The analysis of furnace wall deposits in a low-NO_x waste wood-fired bubbling fluidised bed boiler

Yousef Alipour, Peter Viklund and Pamela Henderson

Kurzfassung

Analyse der Wandablagerungen in einer NO_X-armen altholz-gefeuerten stationären Wirbleschichtfeuerung

Zunehmend wird Biomasse als Brennstoff in der Stromerzeugung genutzt. Mit steigendem Preis für naturbelassenes Holz nimmt der Einsatz von Altholz zu. Altholz enthält jedoch mehr Chlor, Zink und Blei, von denen angenommen wird, dass sie eine Erhöhung der Korrosionsraten verursachen.

Korrosionsprobleme traten an den Kesselwänden von Wirbelschichtkesseln auf, in denen 100 % Altholz unter „Low-NO_X-Verhältnissen“ verbrannt wurde. In einem ersten Schritt zum Verständnis der Auswirkungen des Brennstoffs wurden Ablagerungen an verschiedenen Positionen der unteren Kesselwände gesammelt und analysiert. Ein großer Teil dieser Kesselwände war mit der Nickel-Basis-Legierung Alloy 625 beschichtet.

Es gab beträchtliche Unterschiede in der Zusammensetzung der unterschiedlichen Ablagerungen, aber ein höherer Kaliumgehalt war immer mit einem hohen Chlorgehalt verbunden. In sämtlichen Proben wurden Chlor (bis 27 Atom-%), Kalium und Schwefel gefunden. Darüber hinaus konnte in den meisten Proben (19 von 20) Natrium nachgewiesen werden. Außerdem wurde Zink in 15 von 20 Proben in geringen Konzentrationen gefunden und Blei wurde in 7 von 20 Proben bei niedrigen durchschnittlichen Konzentrationen gemessen. Lokal gab es allerdings hohen Konzentrationen.

Durch Röntgenbeugungsanalysen (XRD) wurde die Anwesenheit von Kalium-Blei-Verbindungen, wie $K_2Pb(CrO_4)_2$, in den Ablagerungen nachgewiesen, und eine erste Prüfung der nickelbeschichteten Rohre hat gezeigt, dass Blei stark konzentriert in Pits an der Korrosionfront auftritt.

Authors

Dipl.-Ing. Yousef Alipour
Division of Surface and Corrosion Science
KTH Royal Institute of Technology
Stockholm/Sweden

Dr.- Ing. Peter Viklund
Swerea – KIMAB
Kista/Sweden

Professor Pamela Henderson
Vattenfall Research and Development
Stockholm/Sweden

Introduction

In recent years there has been a large increase in the amount of biomass being utilised in electricity generation. As the price of virgin wood continues to rise, more waste wood is being used. Waste wood, (also known as recycled wood), consists of by-products from consumption, the major sources being demolition and construction of buildings. However, waste wood often contains traces of paint or plastics which gives rise to an increase in the amount of chlorine, zinc and lead in the fuel and increases the corrosion risk to boiler components.

Vattenfall in Sweden has been utilising wood-based biofuels for more than two decades and has solved many of the corrosion problems associated with wood and waste wood. For example superheater corrosion is mitigated by the use of the patented “ChlorOut” solution, [1], often in combination with a change of material to an austenitic stainless steel, [2]. However, “ChlorOut” is sprayed into the boiler after combustion and tubes of stainless steel cannot be used for the construction of furnace walls.

Problems have been experienced with furnace wall corrosion with waste wood, in combination with low-NO_x combustion. An air-curtain has been installed in the furnace region, but this seems not to have mitigated the problem. Rather, the corrosion problem in the furnace region has been solved by weld overlay coating with a nickel-based alloy, usually IN 625, but these overlay coatings are expensive and other ways are being sought to reduce the costs of corrosion in the lower furnace region, above the refractory. Within the Swedish framework programme “KME”, [3] which is part funded by the Swedish energy agency, a project has been started to specifically look at furnace wall corrosion with the aim of reducing it at present and future steam parameters.

As first step in the project, the deposits formed on the furnace walls have been characterised and the results are reported here. Special attention has been paid to the elements of sulphur, chlorine, potassium, sodium, zinc, and lead, which are corrosive or form corrosive salts. In particular, zinc and lead chlorides have been found to increase the corrosion rate of boiler steels and a mixture of these chlorides in an alkali chloride containing deposit gives rise to low melting point mixtures, causing corrosion at temperatures as low as 250 °C, [8]. Work will continue with evaluation of coated and uncoated tubes cut from the furnace walls, short-term deposit and flue gas measurements and long-term corrosion testing.

The Idbäcken combined heat and power (CHP) boiler

The Idbäcken plant, owned and operated by Vattenfall AB, is situated 120 km south of Stockholm and supplies energy to Nyköping, a town of 30,000 inhabitants. The plant consists of a bubbling fluidised bed (BFB) steam boiler (boiler 3) for CHP operation, two circulating fluidised bed (CFB) boilers for hot water production and a hot water accumulator. The plant has been in operation since the end of 1994. The CHP boiler, the subject of this investigation, originally operated on a mixture of biomass and coal, but over the years the amount of coal has been reduced and the amount of waste wood increased. Since the summer of 2008, the plant has been operated on 100 % waste wood. The waste wood is sourced from Sweden, Great Britain, and Norway.

The CHP unit produces 35 MW of electricity and 69 MW of heat. A flue-gas condenser yields 12 MW additional heat at full boiler load. The final steam temperature is 540 °C and the pressure 140 bar.

The boiler runs at relatively low oxygen levels, 2 to 2.5 %, but these can sometimes be as low as 1 %. This is in order to increase efficiency and reduce NO_x emissions (and the Swedish NO_x tariff which is about 5 Euros per kg). These levels are measured after superheaters. In some parts of the furnace, which is designed with staged combustion, oxygen levels of less than 0.5 % have been measured. The control of the oxygen levels comes at a cost as it is known that chlorine-rich fuels cause more corrosion at reducing and low oxygen conditions, below 0.5 %, [4].

Corrosion in the boiler

As mentioned in the Introduction, problems with superheater corrosion in the

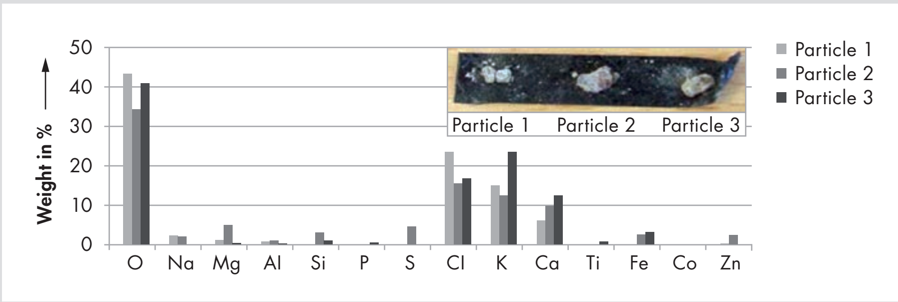


Fig. 1. EDS chemical analysis from deposit F3 (front wall position 3), showing results from the three separate analyses. Within an individual deposit sample/position the spread in chemical composition was low.

plant have been solved and a lifetime of 10 years was achieved for the final superheater with 540 °C steam. However, furnace wall corrosion has increased dramatically over the years. The average metal loss over a period of 9 years from start of operation in 1994 to 2003 was found to be 0.6 mm, i.e. a metal loss rate of 60 to 70 µm per year. In 2006 the average metal loss over the 12 year period since start-up amounted to 1.5 mm, i.e. an increase in 0.9 mm over a three year period. This is equivalent to a metal loss rate of 300 µm per year in the period 2003 to 2006.

The furnace walls were completely replaced in 2008 and the corrosion rate continues to be high when firing 100 % waste wood at moderate to low oxygen levels. Locally, metal loss rates of 1.5 mm per year have been measured in the worst affected areas. With an operating time of 6,500 to 7,000 hours per year this amounts to a metal loss rate of 0.2 mm per 1,000 h. The parts of the walls with the highest corrosion rates have been weld overlay coated with a nickel-based alloy and work is being performed to systematically study the problem and reduce corrosion costs by means other than altering the fuel or operational mode of the boiler.

As a first step in identifying the corrosion mechanisms, deposits were taken from a large number of positions on the furnace wall and chemically analysed. Most of the deposits were from areas in the boiler between the secondary and tertiary air ports (height 11.5 to 18 m), where corrosion is worst. Two samples were taken from above the tertiary air ports at a height of 22 metres (samples F6 and F7 on the front wall). The deposits were removed only from the tubes and not the fins between the tubes on the membrane wall.

The parts of the deposit nearest the tube were analysed using energy dispersive x-ray spectroscopy (EDS). The scanned area was 2.5 x 2 mm in each case (corresponding to a magnification of 50 X) and three separate areas (or pieces of deposit) were analysed for each deposit position. Some deposits were chosen for further examination at higher magnifications and some by x-ray diffraction (XRD).

Results

The deposits were mounted on carbon tape for SEM analysis, so the carbon counts were removed from the analyses presented here. However, they were in the range 5 to 10 weight % for most particles. The spread in chemical composition results was low within individual deposit samples (individual positions on the furnace wall), as shown in Figure 1.

The average content of key elements that are thought to be corrosive or form corrosive salts in the deposits (sulphur, chlorine, potassium, sodium, zinc and lead) and their position on the four furnace walls are shown in Figures 2 to 5.

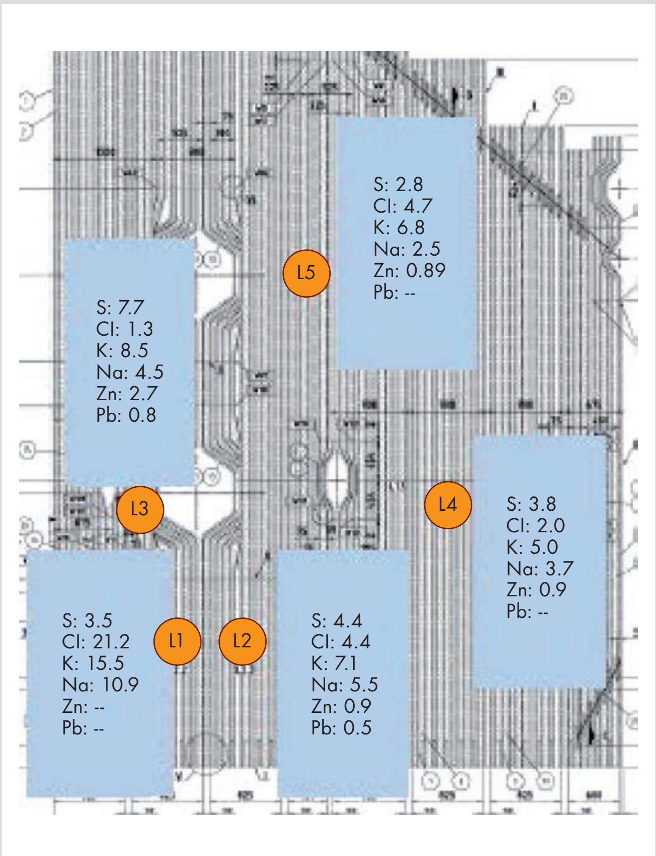


Fig. 3. Sketch of left wall showing the positions, L1 to L5, from where deposits were removed and chemical composition in atomic % of key elements in the deposits.

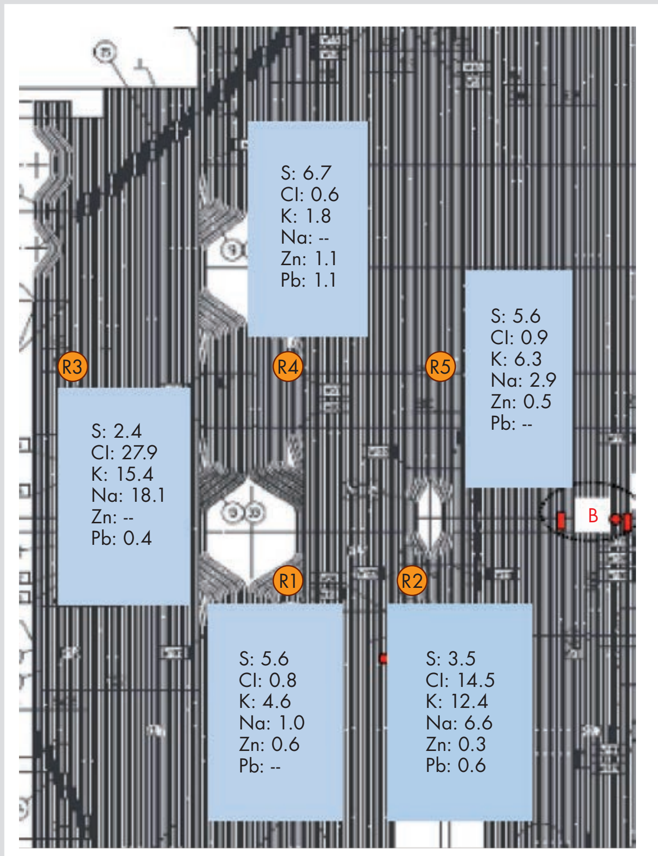


Fig. 2. Sketch of the right wall showing the positions, R1 to R5, from where deposits were removed and chemical composition in atomic % of key elements in the deposits.

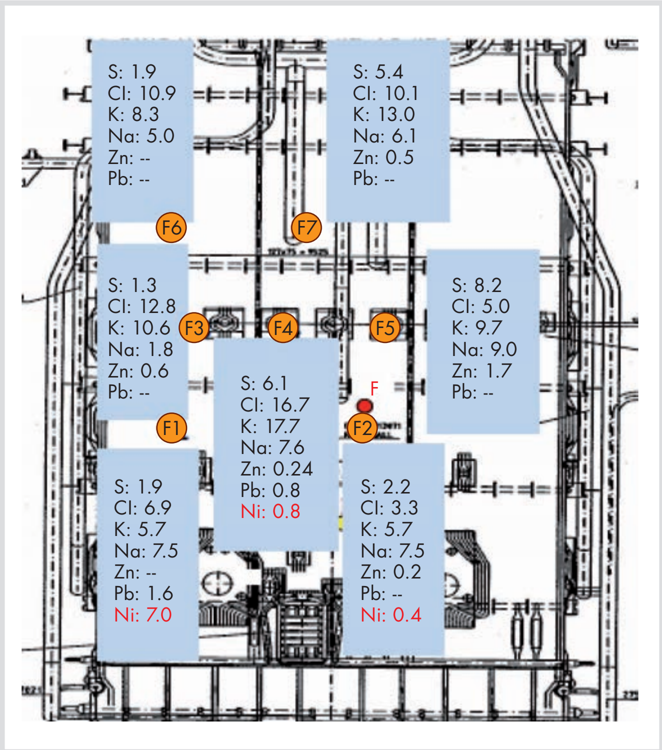


Fig. 4. Sketch of front wall showing the positions, F1 to F7, from where deposits were removed and chemical composition in atomic % of key elements in the deposits. The nickel comes from the Alloy 625 coating which had found its way into the deposits. F6 and F7 are above the tertiary air ports.

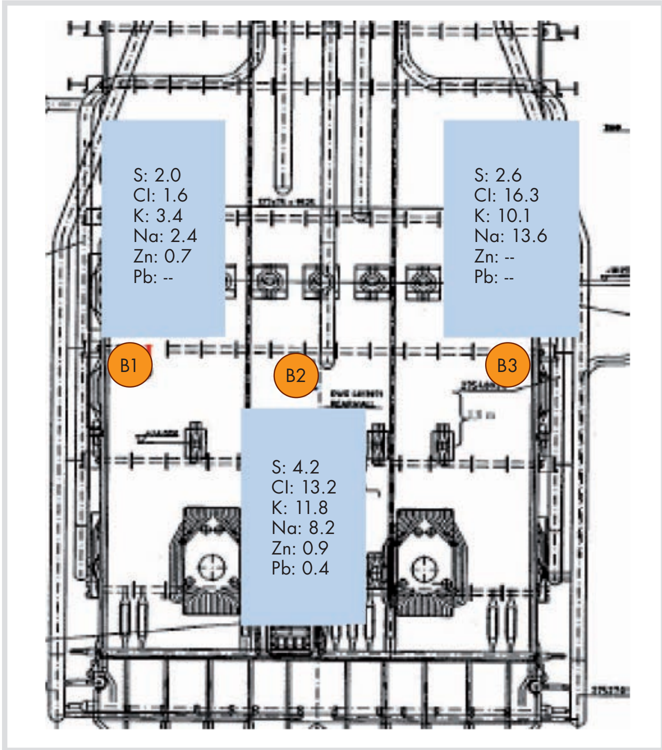


Fig. 5. Sketch of back wall showing the positions, B1 to B3, from where deposits were removed and chemical composition in atomic % of key elements in the deposits.

Table 1. Compounds identified by x-ray diffraction in deposits R4, F1 and R2.

	Compounds detected
R4. low chlorine. high Pb. Cl = 0.6, Pb = 1.1 at %	
Strong intensity/high concentrations	$(K,Na)\ SO_4$, $K_2Pb\ (SO_4)_2$
Medium intensity/medium concentrations	Pb_2OSO_4
F1. medium chlorine. high Pb. Cl = 6.9, Pb = 1.6 at %	
Strong intensity/high concentrations	KCl
Medium intensity/medium concentrations	NaCl, $K_3Na\ (SO_4)_2$, NiO, $K_2Pb\ (CrO_4)_2$
R2. high chlorine. med-low Pb. Cl = 14.5, Pb = 0.6 at %	
Strong intensity/high concentrations	KCl
Medium intensity/medium concentrations	NaCl, $K_3Na\ (SO_4)_2$, NiO, $Cr_{1.6}Fe_{1.4}O_4$

Table 2. Mean values of key elements in forest residues and waste wood (demolition wood) and the spread in waste wood analyses. From 16 analyses of forest residues and 12 analyses of waste wood. Data reproduced from [5].

Parameter	Forest residues	Waste wood	Waste wood spread
Total moisture (weight %)	44	23	11 to 39
Total ash (weight % dry)	2.6	5.8	3.2 to 15
C (wt %) dry ash-free	51	52	50 to 56
N (wt %) dry ash-free	0.4	1.2	0.12 - 1.5
S (wt %) dry ash-free	0.04	0.08	0.04 to 0.3
Cl (wt %) dry ash-free	0.02	0.06	0.04 to 0.22
K (wt %) in ash	7.2	2.0	1.0 to 2.6
Na (wt %) in ash	0.7	1.4	0.6 to 1.9
Zn (mg/kg) in ash	2,047	10,393	2,420 to 184,167
Pb (mg/kg) in ash	63	544	140 to 28,611

There was considerable spread in the composition, depending on the position, but a higher K content was always associated with a high Cl content. Cl was found in all the deposit samples, sometimes at very high levels (27 atomic %). K and S were found in all the deposits samples and Na was found in most samples (19 of 20). Zn was found in 15 of 20 samples at low concentrations. Pb was found in 7 of 20 samples at low average concentrations, but high concentrations locally.

Scanning electron microscopy showed that lead, when it was present in a deposit, was heterogeneously distributed and could be observed as "islands" of pure lead or in mixtures containing oxygen, for example Pb-Cl-O mixtures or Pb-K-S-O mixtures. Figure 6 shows an "island" of a lead mixture in a "sea" of alkali chloride.

Zinc was less frequently observed, but was seen as crystals of zinc chloride as shown in Figure 7.

Results of x-ray diffraction on deposits with low, medium and high chlorine levels are given in Table 1.

In the sample with a low chlorine content, sulphates dominated the x-ray diffraction results. As expected, potassium chloride dominated in deposits with medium to high chlorine contents. Potassium-lead compounds, such as potassium-lead chromate were also detected.

Initial metallographic investigation of corroded Ni-alloy coated tubes, using SEM and wave-length dispersive x-ray

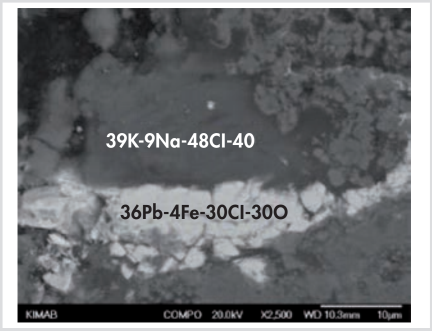


Fig. 6. Section of a deposit showing lead concentrated as a Pb-Cl-O mixture. Analysis in atomic %´.

spectroscopy (WDS), revealed that lead was greatly concentrated at the corrosion front in the pits (Figure 8). The tube section shown in Figure 8 was located near deposit sample R2.

Discussion

It is known that co-firing wood fuel with sulphur or a small amount of coal decreases the corrosion rate [6, 7]. The removal of coal from the fuel mix in the power plant therefore contributed to an increase in the corrosion rate. The switch from forest residues to waste wood increased the problem further adding approximately 5 Euro/MWh to maintenance costs at the plant in Nyköping. However, waste wood is approximately half the price of forest residues, about 10 Euros/MWh as opposed to 20 Euros/MWh for forest residues, and so the overall costs are reduced.

Table 2 shows the key elements which form corrosive salts in forest residues and waste wood. Waste wood contains more chlorine, zinc and lead than forest residues, although it also contains less potassium. Laboratory studies have shown, though, that NaCl and KCl are equally corrosive, [8] and a number of the deposits analysed in this study contained up to 30 atomic percent alkali chloride.

It is thought that both alkali and chlorine take part in the corrosion process. Cl corrosion may occur by diffusion of gaseous Cl (so-called active oxidation), [9] or by diffusion of chloride ions through the oxide scale [10]. Potassium has been found to react with the protective chromium scale to form the unprotective K_2CrO_4, [11] Chlorides of Ca and Na react in a similar way, [14, 15].

In a laboratory study it was observed that stainless steels exposed to lead chloride, $PbCl_2$ showed accelerated corrosion due to the formation of lead chromate, $PbCrO_4$, whereas $ZnCl_2$ was found to have only a marginal effect on the corrosion rate and no chromate was detected. Both $PbCl_2$ and $ZnCl_2$ increased the corrosion rate on a low alloyed steel, but $PbCl_2$ was far the more aggressive, [8,12]. In this study it has been found that lead and potassium together react with the chromia scale to form $K_2Pb(CrO_4)_2$. The presence of $K_2Pb(SO_4)_2$ also shows that potassium and lead are reacting together.

Nickel-based alloys, such as Alloy 625, are widely used in waste incineration plants because of their resistance to chloride corrosion. The *Gibbs* free energy of formation of $NiCl_2$ is less negative than that of $CrCl_2$ or $FeCl_2$ and therefore Ni is more resistant to chloride formation than Cr or Fe, [13]. Coating with Alloy 625 has helped to reduce the corrosion rate of the wall tubes in the boiler at the Idbäcken plant and preliminary results (shown in Figure 8) show that there is very little Cl at the corrosion front. However the alloy is not immune from attack. Our results so far indicate that although only small amounts of Zn and Pb are found in the deposits on the furnace walls the Pb, together with K, is highly active in the corrosion process on the nickel-based alloy coating.

Corrosion tests with other alloys are being performed in order to find more cost effective protection systems

Conclusions

Deposits were taken from the lower part of the furnace walls of a low NO_x boiler running on recycled wood, which is experiencing corrosion problems. The deposits showed a wide spread in chemical composition , although Cl was found in all the samples, sometimes at very high levels (27 atomic %). K and S were found in all the deposits samples and Na was found in most. A higher K content was always associated with a high Cl content. Zn was found in three-quarters of the samples at low concentrations and Pb was found in a third of the samples at low average concentrations, but high concentrations locally.

X-ray diffraction revealed the presence of K-Pb compounds such as $K_2Pb(SO_4)_2$ and $K_2Pb(CrO_4)_2$, Cr in the latter coming from coated tubes.

Coating the furnace wall tubes with the Ni-base alloy, Alloy 625, reduced the corrosion rate and metallographic examination using SEM and WDS showed that there was very little chlorine at the corrosion front in this alloy. However, although only small amounts of lead were found generally in the deposits, the lead together with potassium, was concentrated at the corrosion front in the pits and appeared to be highly active in the corrosion process on the nickel-based alloy coating.

Acknowledgements

This project was funded by the KME Materials Technology Consortium (project KME-508) which is financed by energy

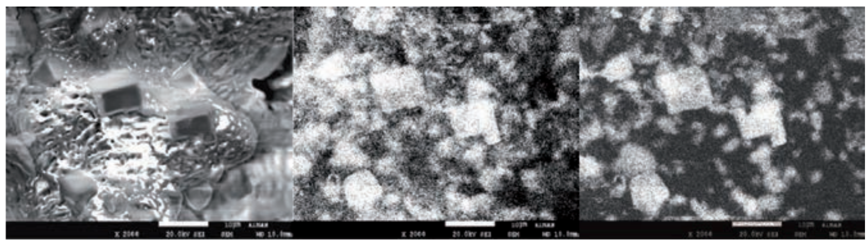
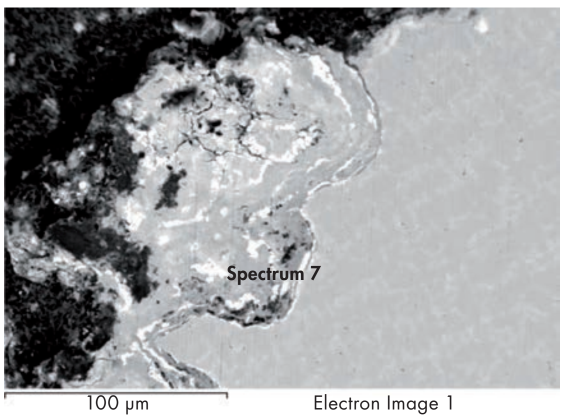


Fig. 7. Crystals of zinc chloride from sample L3, which contained the highest amount of zinc of all analysed samples. The marker bar is 10 µm.



Element	Wt %	At %
O K	19.99	51.68
S K	5.60	7.23
Cl K	0.46	0.54
K K	5.09	5.39
Cr K	4.92	3.91
Fe K	0.41	0.30
Ni K	35.32	24.88
Zn K	1.03	0.63
Pb M	27.22	5.43

Fig. 8. A section through the surface of weld overlay IN 625 and the chemical composition of the analysed spot. The micrograph shows a pit filled with a mixture of deposit and corrosion products, with the un-corroded alloy on the right and the outer surface on the left. The spot analysis was made by WDS.

and materials companies and by the Swedish Energy Authority. We are grateful for the help given by *Christer Forsberg* (formerly *Andersson*), *Anders Hjörnhede* and *Seppo Simola*.

References

[1] *Henderson, P.J., Kassman, K., and Andersson, C.*: The use of fuel additives in wood and waste wood-fired boilers to reduce corrosion and fouling problems. VGB PowerTech, pp 58-62, vol 84, no 6, (2004).

[2] *Henderson, P., Szakalos, P., Pettersson, R. Andersson, C. and Högberg, J.*: Reducing superheater corrosion in wood-fired boilers. Materials and Corrosion, 57, pp 128–134, (2006).

[3] http://www.elforsk.se/Programomraden/El--Varme/KME/

[4] *Davis, C.J., James, P.J., Pinder, L.W., and Mehta, A. K.*: Effects of fuel composition and combustion parameters on furnace wall fireside corrosion in pulverised coal fired boilers, Materials Science Forum, 369-272, 857-864. Trans Tech Publications, (2001).

[5] *Strömberg, B. and Svärd, S.H.*: Fuel Handbook 2012. Värmeforsk report 1234, (2012). Downloaded from www.varmeforsk.se/rapporter?action=show&id=2782 (In Swedish). An earlier version (2006), translated into English, is available at www.varmeforsk.se/reports?action=show&id=1945

[6] *Henderson, P.J., Ljung P., Eriksson, Th., Westberg S-B, Hildenwall, B., and T. Åbyhammar, T.*: Corrosion testing of superheater steels for biomass-fired boilers and the effects of co-firing with coal. Proc Conf "Advanced Materials för 21st Century Turbines and Power Plant". pp 1094-1104. Eds. A. Strang et al. Book 736, IOM Communications, London, UK, (2000).

[7] *Montgomery, M. and Larsen, O.H.*: Field test corrosion experiments in Denmark with biomass fuels Part II: Co-firing. Materials and Corrosion, 53, pp 185–194 (2002).

[8] *Enestam, S*: Corrosivity of hot flue gases in the fluidized bed combustion of recovered waste wood. Academic dissertation. Report 11-04 Åbo Akademi, (2011).

[9] *Grabke, H.J., Reese, E., Spiegel, M.*: The effects of chlorides, hydrogen chloride, and sulfur dioxide in the oxidation of steels below deposits Corrosion Science, 37, pp. 1023–43, (1995).

[10] *Folkeson, N., Jonsson, T. Halvarsson, M. Johansson, L.-G., Svensson J.-E.*: The influence of small amounts of KCl(s) on the high temperature corrosion of a Fe-2.25Cr-1Mo steel at 400 and 500 °C. Materials and Corrosion, 62, pp. 606–610, (2011).

[11] *Pettersson, J., Asteman, H., Svensson, J.-E., Johansson, L.-G.*: KCl Induced Corrosion of a 304-type Austenitic Stainless Steel at 600 °C; The Role of Potassium. Oxidation of Metals, 2005. 64, pp. 23–41, (2005).

[12] *Bankiewicz, D., Enestam, S., Yrjas, P., and Hupa, M.*: Experimental studies of Zn and Pb induced high temperature corrosion of two commercial boiler steels. Fuel Processing Technology, in press (2012).

[13] *Zahs, A., Spiegel, M., Grabke, H.J.*: Chloridation and oxidation of iron, chromium, nickel and their alloys in chloridizing and oxidizing atmospheres at 400-700 °C. Corrosion Science, 42, pp 1093–1122, (2000).

[14] *Folkeson, N., et al.*: Fireside corrosion of stainless and low alloyed steels in a Waste-fired CFB Boiler. Materials Science Forum, 595–598, pp 289-297, (2008).

[15] *Karlsson, S., Pettersson J., Johansson L.-G., Svensson, S.-E.*: Alkali Induced High Temperature Corrosion of Stainless Steel: The Influence of NaCl, KCl and $CaCl_2$. Oxid. Met. 78, pp 83–102, (2012).

InfoExpert

VGB PowerTech-DVD

More than 12,000 digitalised pages with data and expertise
(incl. search function for all documents)

Please fill in and return by mail or fax

I would like to order the VGB PowerTech-DVD 1990 to 2011 (single user license).

- ☐ Euro 950.–* (Subscriber of VGB PowerTech Journal [1]
- ☐ Euro 1950.–* (Non-subscriber of VGB PowerTech Journal [2]
  Plus postage, Germany Euro 7.50 and VAT
- ☐ Network license (corporate license), VGB members' edition (InfoExpert) and education license on request (phone: +49 201 8128-200).

* Plus VAT.
Annual update [1] Euro 150.–; [2] Euro 350.–
The update has to be ordered annually.

Return by fax or in business envelope with window to
VGB PowerTech Service GmbH
Fax No. +49 201 8128-329

Name, First Name

Street

Postal Code City Country

Phone/Fax

Date 1st Signature

Cancellation: This order may be cancelled within 14 days. A notice must be sent to to VGB PowerTech Service GmbH within this period. The deadline will be observed by due mailing. I agree to the terms with my 2nd signature.

Date 2nd Signature