and the sulphidation process. It would seem that sulphidation corrosion is quite common, since evidence of it was encountered in all the three investigated cases of superheater corrosion. In the Valdiva and Nueva Aldea mills, the sulphidation corrosion was deemed to be rather light, but in the Burgo Ardennes mill it was more severe. The occurrence of carryover is difficult to

quantify and control since there exist no instrumentation that can alert the operators when it does occur.

The most commonly used steel in the superheaters today is the SA213T22 steel with 2,25 % Cr and 1 % Mo. This is a cheap steel with high strength at elevated temperatures, but less good corrosion resistance properties. The use of more expensive materials for the superheater tubes, for example compound or high grade austenitic stainless steel would most likely decrease the damages to the superheater tubes. Although it may be uneconomical to use these costly materials in the entire superheaters, using them in commonly affected areas would increase the life time of the entire superheater. One such typical area is the outlet tubes of the superheater panels.

The maintenances costs of a boiler are very much defined during the initial stages of a new boiler project. Unfortunately the focus of the project organization is too often to keep the initial costs down with the result that the maintenance aspect of the project is not given careful consideration. In the cases 4-6 it was seen that unnecessary design flaws resulted in high repair costs once the boilers had been taken into operation.

In the case of the superheater corrosion (case 4) the repair costs were estimated to be approximately 1'000'000 USD (excluding the costs of the extra outage time). A more reliable design which would have reduced the corrosion, or eliminated it completely, would have had an initial cost of about 330'000 USD more than the design used.

In the case of the superheater ties (case 5) a design that would have prevented the extreme wastage of ties would have had an initial cost approximately 275'468 USD higher than the design used today. This can be compared to the replacement costs of 107'000 USD/outage (excluding the costs of extra outage time) as is the case with the used design. When the cost of the extra outage time is not taken into account the internal rent would have to be larger than 38 % in order for the cheaper design to be more cost effective throughput the life cycle of the boiler. If the cost of the extra outage time is taken into account however, the cheaper design is much more expensive throughout the boilers life cycle.

The design flaw of the sootblower wall boxes that was reviewed (case 6), did apart from creating a risk of unplanned shut downs, also cause the yearly maintenance cost to become 5'000-10'000 USD. When the risk of experiencing unplanned shut downs was deemed as serious as to motivate a change of design, the cost of this change was estimated to have been 840'000 USD.

When the steps of the buying process are considered, it becomes clear that the involvement of maintenance personnel is slim in the early stages of the project, when the purchase of the major components is considered. The project organizations can thus be said to often be production oriented and to place less weight on the maintenance aspects of the boiler. Since the major components are what largely define the future maintenance costs, earlier involvement of maintenance personnel could help in reducing future maintenance costs by giving more focus to the maintenance aspects of the boiler. When considering the future costs, not only repair costs should be considered. Time aspects are also very important since prolonged outages are very costly and problems that in themselves are not very expensive to correct, may require that extra time be added to the annual maintenance shut downs. An estimate of the cost of extra outage time was calculated to be about 1'000'000 USD/day for a boiler size of 4 000 tds/24h.

As seen in case 7 (Access) the consequences of an emphasis on production does not always result in high visible costs as in the cases 4-6, while still complicating the maintenance works during a shut down.

The implications are that an initially cheaper purchase may actually turn out to be more costly than an initially more expensive design, when the lifetime of the boiler is considered. Managers would thus be wise to put more consideration into the maintenance aspects when planning for a new boiler.

14 Acknowledgements

Special thanks to all those who made this thesis possible and who have contributed with valuable input and information.

Thomas Eilersson Kari Haaga Anton Bjurenstedt Benny Gustavsson Paul Praszkier

And last but not least to all the personnel at

Celulosa Arauco y Constitución S.A. who have taken their time to share information, experiences and ideas.
15 References

Ahlmann, H. R. *From traditional practice to the new understanding: The significance of life cycle profit concept in the management of industrial enterprises.* Lund: Lund University Institute of Technology.

Almar-Naess, A. (1983). Metalliske Materialer. Trodheim: Tapir Forlag.

Andersson, L. (2010). *Examination and analysis of tube samples from secondary superheater, panel 16. Celulosa Arauco y Constitucion S.A., Nueva Aldea.* Göteborg: Safe Control Materialteknik.

Aracruz Cellulose S.A. (n.d.). Aracruz, Brazil.

ASME. (2007). ASME Boiler & Pressure Vessel Code, Section II.

Barringer, P. H. (1997). *Availability, Reliability, Maintainability, and Capability.* Texas - USA: Barringer & Associates, Inc.

Blanchard, B. S., & Fabrycky, W. J. (1997). *Systems Engineering and Analysis.* New Jersey, USA: Prentice Hall Inc.

Borg, O. F. (1986). Yrkesbok C III - Sulfatmassetillverkning (kokning, tvättning, återvinning). Markaryd: Sveriges Skogsindustriförbund.

Bruno, F. (1995). The significance of superheater tube corrosion on the steam temperature of Kraft recovery boilers. *Pulp & Paper Industry Corrosion Problems*, *8*, 138-149.

Carlson, C. (2010, November). Maintenance coordinator - Arauco Constitución.

Celulosa Arauco y Constitución S.A. (n.d.). Chile.

Eilersson, T., Lejonberg, A., & Praszkier, P. (1995). Black Liquor Recovery Boiler Superheater Gas Side Corrosion. *International Symposium on Corrosion in the Pulp & Paper Industry*, *8*, 158-164.

Falk, I. (1986). Pannrevisioner. Halmstad: Studsvik.

Folkeson, N. (2010). *Chlorine Induced Corrosion in Biomass and Waste Fired Boilers: Laboratory and Field Investigations*. Göteborg: Chalmers University of Technology.

Gale, W., & Totemeier, T. (2006). Smithells Metals Reference Book (8th Edition). Elsevier.

Götaverken Energy. (1989, 03 29). Internal PM by Thomas Eilersson. Göteborg, Västra Götaland, Sweden.

Haaga, K. (2004). High Pressure Boilers. Kvaerner Power OY.

Hagberg, L., & Henriksson, T. (1994). *Lönsamt Underhåll - 8 steg till säkrad produktion*. Lund: Mentor Gruppen AB.

Hough, R. P. (1992). *Chemical Recovery in the Alkaline Pulping Processes* (3:rd edition ed.). Atlanta, USA: Tappi Press.

Khanna, A. (2002). Introduction to High Temperature Oxidation and Corrosion. ASM International.

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

Ljungberg, Ö. (1997). TPM - Totalt Produktivt Underhåll. Vimmerby: TPM Institutet AB.

Metso Power AB. (n.d.). Sweden.

Montgomery, V. M., & Karlsson, A. (1995, April). Bericht über das Oxidation von neun Sthaltypen in dampfseitigen Verhältnissen. *Themenvorschau Heft 4*.

Nigel Slack, S. C. (2007). *Operations Management*. Essex, England: Pearson Education Limited.

Pettersson, J. (2008). *Alkali Induced High Temperature Corrosion of Stainless Steel*. Göteborg, Sweden: Majornas CopyPrint.

Port, R. D., & Herro, H. M. (1991). The Nalco Guide to Boiler Failure Analysis. USA: McGraw-Hill Inc.

Safe Control Boiler Service. (2009). ANALYSIS & RECOMMENDATIONS FOR THE TERTIARY SUPERHEATER IN THE VALDIVIA RECOVERY BOILER. Göteborg: Safe Control - Boiler Service.

Salmenoja, K. (2001). *Field and Laboratory Studies on Chlorine-induced Superheater Corrosion in Boilers Fired with Biofuels*. Åbo, Finland: Åbo Akademi.

Skrifvars, B.-J., Hupa, M., Salmenoja, K., Backman, R., & Vakkilainen, E. (2008). Corrosion of superheater steel materials under alkali salt deposits. Part 1: The effect of salt deposit composition and temperature.

Skärvad, P.-H., & Olsson, J. (2005). Företagsekonomi 100. Malmö: Liber Ekonomi.

Stapelberg, R. F. (2009). *Handbook of Reliability, Availability, Maintainability and Safety in Engineering Design*. London, England: Springer-Verlag London Limited.

Wensle, A. (1996). *Superheater Tube Corrosion No.14 Power Boiler Kimberley-Clark Everett, WA.* Bacon Donaldson Consulting Engineers.

Wilson, A. (1999). Asset Maintenance Management. Oxford: Alden Press.