INCREASED FUEL FLEXIBILITY AND PERFORMANCE FOR BOILERS WITH CHALLENGING FUELS

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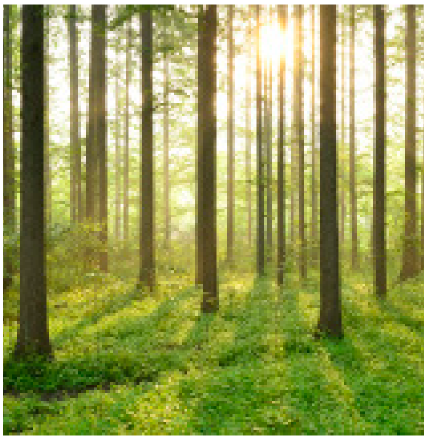
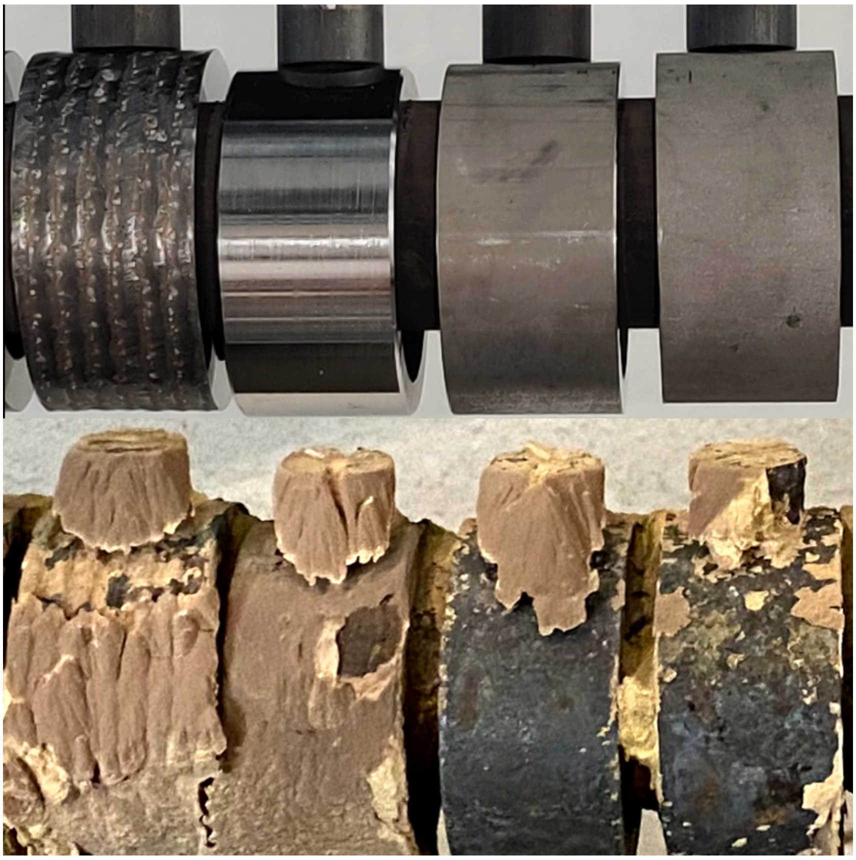


KME
CONSORTIUM MATERIALS TECHNOLOGY
for thermal energy processes



Energiforsk

Increased fuel flexibility and performance for boilers with challenging fuels

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Foreword

The project has been performed within the framework of the materials technology research programme KME, Consortium materials technology for thermal energy processes, period 2018-2023. The consortium is at the forefront of developing material technology to create maximum efficiency for energy conversion of renewable fuels and waste.

KME was established 1997 and is a multi-cliental group of companies over the entire value chain, including stakeholders from the material producers, manufacturers of systems and components for energy conversion and energy industry (utilities), that are interested in materials technology research. The consortium is managed by Energiforsk.

The programme activities are characterised by long term industry and demand driven research, and contribute to the development of thermal energy processes for efficient utilisation of renewable fuels and waste in power and heat production. The KME goals are to bring about cost-effective materials solutions for increased availability and power production, improved fuel flexibility and improved operating flexibility, with low environmental impact.

The specific project has focused on to understand which material challenges are most critical for the operational performance of boilers, and investigated corrosion performance of cooled and uncooled metallic parts as well as the deterioration and corrosion of refractory materials. Rikard Norling, RISE, has been the project leader. Alice Moya Núñez and Melina da Silva, RISE, Thomas Höjer, Calderys, Anna Jonasson, E.ON, and Peter Gewert, Mälarenergi, have been project participants and co-authors of the report. The industry has participated in the project through own investment (60 %) and the Swedish Energy Agency has financed the academic partners (40 %). Participating project partners were RISE, Calderys, Energiforsk, E.ON, Falu Energi & Vatten, Kanthal, MH Engineering, Mälarenergi, Stockholm Exergi, University West, Valmet, and Vattenfall.

Energiforsk would like to thank all the participants for a well performed project.

Bertil Wahlund, Energiforsk

Summary

The KME-802 project ***named Increased fuel flexibility and performance for boilers with challenging fuels*** **has aimed to understand which material challenges are most critical for the operational performance of boilers. To achieve this objective, the corrosion performance of cooled and uncooled metallic parts has been investigated in detail by metallographic evaluation of materials, either retrieved from boilers or from candidate materials exposed to field conditions. The deterioration and corrosion of refractory materials was also addressed as part of the material challenges, by the analysis of samples exposed in boiler and laboratory conditions with respect to the changes in structure or chemistry.**

It is considered that the project has made significant steps towards fulfilling a number of challenging project goals. Some of the more important of these are:

- To obtain new knowledge on how heavy metals in deposits influence corrosion of cooled parts in boilers, that is when exposed to a heat flux causing a temperature gradient.
- To gain an understanding of the corrosion performance and processes related to the use of new or improved coating materials with the purpose of allowing implementation or further improvements.
- To identify, if possible, 1-2 coating candidates that appear to have the potential to improve the life performance by 20 %.
- To identify, if possible, 1-2 refractory material candidates that appear to have the potential to improve the life performance by 20 % or decrease the need of replacements correspondingly.

In particular it is worth highlighting, a field test performed with uncooled specimens, which were done in a boiler inside the manifold duct just before the vertical empty pass where the temperature was approximately 900 °C and the flue gas flow was considered somewhat erosive. It showed that the coating Amdry 510 applied by HVOF had the best behaviour of all the tested materials. Amongst the surpassed tested materials was solid 253 MA, which is a state-of-the-art material for these conditions, as well as alloy 625. Thus, it can be concluded that HVOF applied Amdry 510 coating, which is a new material for this application, has the potential to improve material performance for uncooled parts.

Keywords

Combustion, boiler, corrosion, heavy metals, thermal spray coating, overlay weld, refractory

Förbränning, panna, korrosion, tungmetaller, termiskt sprutad beläggning, påläggssvets, murverk

Sammanfattning

Projektet KME-802 benämnt *Ökad bränsleflexibilitet och driftprestanda för pannor med utmanande bränslen* har syftat till att förstå vilka materialutmaningar som är de mest kritiska för pannors driftprestanda. För att uppnå detta mål har korrosionsprestandan hos kylda och okylda metalldelar undersökts i detalj genom metallografisk utvärdering av material, antingen tagna från pannor eller från kandidatmaterial exponerade för fältförhållanden. Nedbrytning och korrosion av murverk som är en del av materialutmaningarna har också behandlats genom analys av prover exponerade i pann- och laboratorieförhållanden med avseende på förändringar i struktur eller kemi.

Det bedöms att projektet har tagit betydande steg mot att uppfylla ett antal utmanande projektmål. Några av de viktigare av dessa är:

- Erhålla ny kunskap om hur tungmetaller i avlagringar inverkar på korrosionen av kylda delar i pannor, d.v.s. när de utsätts för ett värmeflöde som skapar en temperaturgradient.
- Uppnå en förståelse för hur korrosionsprestanda och -processer relaterade till användningen av nya eller förbättrade beläggningsmaterial med syftet att tillåta implementering eller ytterligare förbättringar.
- Identifiera försåvitt möjligt 1-2 kandidater till beläggningar, vilka förefaller att ha potential att förbättra livslängdsprestandan med 20 %.
- Identifiera försåvitt möjligt 1-2 kandidater till eldfasta material (s.k. murverk), vilka förefaller att ha potential att förbättra livslängdsprestandan med 20 % eller att minska behovet av utbyten motsvarande.

Det är särskilt värt att lyfta fram ett fälttest utfört med okylda prover, som gjordes i en panna inuti kanalen strax före det vertikala tomdraget där temperaturen var cirka 900 °C och gasflödet ansågs vara något erosivt. Resultaten visade att beläggningen Amdry 510 applicerad med HVOF hade det bästa beteendet av alla testade material. Bland de överträffade testade materialen fanns solid 253 MA, som är ett högpresterande material för dessa förhållanden, samt legering 625. Därmed kan man dra slutsatsen att HVOF applicerad Amdry 510-beläggning, som är ett nytt material för denna applikation, har potential att förbättra materialprestanda för okylda delar.

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1 Introduction

Aiming to diminish the effects of anthropogenic climate change, the fossil-fuel reliance must be reduced to a minimum. Alternative fuels such as biomass and waste-based fuels are readily available for firing or gasification purposes, and their use imply a reduced environmental impact compared to fossil fuels. Despite great advantages, the use of biomass or waste-based fuels can lead to elevated corrosion risks, due to the uncontrolled nature of their compositions. Alkali metals and chlorides are often present in these types of fuels, which are known to cause in certain conditions catastrophic damage of boiler components. These materials challenges must be addressed to enhance the performance and ensure the reliability of biomass or waste-fired boilers.

The KME-802 project named *Increased fuel flexibility and performance for boilers with challenging fuels* aims to understand which material challenges are most critical for the operational performance of boilers. To achieve this objective, the corrosion performance of cooled and uncooled metallic parts has been investigated in detail by metallographic evaluation of materials, either retrieved from boilers or from candidate materials exposed to field conditions. The deterioration and corrosion of refractory materials was also addressed as part of the material challenges, by the analysis of samples exposed in boiler and laboratory conditions with respect to the changes in structure or chemistry.

Work Package 1 (WP1): "Challenges and possibilities"

This work package deals with the general understanding of the challenges related to the combustion of fuels containing heavy metals or waste. The project group included different partners that brought their unique experience in boiler performance and operational conditions. The outcome of this work package is a summary of the compiled answers to surveys sent to the partners.

Work Package 2 (WP2): "Performance of cooled metallic parts"

This work package focusses on the cooled furnace metallic parts and how the heat fluxes can exacerbate their deterioration and corrosion in the harsh boiler environment. Deleterious compounds can condense on top of boiler parts, primarily furnace walls and superheaters, due to the temperature gradients, imposing challenging conditions for the metallic materials. In this work package, metallographic investigations were performed in materials exposed to cooled conditions in field exposures, in order to assess the performance of new overlay weld coatings.

Work Package 3 (WP3):" Performance of uncooled metallic parts"

This work package assessed uncooled metallic parts from boilers with respect to their corrosion resistance. These components such as cyclone vortex finder, supports, hangers, plates, refractory anchors and nozzles, habitually exhibit shorter lifespans. The challenges for uncooled parts differ significantly from cooled parts (WP2), not only by the fact that materials are exposed to higher temperatures but also through the effect in the condensation of deleterious species in the flue gas. This work package aims to gain understanding of the corrosion behaviour of such components, including a metallographic investigation of retrieved samples from boiler systems and the assessment of the performance of new advanced coating materials for high temperature applications.

Work Package 4 (WP4): "Refractories"

Refractory materials in boiler applications with challenging fuels tend to have limited lifetimes, which has been related to the presence of heavy metals, alkali metals, and chlorides in the flue gas. This work package deals with the deterioration of refractory materials due to heavy metals, with focus in potential structural and chemical changes. The investigation included the use of non-destructive chemical analysis on site, as well as the microstructural analysis of field specimens. Lastly, cup tests were performed to investigate the corrosion of selected refractory materials to chemical reactive slags.

Work Package 5 (WP5): "Excellence in performance"

An overarching aim of this project is to understand which material challenges are most critical towards increased fuel flexibility and operational performance of boilers with challenging fuels. It is also aimed to find ways to handle these. The possibility of overcoming several of the challenges requires materials with improved capabilities to withstand erosion-corrosion. Field tests with new metallic coating materials and refractories provide information of which materials have potential to significantly improve material performance. An important design question in boilers is whether to put refractory on the upper parts of the water walls of the furnace and some following flue gas paths with high gas temperature. Investigating both metallic coating materials and refractories in the same project provides a unique insight into this choice. As a whole it provides opportunities to achieve excellence in performance.

Work Package 6 (WP6): "Co-operation and communication"

A vital part of the project is the communication of industrial needs to the academic researchers and the dissemination of results from the researchers back to industry. The purpose of this work package is to ensure efficient co-operation and results dissemination, collaboration and continuous knowledge exchange between the academia, institutes, and the industry stakeholders, in different stages of the value chain.

2 WP1 – Challenges and possibilities

2.1 INTRODUCTION TO WP1

In the scope of KME 802 work-package 1 "Challenges and possibilities" surveys were sent out to the boiler owners involved in the project. Questions were asked about the normal functioning of the boiler, the materials used inside the boilers and reported frequent corrosion and erosion problems. The survey was divided into several categories: general information about boiler (materials, fuel, placement of superheaters, gas temperature, etc); typical lifespan, corrosion rate and damage of the different components; typical appearance and spread of damages and corrosion; breakdowns and other types of issues. The aim was to identify common challenges but also differences to share the experiences and knowledge.

List of boiler owners or sites involved in investigation:

- Vattenfall Jordbro
- E.ON Händelö P14, P15
- Mälarenergi Västerås P5, P6, P7
- Stockholm Exergi Värtaverket

Table 1 shows a list of the details regarding the sites involved in the investigation.

Table 1 List of sites involved in the investigation.

Boiler	Type	Manufacturer, Year	Thermal effect (MW)	Superheater (min-max gas temperature at SH in flue gas path), sootblowing type	Empty pass, sootblowing type	Refractory
Jordbro	Bio fuel, BFB	Valmet, 2009	65	2 superheaters (460-760°C), steam	Yes, water	Calderys
Händelö, P14	Waste-to-energy, CFB	Kvaerner Power, 2002	75	3 superheaters (345-580°C), steam	Yes, water	Calderys
Händelö, P15	Waste-to-energy, CFB	Foster Wheeler, 2010	85	3 superheaters (350-690°C), *slag*	Yes, water	Calderys
ME Västerås, P5	Bio fuel, CFB	Foster Wheeler, 2000	180	3 superheaters (585-738°C), steam	No	Calderys
ME Västerås, P6	Waste-to-energy, CFB	Valmet, 2014	160	3 superheaters (360-560 °C), steam	Yes, water	Calderys
ME Västerås, P7	Bio fuel, CFB	Sumitomo Foster Wheeler, 2019	150	3 superheaters (523-724°C), steam	No	Calderys
Värtaverket, P8	Bio fuel, CFB	Andritz, 2016	345	3 superheaters (530-920°C), steam	No	Junger+Gräter

BFB: bubbling fluidised bed, CFB: circular fluidised bed.

2.2 COMMON CHALLENGES IDENTIFIED

2.2.1 Furnace

Refractory materials are often replaced inside the furnace at each revision stop, however none of the boiler owner report major replacements but rather small pieces which have detached from the walls or cracks. Maintenance of the refractory around fuel intakes occurs more often than the rest of the chamber (P15). The material detachments are often related to severe degradation of studding (refractory anchor) material (P6, P15, Jordbro).

Figure 1 Examples of corroded studdings in a detached piece from P6 chamber roof.

Vattenfall has observed issues with attachment of new refractory materials when the temperature rise is too high at the gas turning point at the bottom of the empty pass, then refractory materials are likely to detach.

Some parts of the chamber have Inconel 625 overlay-weld, for example Mälarenergi P7 3 m of the wall from “kick-out” is covered and about 90 m^2 in P6, the rest of the walls are covered with Calderys refractory materials. In P6 the refractory materials on the roof were removed due to corroded studdings (see Figure 1) and replaced with ChromeClad and Tube Armor, and the edges were covered with refractory materials. E.ON has also used 625 as base material or overlay for exposed tubes, until the tubes were integrated to the walls. The observed corrosion and erosion problems for the tubes were considerably reduced after the modification. In Värtaverket, eroded tubes close to edges have been coated with NiCrMo-3 (alloy 625). In Jordbro, Inconel 625 as overlay weld is used since 2018 on 16Mo3 screen tubes before the empty pass where the erosion is high. For P15 tube shields are used on the screen tubes before the empty pass.

2.2.2 Cyclones

Erosion problems on the refractory materials for the cyclone inlets were observed for waste-to-energy boilers Händelö P15, Händelö P14 and Mälarenergi P6. This leads to smaller repairs every year in P15. Replacements of refractory occur in Händelö P14 every 3 years. Erosion problems in cyclones around the target zones have been reported in Värtaverket P8 and lead to yearly replacements of the refractory materials. Erosion attack was visible in Mälarenergi P6 after 6 years; 20-25 mm of material has eroded. Full replacement was done in Mälarenergi P6 after 7 years under the 2021 revision. Figure 2 shows example of material damage in cyclones.

Figure 2 Material damage in cyclones. Left: P15 vortex finder (after undisclosed operation time). Right: P6 cyclone target area (after 6 years operation time).

2.2.3 Superheater tubes and tube shields

Leaks in the tubes is the most common reason for unscheduled stop in the boilers. Some of the leaks have been recently observed in the superheaters (P15) or close to the cyclone (Värtaverket). The leaks are caused by erosion and corrosion of tubes. Maintenance of the tubes and tube sheets for the superheaters include overlay welds, removal of slag and replacement of tube shields (every 2 years in P14). The corrosion rates of tubes and tubes shields have been considerably reduced with ChlorOut additions in Jordbro boiler (see Figure 3).

Figure 3 Corroded and eroded tubes with tube shield in P15 (left), SH3 in P14 (middle) and SH2 with ChlorOut additions in Jordbro.

2.2.4 Sooting techniques

Soot blowers are affecting the material lifespan of the boiler and causing some of the erosion, however, is necessary for thermal transfer and to avoid clogging. The frequency of the steam sooting procedures is continuously discussed at E.ON to find the proper balance between thermal effect and material degradation.

The slag issues can be solved by water sooting close to screen tubes and further down in the incineration chamber. This is done for example at Jordbro, where the risk for wet ash and clogging is also monitored when water sooting is used.

In for example Jordbro boiler, explosion cleaning is applied in incineration chamber, empty pass and superheater under maintenance stop and there is a risk for refractory material to detach.

2.2.5 Changes in fuel humidity

E.ON has observed that the waste fuel is less and less humid, most probably due to better waste sorting and reduction of bio-waste and plastic materials in the fuel. The calorific heat value of the fuel has therefore increased. This resulted in changes of refractory materials and usage of SiC based refractories to ensure heat exchange with the tube walls. One alternative is water spraying on the fuel but has not been implemented in the boiler.

The changes in the waste fuel, in particular reduction of plastic waste in the fuel was also confirmed by Stockholm Exergi.

2.3 SUMMARY OF WP1 AND FUTURE RESEARCH POSSIBILITIES

In this study, information about challenges for seven different boilers have been collected. Five types of challenges have been identified: studding materials for attachment of refractory materials in the furnace, erosion patterns of refractory materials in cyclone, erosion and corrosion of tube and tubes shields in superheater, sooting strategies and changing in the waste fuel composition and humidity which affects the incineration of the fuel.

These observations are an opportunity for new research topics for long-term tackling of these identified challenges. For refractories and studding materials, investigation of different materials could be carried out to find some with better corrosion resistance and avoid detachment of refractories. For the refractories themselves, erosion resistant refractories could be investigated and placed inside boilers where the erosion is more pronounced. Different sooting techniques are available and used by boiler owners to balance functioning of the boiler by removal of slag and limiting the erosion and corrosion of the materials. Here different strategies for different part of the boiler could be investigated and what is the impact on corrosion and erosion resistance could be evaluated. Finally, changes in the fuel composition due to changes in our society could be further investigated together with material testing. Predictions on how fuel will evolve and what will be the impact on the functioning of boilers could be made and help future development of boilers.

The reflexions and suggestions that were acquired in this WP have been valuable input to the other work packages and been considered during planning and execution of these when applicable.

3 WP2 – Performance of cooled metallic parts

3.1 INTRODUCTION TO WP2

The main objective of this work package was to obtain new knowledge on how heavy metals in deposits might influence the corrosion of cooled parts in boilers. The cooled parts are exposed to a heat flux during operation, which in turn induces a temperature gradient that might affect the way detrimental substances condense and deposit. These effects might enhance the degradation of cooled or semi-cooled parts in the boiler. It is important to note the inherent difficulty of replicating the transient conditions of the boiler in laboratory exposures, therefore field exposures and their assessment were prioritized in this WP.

WP1 interviews pointed to different issues that were in part investigated further in this work package. A tube shield investigation regarding the corrosion resistance of overlay welds was also performed within this WP, related to the project HÖG-FECRALCLAD *Svetsbarhet och korrosionbeständinghet av nya FeCrAl-legeringar (funded by Stiftelsen för Kunskaps och Kompetensutveckling)*. The shields aim is to increase the lifetime of tubes that are exposed to a temperature gradient and harsh conditions from the flue gas, including corrosion by alkali metals and erosion from particles entrained in the gas. Metallographic investigations were carried out in order to evaluate the behaviour of selected materials exposed to boiler conditions.

3.2 MÄLARENERGI P6 – DEPOSITS

In an effort to gain knowledge from the common failure cases investigated in WP1, the boiler P6 at Mälarenergi was selected to collect deposits or oxide flakes to be characterized through a metallographic assessment.

At the waste-fired plant designated Mälarenergi P6 some deposits were collected from the waterwalls. A cross section of one deposit was analysed using SEM/EDS (see Figure 4 and Figure 5). The inner side of the deposit (not exposed to flue gas) shows iron oxides and elevated concentrations of Cl and Zn. The outer side of the deposit (exposed to flue gas) indicates much higher concentrations of Pb.

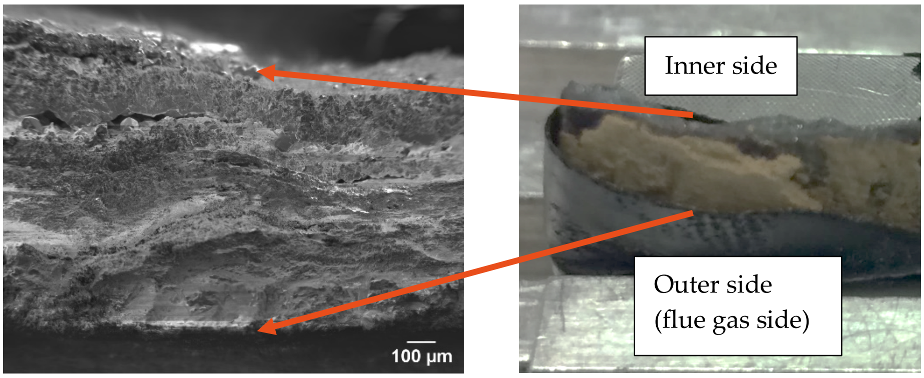

Figure 4 SEM image of cross section of deposit collected from boiler P6 at Mälarenergi (left) and its corresponding photograph showing the inner side of the deposit and the outer side (exposed to flue gas).

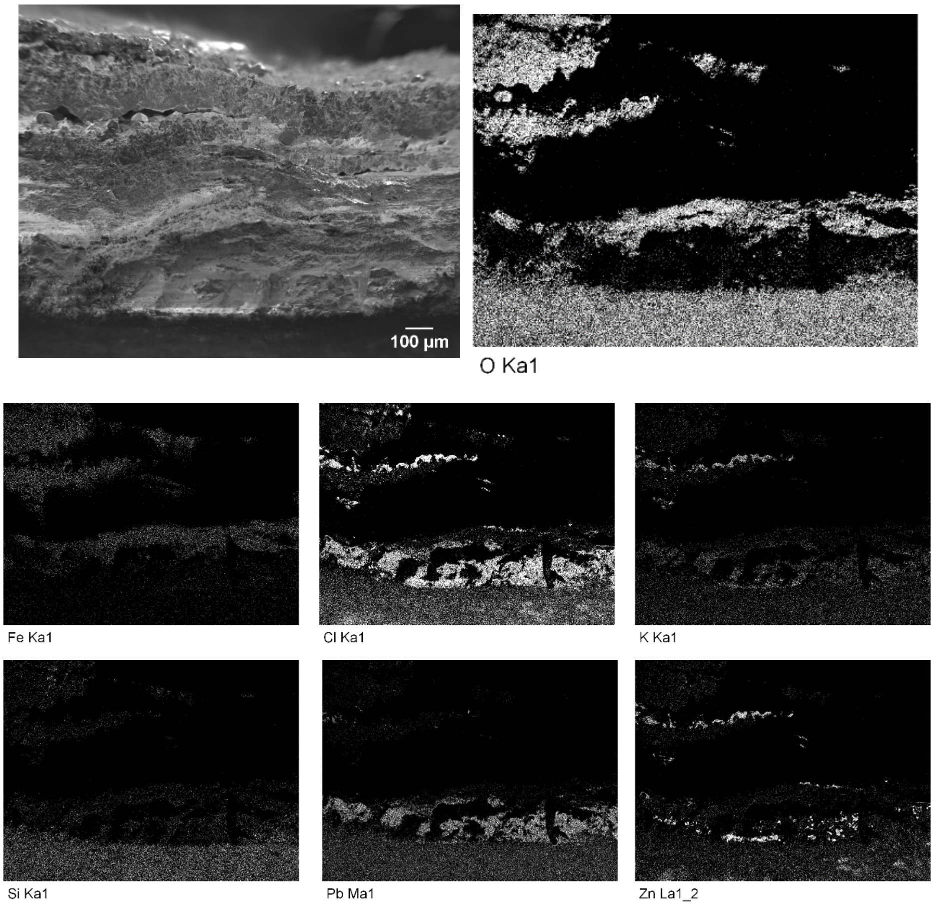

Figure 5 SEM image and its corresponding elemental maps (EDS) of deposit collected from boiler P6 at Mälarenergi (empty pass). Upper side corresponds to the inner side of the deposit/scale, while the bottom side is the outer side that was exposed to flue gas. O, Fe, Cl, K, Si, Pb and Zn maps are depicted. The maps of Pb and Na are indicative only, since the signals overlap with S and Na, respectively.

3.3 FECRALCLAD PROJECT – EVALUATION OF TUBE SHIELDS

Tube shields placed in the evaporator bank were cladded with different alloys and exposed for six months in a waste-fired plant, designated as Händelö P14 E.ON utility in Norrköping, Sweden. The assessed exposure corresponds to the 4th exposure pertaining to the coupled project HÖG-FECRALCLAD (*Svetsbarhet och korrosionbeständinghet av nya FeCrAl-legeringar)*, funded by KK-stiftelsen. Details of the boiler are given in Section 5.2.

The cladding was applied to eight tube shields that were installed in the evaporator bank, at the level designated as 5+, just below the secondary superheater. Four tube shields were placed in the area denominated "floor" and the remaining four in the "roof" area. These designations are arbitrary and, in this case, correspond to the relative position in the chamber, viewed from the manhole (see Figure 6). The gas flows from bottom to top in this position (from *floor* to *roof*). Flue gas temperature measured at the secondary superheaters corresponds to 606 ± 40° C, while water at saturation temperature in the evaporator bank at this position is approximately 281 °C.

Figure 6 Manhole view at level +5 (evaporator bank) in the boiler Händelö P14. The top row of tubes corresponds to the "roof" position, while the bottom row is the "floor" position.

Table 2 Summary of the exposed materials and their relative positions inside the evaporator bank. The substrate material for all the tube shields corresponds to a low-alloyed steel grade EN 10028 16Mo3.

Convection bank 1 ("roof")	Cladding alloy
Tube #12	Sanicro 60
Tube #13	L197
Tube #18	Kanthal® APMT
Tube #21	L198

Convection bank 2 ("floor")	Cladding alloy
Tube #6	Sanicro 60
Tube #7	L198
Tube #8	L197
Tube #9	Kanthal® APMT

The tube shields were cladded using a welding (mechanized gas metal arc welding) procedure explained in detail elsewhere[1]. The substrate corresponds to a low-alloyed steel grade EN 10028 16Mo3, which is typical for this kind of application. Three FeCrAl alloys by Kanthal® containing rare earth elements were chosen as candidate materials, including Kanthal® APMT™, L197 and L198. Additionally, a nickel-based alloy Sanicro 60 (a variant of alloy 625) was chosen as reference material. See Table 6 for exposure positions of each material.

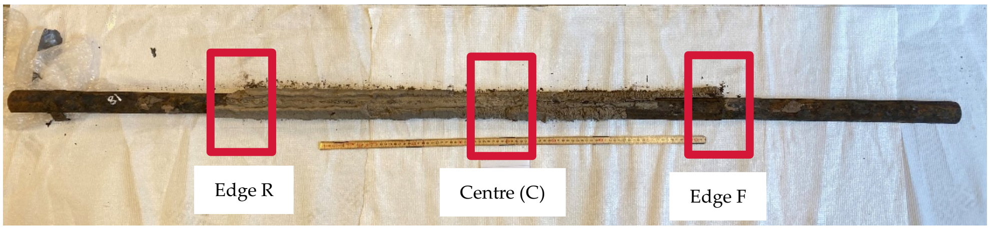

Figure 7 One of the cladded tubes corresponding to the project FECRALCLAD (exposure #4), exposed for 6 months in the boiler Händelö P14. The middle zone of each tube was cladded with the candidate materials by mechanized gas metal arc welding. After exposure, cross sections of three areas of the cladded section of the tubes were carefully removed for examination. The edge "R" corresponds to the end of the tube oriented towards the rear-wall of the boiler, while the edge "F" is towards the front-wall.

After retrieval from the P14 boiler, the cladded tube shields were cut into cross sections for further examination. The area of the remaining cladding material was measured using a standard image software (ImageJ). From these values and from the original cladding thickness, a thickness loss was determined. Then, the results were extrapolated to a yearly basis, as a corrosion rate or metal loss for each examined tube shield. Figure 8 shows an example of a cross section with the remaining cladding area in dashed lines, the substrate material for each specimen was also measured in the same manner. Figure 9 and Figure 10 show the normalised corrosion rate or loss of material of the overlay clad for all the tube shields (*floor* and *roof* positions), with respect to the largest value. Generally, tube shields located in the *roof* position exhibited a higher coating loss rate than the ones at the *floor* position, which could be explained by the gas direction, carrying particles that can enhance the erosion rate of the coatings. Figure 11 and Figure 12 show the normalised corrosion rate or metal loss of the substrate material for all the tube shields, indicating a considerable difference as well between the roof and floor positions.

Overall, the APMT alloy showed a consistent metal loss rate in both positions, as well across the edge and centre sections of the tube. Sanicro 60 exhibited an appreciable metal loss rate in one of the roof specimens (edge R), in comparison to the almost negligible value of its corresponding edge F. A possible explanation is local inhomogeneities in the exposure environment, causing considerable local differences in the corrosion/erosion regime. The other FeCrAl alloys performed similar with respect to each other in terms of metal loss rate, including an increased rate in the centre sections of the tube at the *floor* position. The weld

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[1] M.A. Valiente-Bermejo et al. (2022) *Metal loss and corrosion attack of FeCrAl overlay welds on evaporator tube shields of a waste-fired power plant*. (To be submitted for publication in a scientific journal.)

overlay materials can be ranked from best to worse corrosion-erosion resistance with respect to metal loss as follow: APMT ≈ Sanicro 60 > L197 ≈ L198.

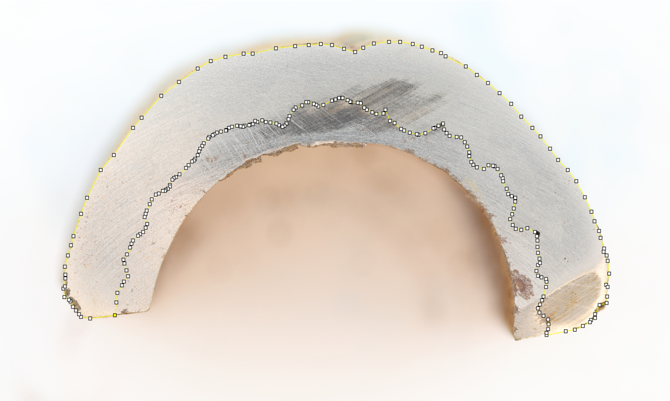

Figure 8 Example of cross section from the edge F area of a cladded tube. The dashed area in the picture corresponds to the remaining cladding.

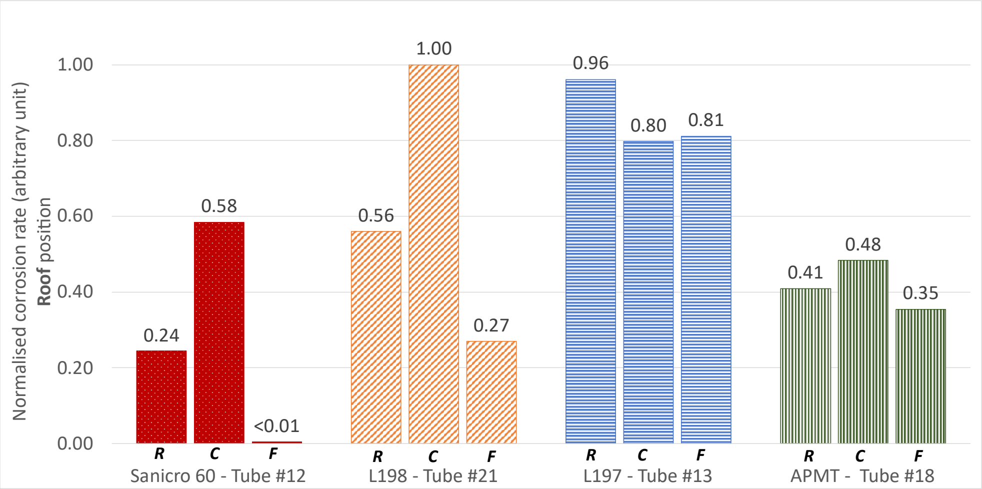

Figure 9 Normalised corrosion rate or metal loss of overlay welds in arbitrary units corresponding to the "*roof*" position described in Figure 6. Sanicro 60, L198, L197 and Kanthal® APMT cladding materials were included in the assessment. The plot shows the corrosion rate of three areas of each tube shield (edge R, edge F and C).

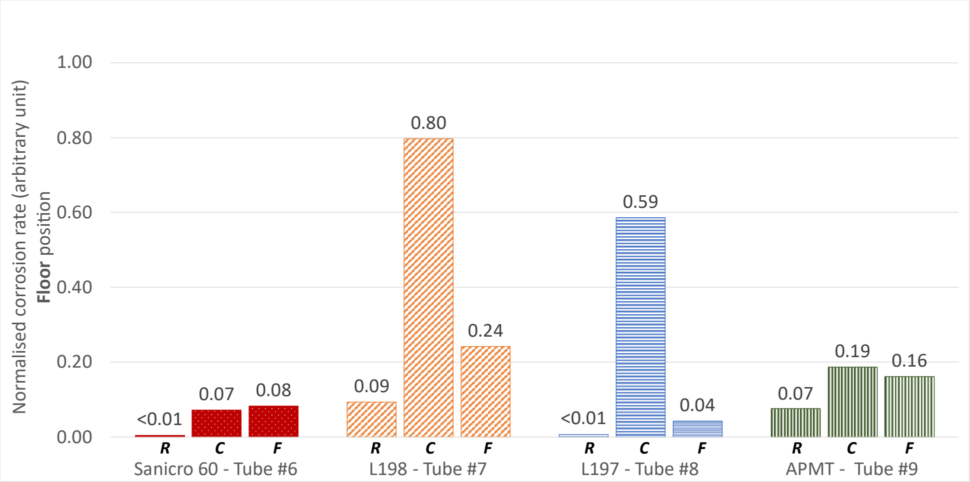

Figure 10 Normalised corrosion rate or metal loss of overlay welds in arbitrary units corresponding to the "*floor*" position described in Figure 6. Sanicro 60, L198, L197 and Kanthal® APMT cladding materials were included in the assessment. The plot shows the corrosion rate of three areas of each tube shield (edge R, edge F and C).

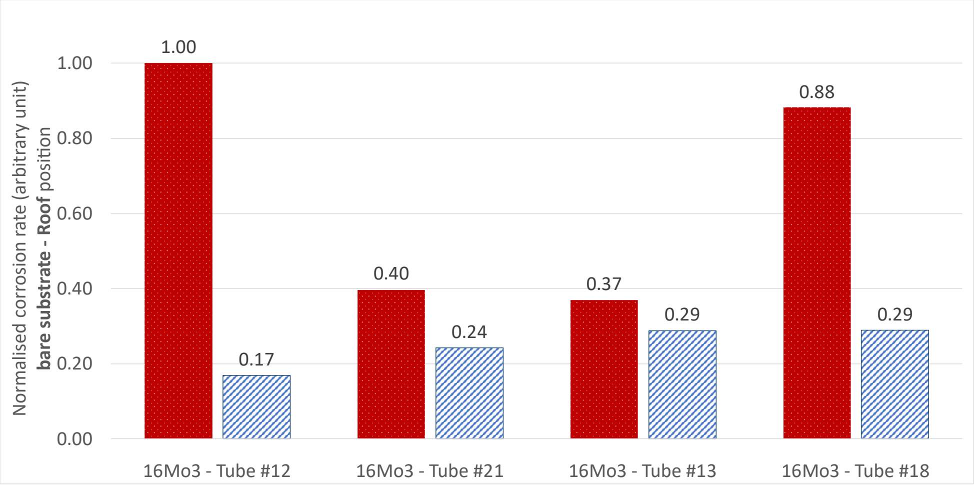

Figure 11 Normalised corrosion rate or metal loss of the bare substrate material (16Mo3) in arbitrary units corresponding to the "*roof*" position described in Figure 6. The plot shows the corrosion rate of the two ends of each tube shield (edge R and edge F) at a position without overlay weld.

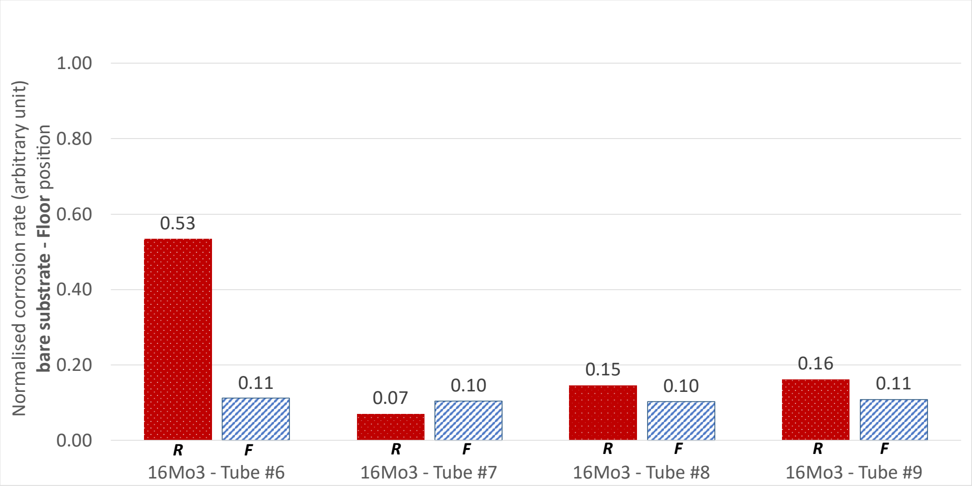

Figure 12 Normalised corrosion rate or metal loss of the bare substrate material (16Mo3) in arbitrary units corresponding to the "*floor*" position described in Figure 6. The plot shows the corrosion rate of the two ends of each tube shield (edge R and edge F) at a position without overlay weld.

The dispersion of the results and the seeming inconsistencies (for example the difference shown by Sanicro 60 roof position between the sides and the centre of the tube), are indicatives of several phenomena not only inside the complex boiler environment, but as well of the challenges during the welding process of the clads.

Figure 13 shows SEM images of typical corrosion attacks for the exposed specimens at the *floor* position. L198 exhibits a corrosion pattern attack along grain boundaries with Cl signal showing deep into the attack. In contrast, L197 shows more defined pits filled with corrosion products containing Al, Cr and Fe oxides, as well as a thin silicon-based oxide layer enveloping the pits. The Cl signal is also visible in this specimen and, given its location, it suggests the formation of metal chlorides and the eventual disruption of an oxide scale. APMT exhibited in general a more uniform corrosion attack, although with some evidence of grain boundary corrosion. Sanicro 60 showed a layered corrosion attack, with primarily a Cr-rich oxide layer in the metallic interface followed by a Ni-rich scale that has been mixed with the deposit. A weak Cl signal is shown cross the metallic interface, strengthening in the upper scale, although no strong evidence that would suggest the formation of metallic chlorides was seen for alloy Sanicro 60.

Further details of this investigation are intended to be published in an article in a scientific journal[1].

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[1] M.A. Valiente-Bermejo et al. (2022) *Metal loss and corrosion attack of FeCrAl overlay welds on evaporator tube shields of a waste-fired power plant*. (To be submitted for publication in a scientific journal.)

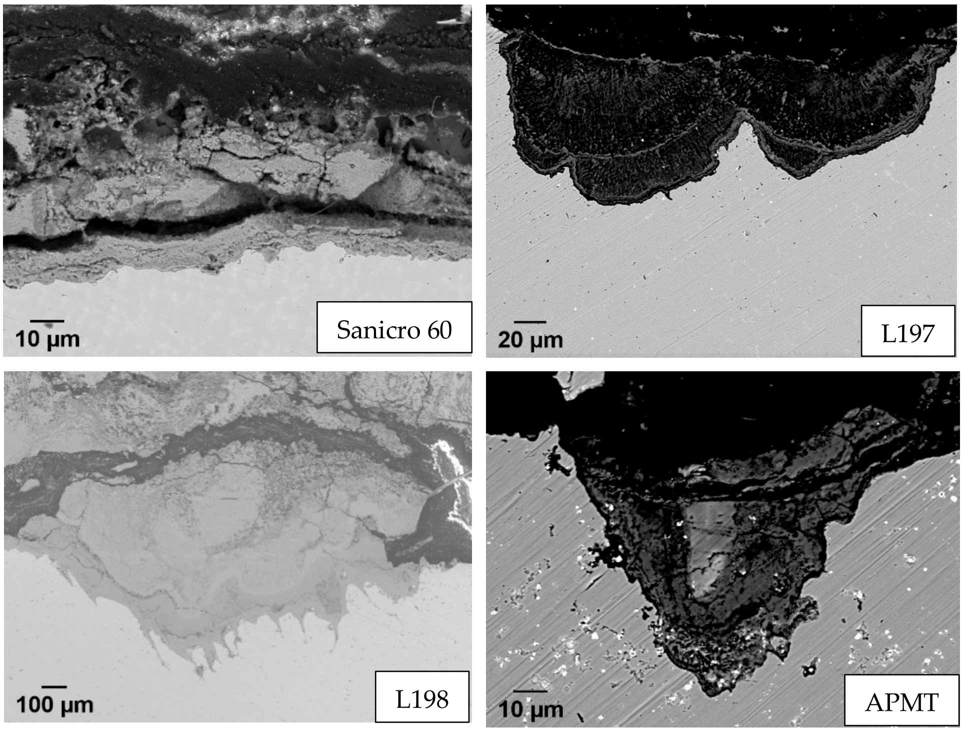


Figure 13 SEM images of the typical corrosion attack morphology exhibited by the overlay weld materials for tube shields after a 6-month exposure in a waste-fired plant.

3.4 CONCLUSIONS WP2

Cooled metallic parts inside boiler system can exhibit extended corrosion attack due to the harsh conditions exacerbated by the imposed temperature gradients. The condensation and deposit of deleterious species, such as alkali metals, will be in part affected by these temperature gradients, therefore new knowledge is required to understand the intertwined mechanisms occurring simultaneously and, in some cases, synergistically. Laboratory exposures to study these phenomena are limited in nature as they cannot replicate accurately all the different variables at hand. Thus, the study of samples retrieved from actual boiler systems, or the field exposure of candidate materials has been chosen to fulfil the objectives of this WP.

A flake was retrieved from the empty pass at Mälarenergi P6 boiler and analysed using SEM/EDS. The results indicate elevated concentrations of Cl, Zn and Pb, as well as the formation of iron-containing oxides.

The field exposure within the HÖG-FECRACLAD project had as an objective to rank candidate FeCrAl alloys with respect to their corrosion-erosion resistance as overlay welds. Sanicro 60 was included as a reference material. These welds were applied to tube shields manufactured from low alloyed steel and exposed during a 6-month period at the evaporator bank in Händelö P14. The metallographic investigation resulted in a materials ranking, considering the overall metal loss (or corrosion-erosion rate) as well as the presence of intergranular corrosion in L198, as follows: Kanthal® APMT ≈ Sanicro 60 > L197 > L198.

4 WP3 – Performance of uncooled metallic parts

4.1 INTRODUCTION TO WP3

The main objective of this work package was to obtain new knowledge and find targeted solutions, by analysing issues identified in WP1, corresponding to uncooled metallic parts of boilers. Many components other than tubing, and that are mostly uncooled, such as cyclone vortex finder, supports, hangers, plates, refractory anchors, and nozzles, frequently experience short life. Being uncooled these parts operate at a high temperatures giving intrinsically different challenges compared to cooled parts, as for example condensed phases in the deposits are expected to be different. It can be noted that air nozzles are somewhat cooled by the air passing through them.

Figure 14 shows a schematic of the positions relative to the boilers where specimens were retrieved for further analysis. Additionally, WP3 should gain new knowledge with respect to the corrosion performance of coatings candidates with the purpose of allowing implementation or further improvements. Metallographic investigations were carried out in order to evaluate the behaviour of selected materials exposed to boiler conditions.

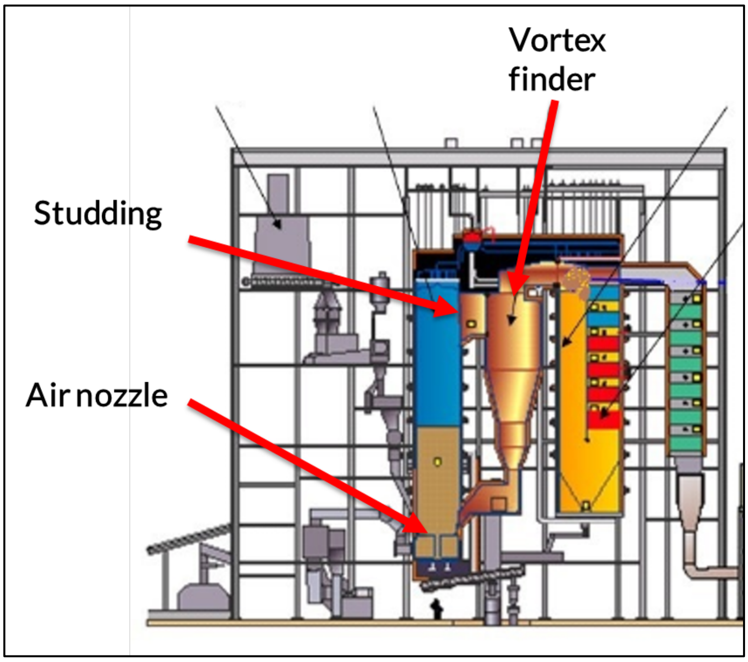


Figure 14 WP3 investigation comprised of specimens retrieved from boilers Händelö P14 and Mälarenergi P6, at the indicated positions (vortex finder, studding, air nozzle).

4.2 HÄNDELÖ P14 – SAMPLES

4.2.1 Studding from the cyclone inlet

Figure 15 shows a piece of studding (refractory anchor) from the boiler Händelö P14, retrieved from the cyclone inlet. The composition of the corrosion products and deposits in the specimen was analysed using SEM/EDS. The encircled area in the right-most picture of Figure 15 shows where the analysis was attempted. Figure 16 and Table 3 show the corresponding SEM image and chemical analysis results. The specimen exhibited low conductivity which resulted in high uncertainty, which is related to its composition, indicating that extensive corrosion has occurred. The composition suggests the presence of iron-based oxides and segregated areas containing Na, S and Ca.

Figure 15 Retrieved studding from boiler Händelö P14. The encircled area corresponds to the chemical analysis shown in Table 3.

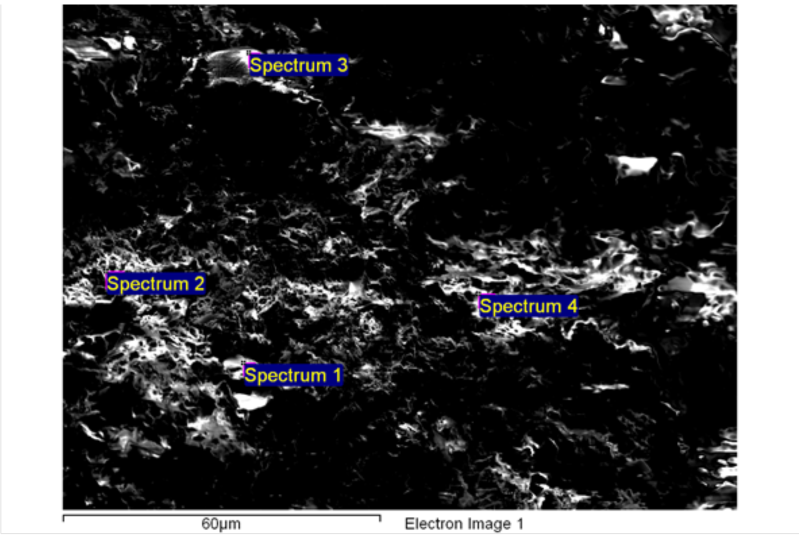


Figure 16 EDS map corresponding to the encircled section in Figure 15. Table 3 shows the corresponding results in weight %.

Table 3 Semi quantitative chemical composition in weight % of spectra in Figure 16.

Spectrum	O	Na	Al	Si	S	K	Ca	Fe	Ni
1	30.30	5.32	0.81	1.10	3.40			39.44	19.64
2	31.73	5.81	0.36	0.71	3.49	0.95	0.96	37.54	18.45
3	23.76	2.76	0.88	0.85	21.24	7.00	26.76	13.30	3.45
4	27.25	0.79	0.28		0.58			46.74	24.37

4.2.2 Cyclone vortex finder

Figure 17 shows the localization at the cyclone vortex finder of Händelö P14 boiler system, where flakes were collected to inspect using SEM/EDS. The examined flake is shown in Figure 18 and exhibits extensive corrosion. The EDS results in Table 4 show localized chromium-containing oxides (Spectrum 1) and the widespread presence of iron-containing oxides.

Figure 17 Cyclone vortex finder in Händelö P14 boiler. Flakes from this area were retrieved for SEM/EDS analysis.

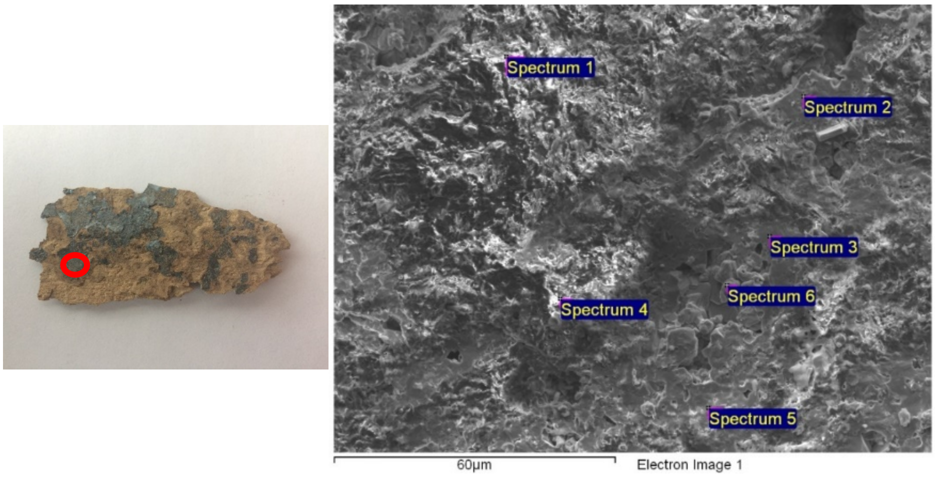


Figure 18 Flake retrieved from the cyclone vortex finder in the Händelö P14 boiler system. The circle in the left picture indicates the analysed area by SEM/EDS. The rightmost SEM (secondary electrons) image indicates the EDS point analyses (Spectrum 1 to 6) showed in Table 4.

Table 4 Semi quantitative chemical composition in weight % of spectra in Figure 18

Spectrum	C	O	Na	Mg	Si	Ca	Cr	Mn	Fe	Ni	Zn
1	0.72	41.31			10.20		47.77				
2	0.72	35.23			0.22		40.60		21.73	1.50	
3	1.18	43.24		0.24	3.78		0.00	0.00	34.13	15.68	1.75
4		45.45			8.32		26.35		14.99	4.89	
5	0.85	38.32	0.41		1.60	1.07	17.80		24.50	15.44	
6	0.95	25.04	0.46		0.47		16.41		34.31	22.35	

4.2.3 Primary air nozzles

A primary air nozzle was retrieved from Händelö P14 boiler system. The top of the injector was cross sectioned to be investigated using SEM/EDS analysis (Figure 19). The results in Figure 20 and the corresponding Table 5 show extensive corrosion attack, including an area containing high concentrations of Pb (Spectrum 1). Figure 21 shows an EDS analysis done in a neighbouring area (Table 6), exhibiting a high concentration of Al and Zn in what appears to be an inclusion (Spectrum 1 and 2), potentially corresponding to a metallic AlZnSi.

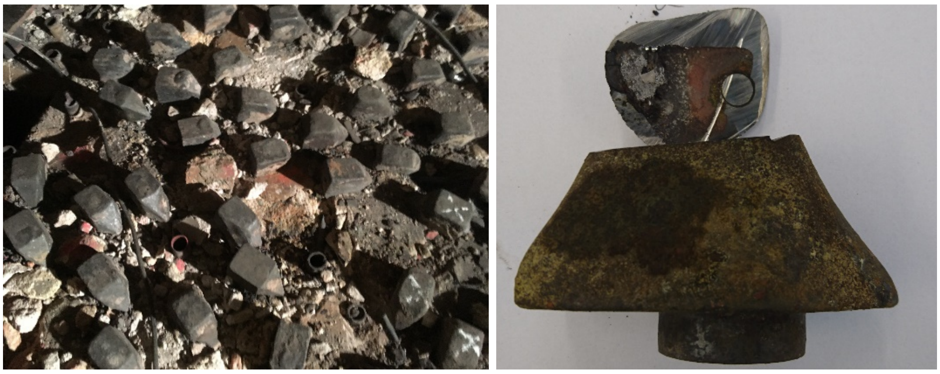


Figure 19 The image to the left shows an arrangement of primary air injectors. The image to the right corresponds to one primary air nozzle specimen collected from the Händelö P14 boiler system. The top part of the nozzle was cross sectioned for further investigation.

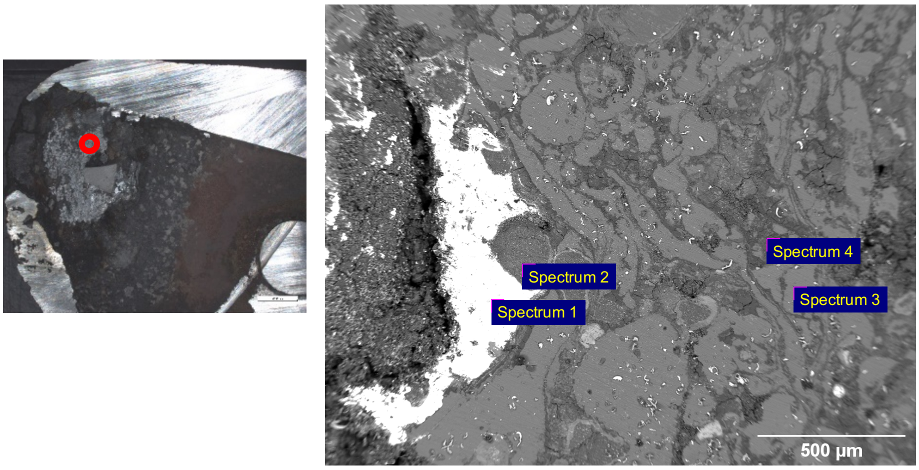


Figure 20 The left image shows a cross section of retrieved primary air nozzle. The encircled area was investigated using SEM/EDS. The rightmost image is the secondary electron SEM image with point analysis (Spectrum 1 to 4) shown in Table 5.

Table 5 Semi quantitative chemical composition in weight % of spectra in Figure 20.

Spectrum	C	O	Na	Al	Si	Cl	K	Ca	Mn	Fe	Zn	Pb
1		5.82		0.55		0.57				1.81		91.25
2	2.90	54.40		1.09	40.48	0.30		0.13		0.27	0.43	
3		2.46		95.53	0.36					0.89	0.76	
4		47.60	3.56	42.42	0.41	1.14	0.66	0.16	1.16	1.02	1.87	

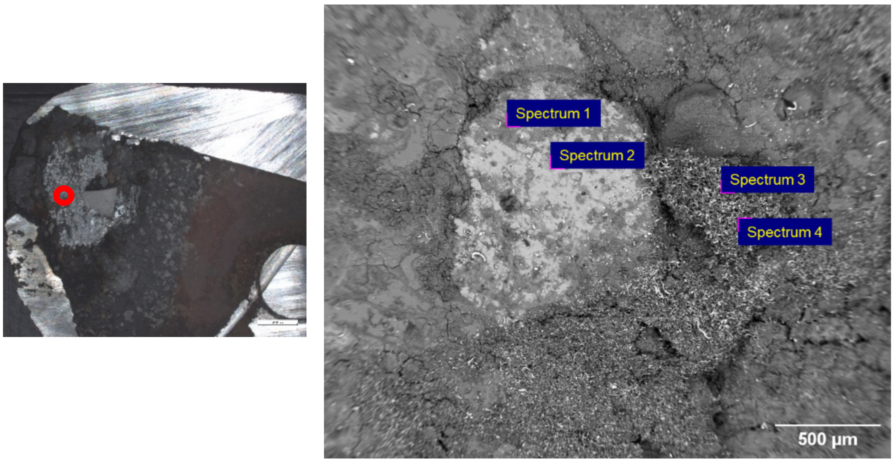


Figure 21 The left image shows a cross section of retrieved primary air nozzle. The encircled area was investigated using SEM/EDS. The rightmost image is the secondary electron SEM image with point analysis (Spectrum 1 to 4) shown in Table 6.

Table 6 Semi quantitative chemical composition in weight % of spectra in Figure 21.

Sp.	C	O	Na	Al	Si	Cl	K	Ca	Cr	Mn	Fe	Ni	Cu	Zn	Mo
1	3.97	43.64		28.86	0.21	0.57	1.37	0.38			0.30		1.11	19.60	
2		8.71		51.98	4.10	3.23				1.54	3.65		0.94	25.85	
3	5.72	6.45	0.46	9.54	10.37			0.74	13.06	1.02	44.65	6.63			1.36
4	9.31	9.10		14.66	7.72	0.27		0.82	11.17	0.84	38.46	6.25			1.41

4.3 MÄLARENERGI P6 – SAMPLES

4.3.1 Cyclone vortex finder I

A specimen from the cyclone vortex finder at Mälarenergi P6 was analysed using SEM/EDS. A cross section of the specimen was mounted in conductive bakelite for analysis and prepared using common metallographic techniques. The vortex finder has been manufactured from 253 MA alloy. Two areas of the cross section were investigated, including the bulk of the specimen.

The results show severe corrosion in the specimen that is likely to be spreading between grain boundaries. Figure 22 shows the cross section of the investigated specimen. Figure 23 shows the corresponding SEM image of the upper area marked by a red circle in Figure 22. The chemical analysis (weight %) is shown in Table 7. The results show clear corrosion products in Spectrum 1 and 2, primarily containing various amounts of Cr, Fe and Ni. The bulk of the material was also investigated using point analysis (see Figure 24), revealing nitriding to a considerable depth of the specimen (spectra 3 and 4 from Table 8).

Figure 22 Specimen corresponding to the cyclone vortex finder (from Mälarenergi P6). The specimen was cut in half upon reception. The cross section was mounted in conductive bakelite (left part of the image) to be analysed using SEM/EDS. The red circle corresponds to the EDS analysed area shown in Figure 23. The bulk of the metal was also analysed using EDS.

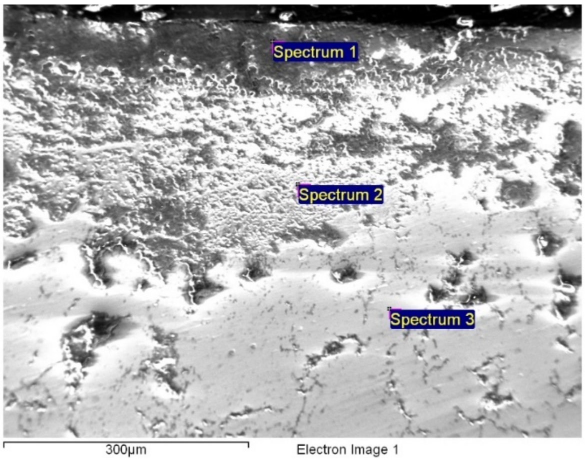


Figure 23 SEM image of upper side of the specimen cyclone vortex finder, retrieved from Mälarenergi P6.

Table 7 Semi quantitative chemical composition in weight % of spectra corresponding to Figure 23.

Spectrum	C	O	Si	Cr	Fe	Ni
1	1.85	33.63	1.08	44.59	13.03	5.81
2	1.54	19.33	0.39	20.02	43.38	15.33
3	0.81	0.57	0.46	11.81	64.53	21.82

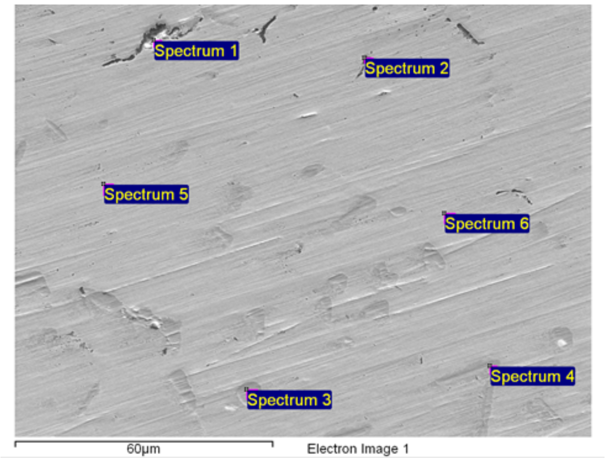


Figure 24 SEM image of bulk material of the cyclone vortex finder sample, retrieved from Mälarenergi P6.

Table 8 Semi quantitative chemical composition in weight % of spectra corresponding to Figure 24 (bulk of the material).

Spectrum	C	N	O	Si	V	Cr	Fe	Ni
1	3.48		31.74	24.95		0.00	33.61	6.23
2	1.55		37.48	30.98		0.00	24.66	5.34
3	0.96	8.44			1.64	83.58	5.38	
4	1.09	8.74			1.15	84.64	4.38	
5	0.70		0.92	1.23		18.44	64.01	14.70
6	0.60		1.23	1.01		15.24	65.86	16.06

4.3.2 Cyclone vortex finder II

A vortex finder at Mälarenergi P6 boiler had to be exchanged due to wear. A piece was cut from the damaged part and analysed by SEM-EDS (see Figure 25). The SEM image with the corresponding EDS analysis is shown in Figure 26 and Table 9. The results show the formation of a chromium oxide layer (Spectrum 3) and evidence of chromium depletion in Spectrum 4.

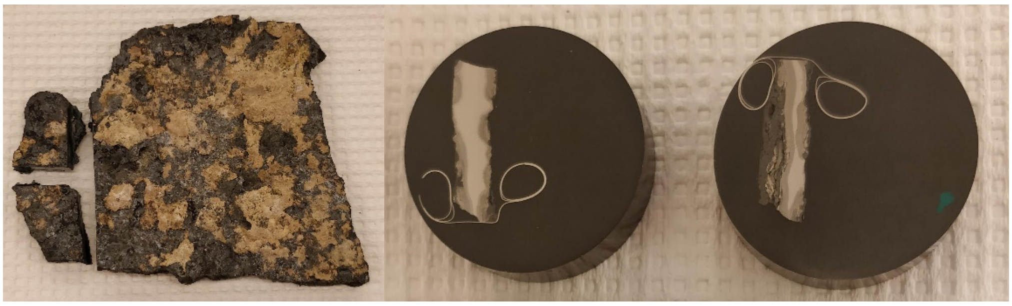


Figure 25 Sample from the cyclone vortex finder, retrieved in Mälarenergi P6 boiler. The sample was cut into two cross sections that were mounted in conductive bakelite for further examination.

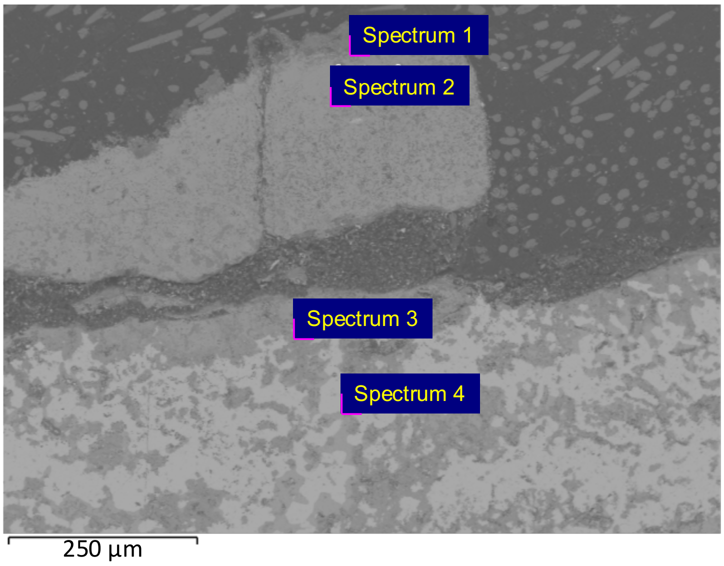


Figure 26 SEM image corresponding to the cyclone vortex finder sample retrieved from Mälarenergi P6. The corresponding compositions for the spectra are shown in Table 9.

Table 9 Semi quantitative chemical composition in weight % of spectra corresponding to Figure 26.

Spectrum	N	O	F	Al	Si	Ti	Cr	Fe	Co	Ni	Mo	W
1	1.32	45.85		36.04		0.23	2.94			0.57	2.78	10.27
2		72.27		8.98		0.38	15.11			2.22		1.04
3	0.9	28.49		0.04			69.13			0.27	0.93	0.25
4		0.9	1.23	0.04	0.13		0.81	61.54	0.7	34.04	0.46	0.16

4.3.3 Primary air nozzles

Primary air nozzles were retrieved from the boiler P6 at Mälarenergi (see Figure 27). The nozzle shows clear evidence of erosive wear, which most likely is corrosion assisted (i.e it has experienced erosion-corrosion).

Figure 27 Primary air nozzle retrieved from Mälarenergi P6 boiler system. The nozzle exhibited evidence of erosive wear.

4.3.4 Studdings

Studdings exhibiting extensive degradation were retrieved from Mälarenergi P6 boiler system (Figure 28). The SEM/EDS results show evidence of a severe type of grain boundary attack.

Figure 28 Studdings retrieved from Mälarenergi P6 boiler system. The right image shows the studdings mounted in conductive bakelite and ground to reveal their cross sections.

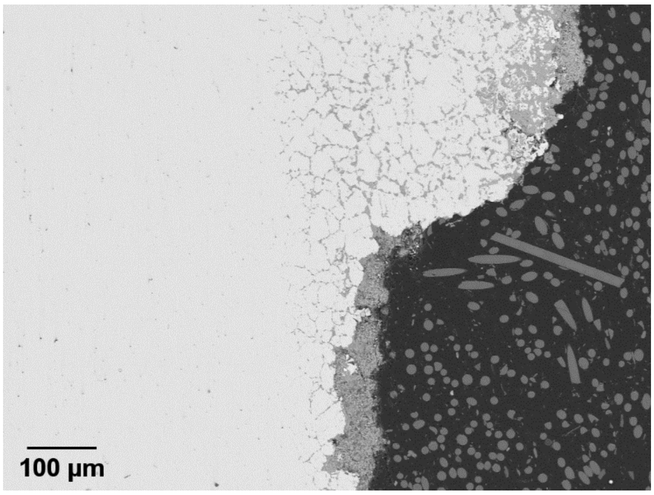


Figure 29 SEM image (Backscattered electrons) of the cross section of a studding from Mälarenergi P6 boiler.

4.4 UNCOOLED PROBE – FIELD EXPOSURE MÄLARENERGI P6

4.4.1 Probe manufacturing and exposure conditions

An uncooled probe was designed and built to perform a field exposure in Mälarenergi P6 boiler system. The objective was to assess the performance of 14 metallic rings of different compositions and coatings (see Table 10 for details). The probe was installed in a manifold duct just before the vertical empty pass (see Figure 30 for a schematic of the location of the exposure. Further details of the boiler are given in Section 5.2. The rings were mounted in the probe (see Figure 31) and were exposed for a total of 99 days. The temperature at this position was typically 890-920 °C and could reach temporarily a maximum of 950 °C. The flue gas flow was considered somewhat erosive at the location. Figure 32 shows the installed probe in the horizontal manifold duct.

The probe was manufactured from the FeCrAl alloy Kanthal® APMT™.

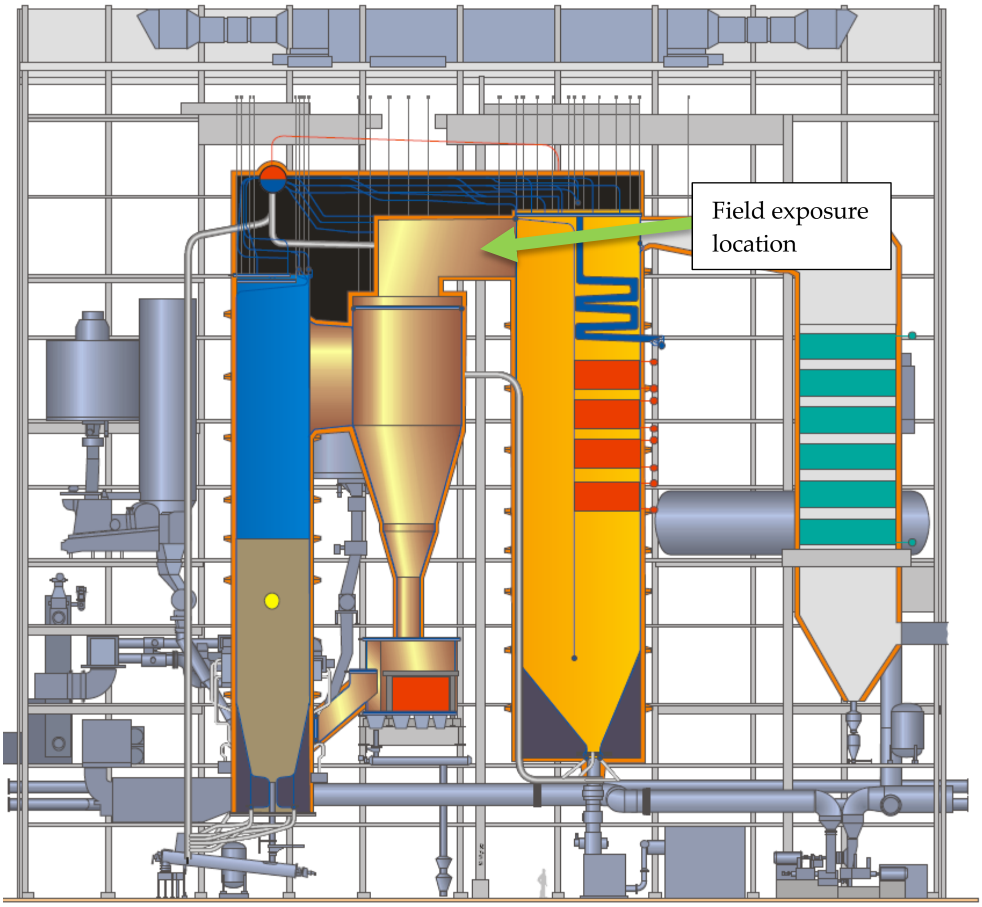


Figure 30 Schematic of location of the field exposure. The probe was installed in a manifold duct just before the vertical empty pass in Mälarenergi P6 boiler system.

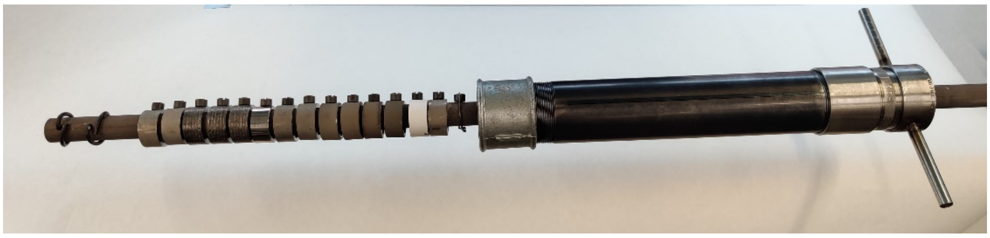


Figure 31 Image of the manufactured probe with mounted specimens (14 rings listed in Table 10).

Figure 32 Installed probe in Mälarenergi P6 boiler system. The probe was mounted into the horizontal manifold duct just before the empty pass.

4.4.2 Materials

The selected test materials are listed in Table 10. Metallic coatings were applied either by overlay welding for specimens #3 to #5 or HVOF (high velocity oxygen fuel) for specimens #9 to #12.

Table 10 Selected test materials.

Specimen number	Base material	Coating	Average original thickness (mm)
#1 (Reference)	253 MA	-	5.15 ± 0.04
#2 (Reference)	Solid Kanthal® APMT	-	6.29 ± 0.14
#3	Solid Kanthal® APMT	Welded Kanthal® APMT	8.03 ± 0.23
#4	Solid Kanthal® APMT	Welded Kanthal® EF100 (earlier referred as L198)	7.89 ± 0.20
#5	Solid Kanthal® APMT	Welded Kanthal® EF101 (earlier referred as L197)	7.93 ± 0.28
#6	Solid 625	-	4.94 ± 0.05
#7 (Reference)	253 MA	-	5.14 ± 0.04
#8 (Reference)	Solid Kanthal® APMT	-	6.33 ± 0.13
#9	253 MA	CorrEr	5.46 ± 0.06
#10	253 MA	Amdry 365-4	5.38 ± 0.04
#11	253 MA	Amdry 510	5.28 ± 0.06
#12	253 MA	Amdry 9700	5.34 ± 0.04
#13	253 MA	Keram	5.50 ± 0.10
#14 (Reference)	253 MA	-	5.15 ± 0.04

4.4.3 Exposure results

The rings were assessed before exposure by measuring their thickness using a calliper (for the welded specimens) or a micrometre (for the solid and spray coated specimens). After exposure the specimens were casted in cold epoxy resin to protect the potential oxide scales and subsequently cross sectioned. The specimens were prepared for examination using standard metallographic techniques. The cross sections were examined using a LOM (Light Optical Microscope brand Zeiss Axio Zoom) and later the images were processed using the software ImageJ. One cross section corresponding to approximately 30° off from the wind side was selected to measure the thickness (see Figure 33). The measurements before and after exposure were compared approximately at the same section of the rings.

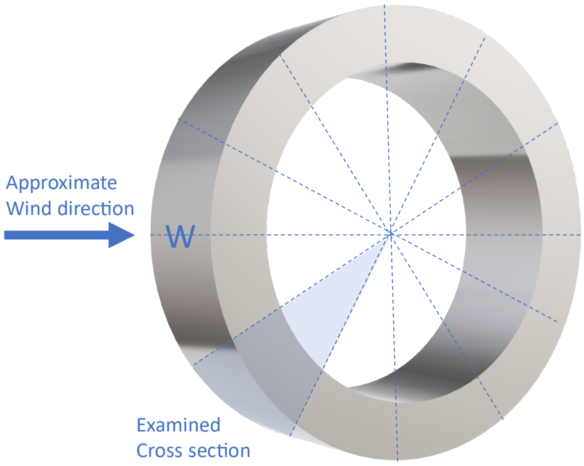


Figure 33 Schematic illustration showing the cross section 30° off from the wind side, which was used to measure the thickness of the ring.

The metallic rings before and after exposure are shown in Figure 34. The results of the loss of material measurements are shown in Figure 35. From Figure 36 to Figure 49, light optical microscope images of the cross sections of each specimen are shown, including a brief comment on their appearance with respect to their corrosion resistance.

The results show that the rings have lost between 0.1 and 1 mm of material. The uncertainty of the material loss taking into consideration the spread of the original thickness results and other deviations, was estimated as ± 0.2 mm for the welded specimens, ± 0.1 mm for the solid specimens, and ± 0.08 mm for the spray coating samples. The reference material 253 MA (uncoated, specimens #1, #7 and #14) exhibited about the same loss of metal in the three positions along the probe (edges and centre position), which indicates that the rings were not subjected to important flow inhomogeneities or temperature variation inside the boiler. Two specimens with welded coatings (welded Kanthal® EF100 #4, welded Kanthal® EF101 #5) exhibited the largest material losses for the metallic materials (see Table 11 Figure 39 and Figure 40), although it was difficult to determine the weld thickness change after exposure given that the weld surface is quite uneven from the beginning. Some internal corrosion was found in the reference material 253 MA however the attack depth was limited to 0.1 mm. The sprayed coating in specimen #10 (Amdry

365-4) exhibited important undermining at the edges (see Figure 45). The specimen #11 (Amdry 510) exhibited no undermining in any of the assessed samples, with visible coating from edge to edge (see Figure 46). The coated ring #12 (Amdry 9700) exhibited some undermining at the edges (see Figure 47). CorrEr coating (#9, see Figure 44) exhibited some porosity in the interface between the coating and the substrate material. Additionally, some corrosion products were found in this area, however it is unclear if they have been lodged in after exposure i.e., during the metallographic preparation process. The cross sections of the ring coated with Keram (Al-based ceramic coating, see Figure 48) had no visible coating when examined with a light optical microscope. For this coating, some decolouration and limited internal attack (0.1 mm deep) can be seen in some of the samples. From all the sprayed-coating samples, Keram exhibited the largest material loss. The solid 625 (#6) specimen exhibited a somewhat irregular surface and a thin corrosion layer underneath the deposit (see Figure 41). Finally, the specimens corresponding to solid APMT (#2 and #8, see Figure 37 and Figure 43 respectively) exhibited limited corrosion attack (at most 0.2 mm deep in localized areas) and a thin corrosion layer beneath the deposit. Considering the measured metal loss and corrosion behaviour as observed by metallography, it was considered that coating Amdry 510 had the best behaviour of all the tested materials.

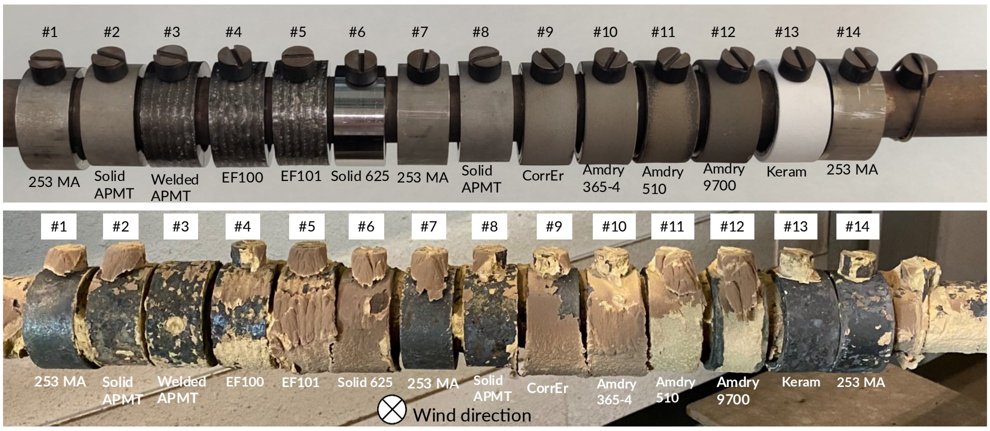


Figure 34 Metallic rings before and after exposure. The rings were fastened to the probe with Kanthal® APMT™ bolts to prevent potential shift during exposure. The bolt corresponding to one of the specimens was lost during the probe installation process and consequently the specimen was rotated approximately 90° with respect to the others. The wind direction is shown in the bottom picture.

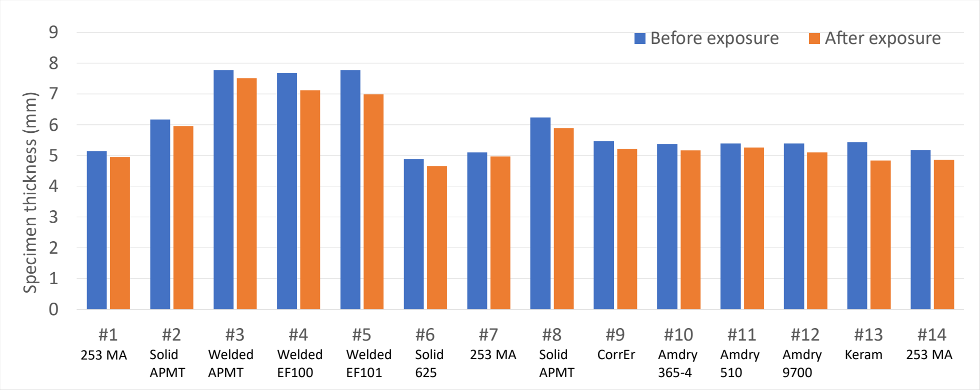


Figure 35 Specimen thickness before and after exposure. Before exposure the specimens were measured with a micrometre (solid and sprayed coated specimens) or a calliper (welded specimens). After exposure, the thickness of the specimens (approximately 30° off from the wind side) was measured using a light optical microscope and the software ImageJ. The horizontal axis refers to the specimen number shown in Table 10 and Figure 34.

Table 11 Thickness loss of exposed specimens.

Specimen number	Thickness loss (mm)
#1 – 253 MA	0.18
#2 – Solid APMT	0.21
#3 – Welded APMT	0.27
#4 – Welded EF100	0.57
#5 – Welded EF101	0.79
#6 – Solid 625	0.24
#7 – 253 MA	0.14
#8 – Solid APMT	0.35
#9 – CorrEr	0.24
#10 – Amdry 365-4	0.21
#11 – Amdry 510	0.13
#12 – Amdry 9700	0.29
#13 – Keram	0.59
#14 – 253 MA	0.32

- #1 253 MA (reference)

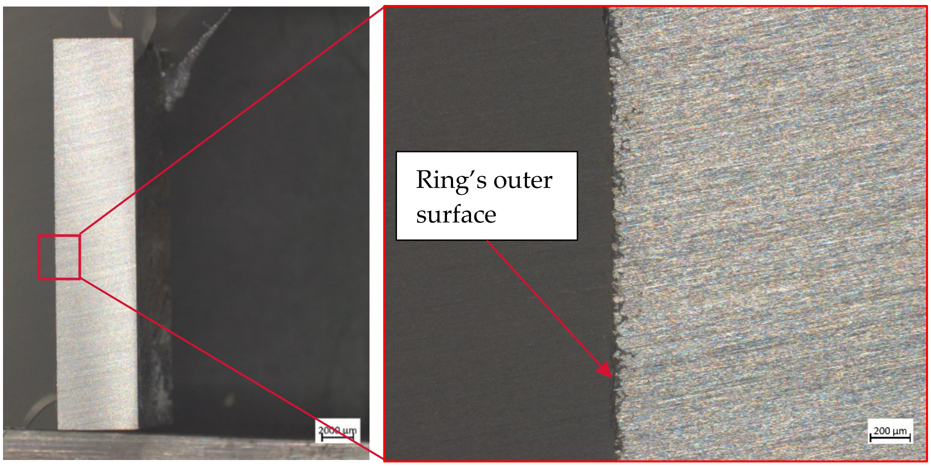


Figure 36 Specimen #1 corresponding to the alloy 253 MA (reference) after exposure. The zoomed in picture to the right shows an indication of internal corrosion attack (about 0.1 mm deep).

- #2 Solid Kanthal® APMT™

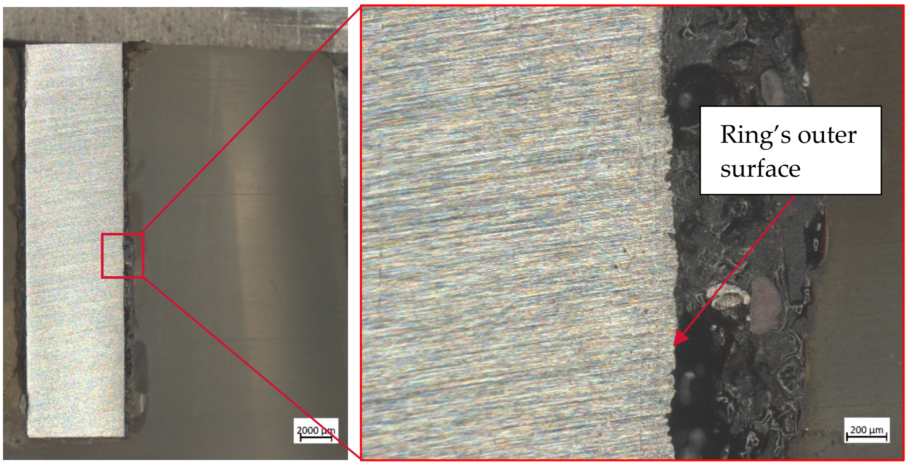


Figure 37 Specimen #2 corresponding to the alloy solid Kanthal® APMT™ after exposure. The zoomed in picture to the right shows negligible corrosion attack.

- #3 Welded Kanthal® APMT™

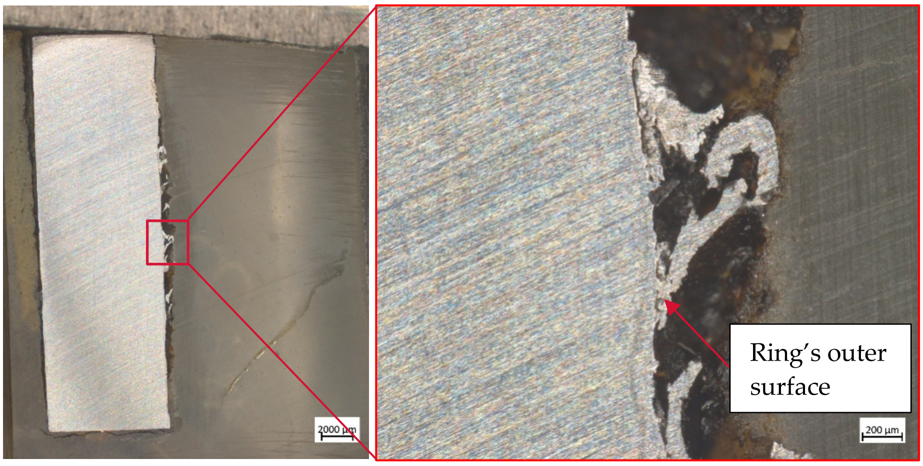


Figure 38 Specimen #3 corresponding to the welded alloy Kanthal® APMT™ after exposure. The zoomed in picture to the right shows remaining welded coating and no signs of internal attack.

- #4 Welded Kanthal® EF100 (also referred to as L198)

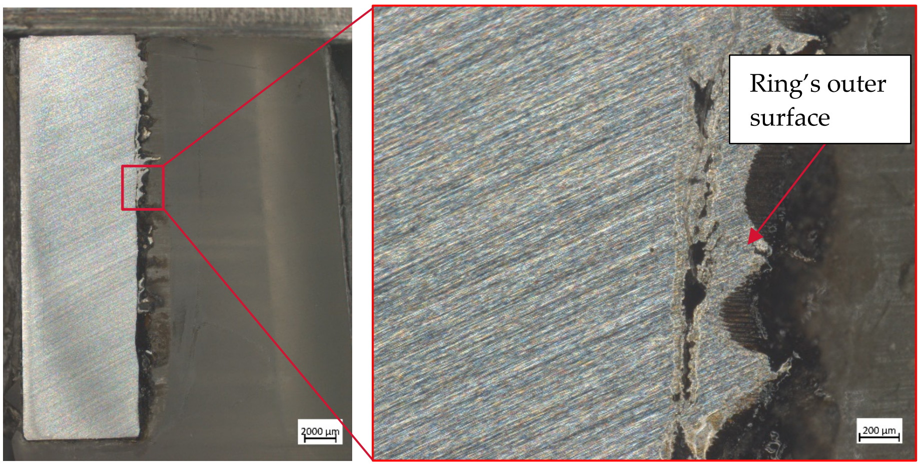


Figure 39 Specimen #4 corresponding to the welded alloy Kanthal® EF100 after exposure. The zoomed in picture to the right shows remaining welded coating and no clear signs of internal attack.

- #5 Welded Kanthal® EF101 (also referred to as L197)

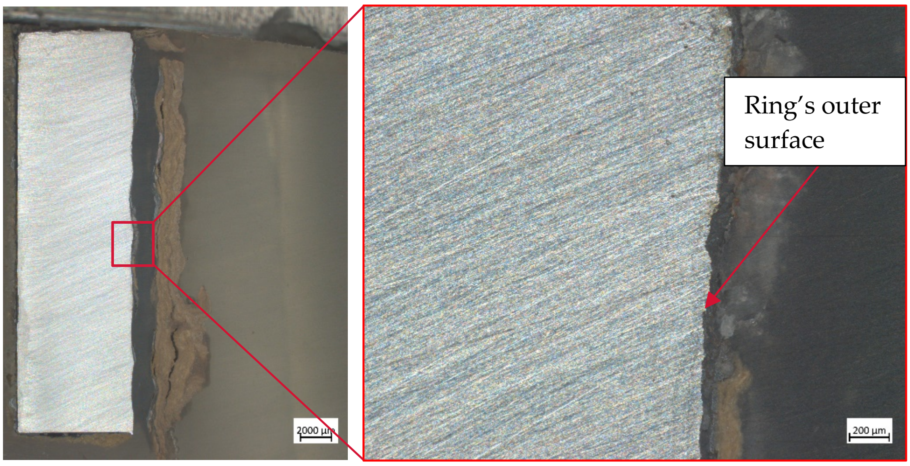


Figure 40 Specimen #5 corresponding to the welded alloy Kanthal® EF101 after exposure. The zoomed in picture to the right shows no signs of internal attack.

- #6 Solid 625

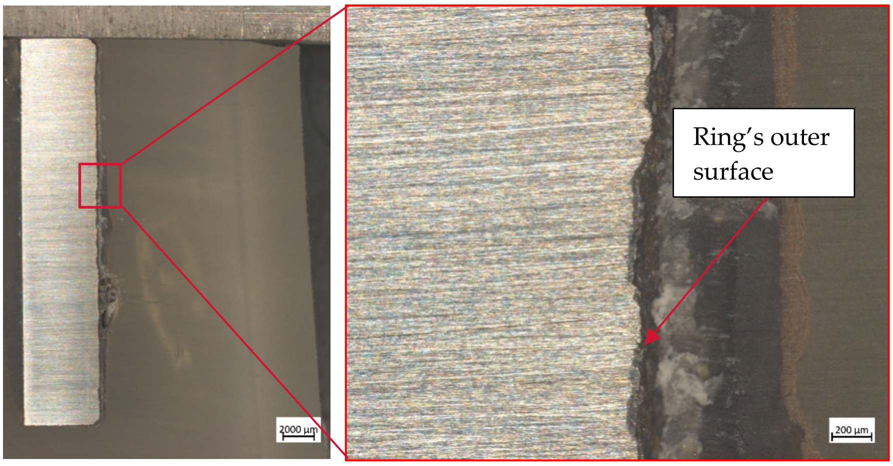


Figure 41 Specimen #6 corresponding to the alloy solid 625 after exposure. The zoomed in picture to the right shows an uneven surface and a thin corrosion layer.

- #7 253 MA (reference)

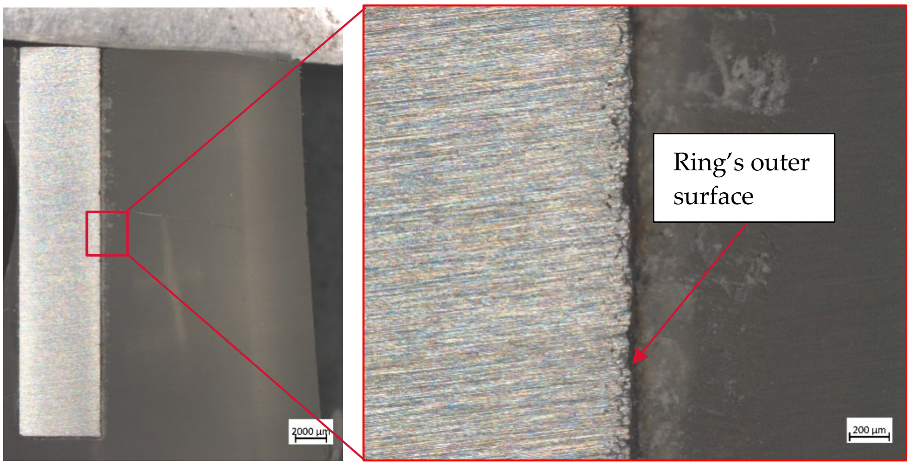


Figure 42 Specimen #7 corresponding to the alloy 253 MA (reference) after exposure. The zoomed in picture to the right shows a similar microstructure as specimen #1 (253 MA), with an internal corrosion attack of about 0.1 mm depth.

- #8 Solid Kanthal® APMT™

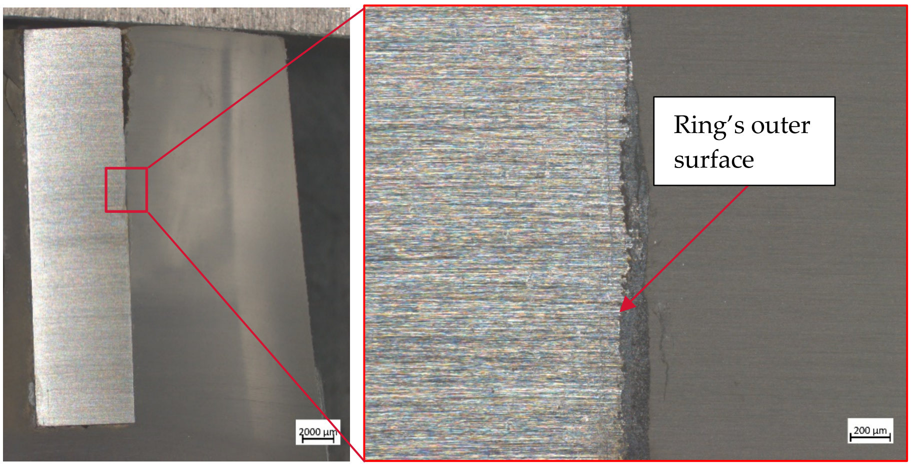


Figure 43 Specimen #8 corresponding to the alloy solid Kanthal® APMT™ after exposure. The zoomed in picture to the right exhibits a thin corrosion/deposit layer.

- #9 CorrEr

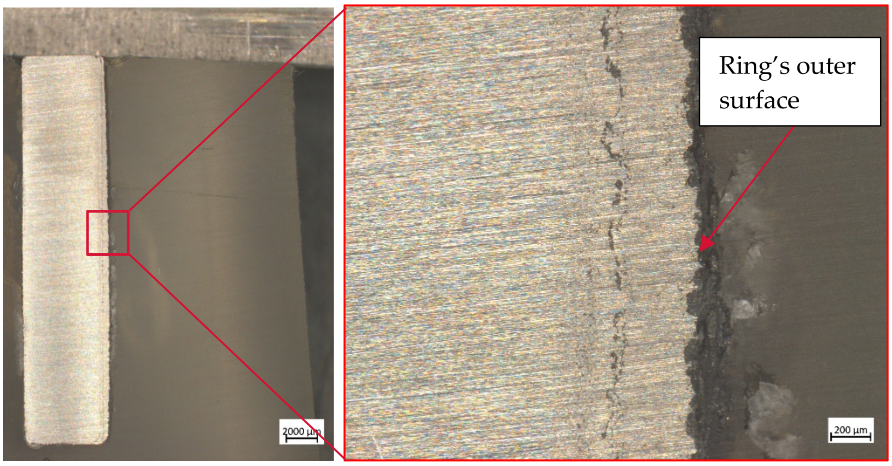


Figure 44 Specimen #9 corresponding to the coating CorrEr on a 253 MA substrate after exposure. The zoomed in picture to the right shows remaining coating (about 0.4 mm thickness) with a thin corrosion/deposit layer on top.

- #10 Amdry 365-4

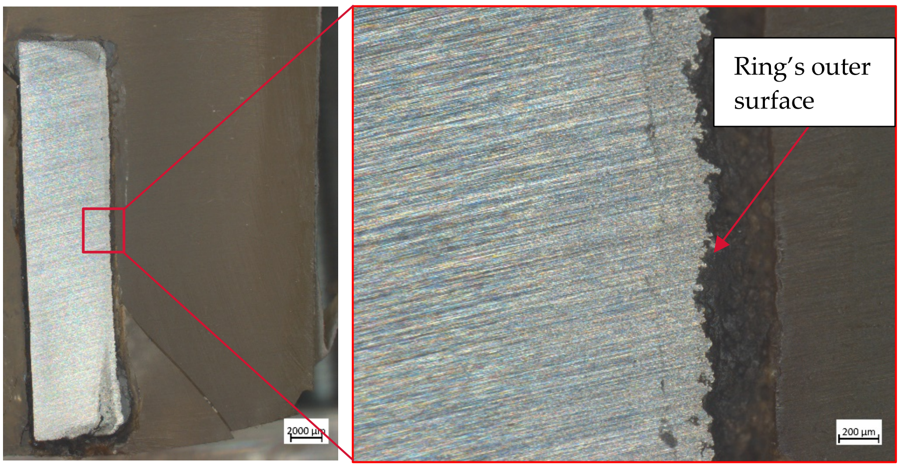


Figure 45 Specimen #10 corresponding to the coating Amdry 365-4 on a 253 MA substrate after exposure. The zoomed in picture to the right shows remaining coating (about 0.25 mm thickness) with a thin corrosion/deposit layer on top. This specimen exhibited some undermining at the edges.

- #11 Amdry 510

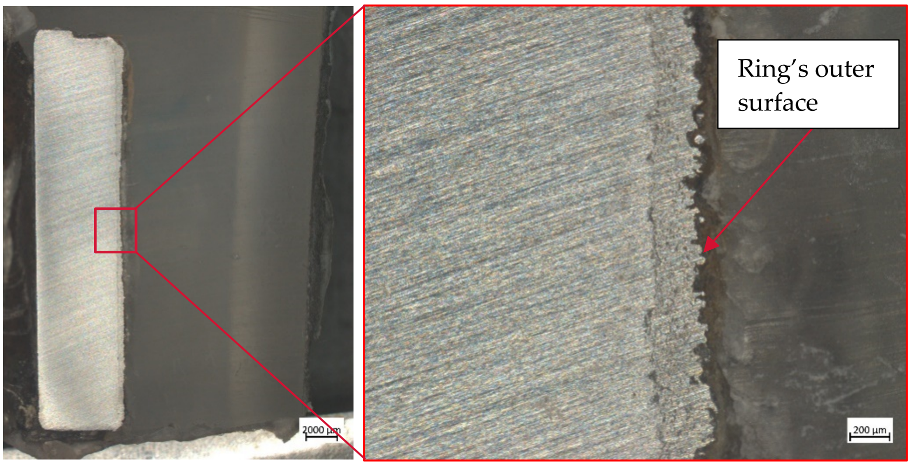


Figure 46 Specimen #11 corresponding to the coating Amdry 510 on a 253 MA substrate after exposure. The zoomed in picture to the right shows remaining coating (about 0.25 mm thickness) with a thin corrosion/deposit layer on top.

- #12 Amdry 9700

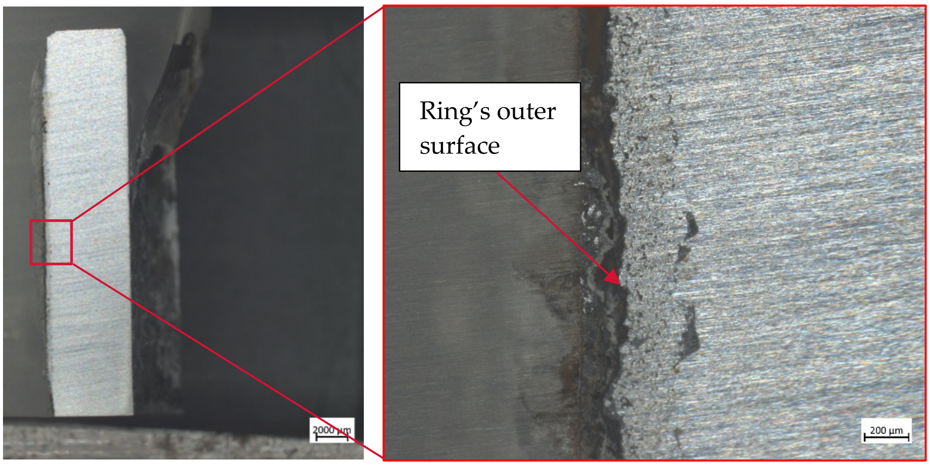


Figure 47 Specimen #12 corresponding to the coating Amdry 9700 on a 253 MA substrate after exposure. The zoomed in picture to the right shows remaining coating (about 0.25 mm thickness) with a thin corrosion/deposit layer on top. In between the coating and the substrate, some areas seem to have become detached.

- #13 Keram (Al oxide based ceramic)

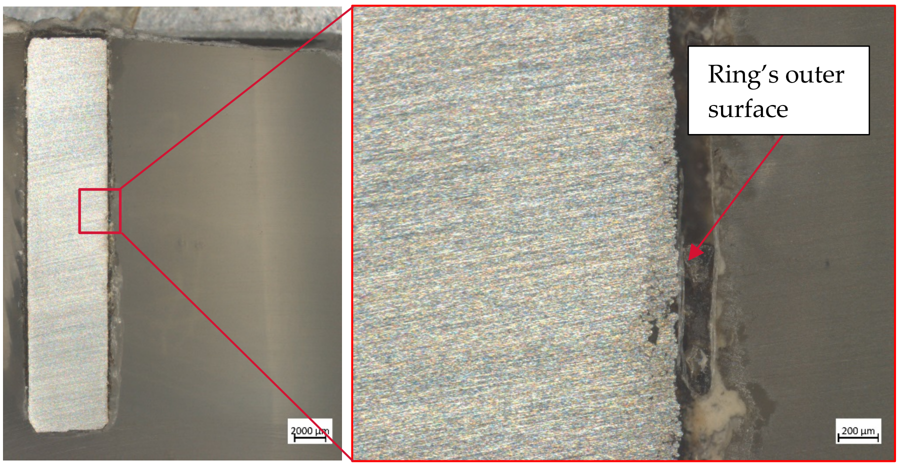


Figure 48 Specimen #13 corresponding to the coating Keram on a 253 MA substrate after exposure. The zoomed in picture to the right shows no signs of ceramic coating. However, an undefined possibly metallic layer of about 0.1 mm thickness is seen.

- #14 253 MA (reference)

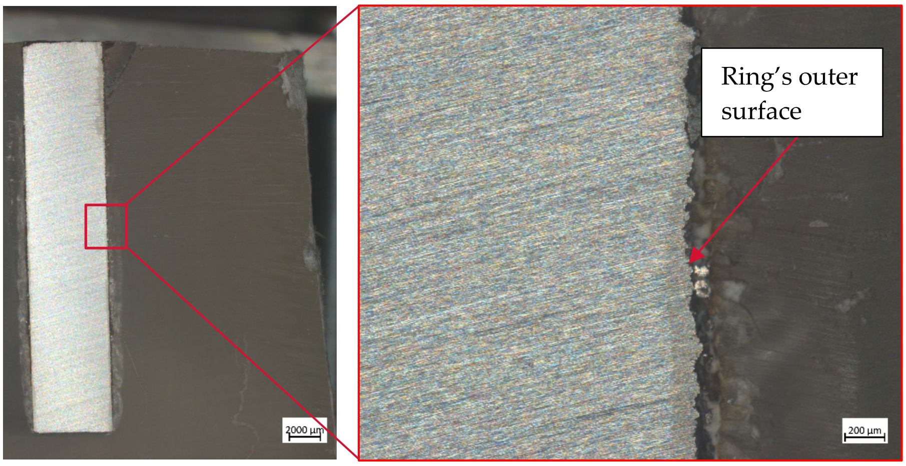


Figure 49 Specimen #14 corresponding to the alloy 253 MA after exposure. The zoomed in picture to the right shows an irregular surface but no internal corrosion attack.

4.5 CONCLUSIONS WP3

Metallic parts in a boiler that are mostly uncooled (i.e. steam or water are not passing through them) face challenges that are intrinsically different compared to those of cooled parts. Depending on their position, temperatures can be much higher, and the composition of deposits is expected to be different, since the condensation conditions are not the same. A number of parts have been retrieved from boilers to investigate various observed issues to help shed light on the degradation types at play. The investigations have encompassed analysing specimens taken from parts such as: cyclone vortex finder, studding (refractory anchor), and air nozzle. In several cases the material degradation, typically by corrosion, was found to be very severe.

The analysis of these parts has given insight into different corrosions behaviours that are occurring. For a vortex finder it was found that significant nitriding had occured to a substantial depth into the material. For air nozzles it was detected exceptional amounts of Pb locally, which is known to be corrosive, as well as what appears to be metallic AlZnSi and may have caused corrosion by presence of molten phases.

To find solutions to some of the difficulties with high degradation rate of uncooled parts it has been investigated which different coating types and material grades could be suitable. A field exposure lasting 99 days was carried out in a boiler, inside the manifold duct just before the vertical empty pass, where the temperature was typically 890-920 °C and could reach temporarily a maximum of 950 °C, and the flue gas flow was considered somewhat erosive. The coating techniques used were overlay welding and HVOF. Considering the measured metal loss and corrosion behaviour as observed by metallography, it was considered that coating Amdry 510 applied by HVOF had the best behaviour of all the tested materials. Although it is worth noting that generally thermal spray coatings' lives are not determined only by their corrosion resistance, other damage mechanisms such as detachment or mechanical damage might come much earlier thus limiting their application. And these factors may not be reflected by a short-term probe test.

Amongst the surpassed tested materials was solid 253 MA, which is a state-of-the-art material for these conditions, as well as solid 625. Welded 625, which is a commonly used coating at much lower temperatures, was not included. However, it is believed that it would not have behaved better than solid 625, since for welded materials the microstructure and local compositional variations are not as optimized. Thus, it can be concluded that HVOF applied Amdry 510 coating has potential to improve material performance significantly for uncooled parts.

5 WP4 – Refractories

5.1 INTRODUCTION TO WP4

An important issue for plant owners is to keep the boilers intact and avoid unplanned shutdowns. One of the main reasons for unwanted shutdowns are tube leakages caused by corrosion, erosion, or a mix of those. To avoid leakages, a lot of work has been done within the area of metallic materials. However, some areas in the boiler are protected by means of refractory materials instead and damage also occurs on these surfaces. Thus, there is a need to increase the knowledge regarding refractory materials and to further develop the methods of inspecting these materials.

In this project, the presence and effect of heavy metals and alkali containing substances on refractory materials is studied using advanced analysis of exposed material (up to several years) with respect to changes in structure or chemistry. Improvements of inspection methods for refractory material in service are also included. The analysis results are put in relation to the data on exposure conditions as provided by the boiler operators.

The idea on follow-up and analysis of refractories being tested has been the same throughout the project. Target area has been chosen and agreed between Calderys/E.ON/RISE. These areas have been identified in each target boiler. The existing refractory on the identified area was demolished and new refractory installed, carefully marked on drawings. From the very same pallet of refractory bags were taken to the Calderys lab to produce a set of casted reference samples (exposure 0 years), standard size test bars, fired in controlled environment for testing and analysis. Later, during a maintenance shutdown, the test areas having been in boiler operation were identified, refractory chiselled out giving as big pieces of refractory as possible. These sample pieces were sent to Calderys lab and RISE for analysis and then benchmarked against the properties of the reference sample.

5.2 BOILERS

Refractory material/specimens were taken from two sites, Händelöverket in Norrköping (owned by E.ON Energiinfrastruktur AB) and from Mälarenergi in Västerås.

5.2.1 Händelöverket (E.ON), Norrköping

Specimens were taken from two boilers, P14 and P15. The two boilers are described below.

P14

The boiler, Figure 50, is a Circulating Fluidised Bed (CFB) boiler with a thermal capacity of 75 MW supplied by Kvaerner Power (today: Valmet). The boiler produces steam, primarily used for production of electricity, industrial process steam, and district heating. Some boiler data are shown in Table 12.

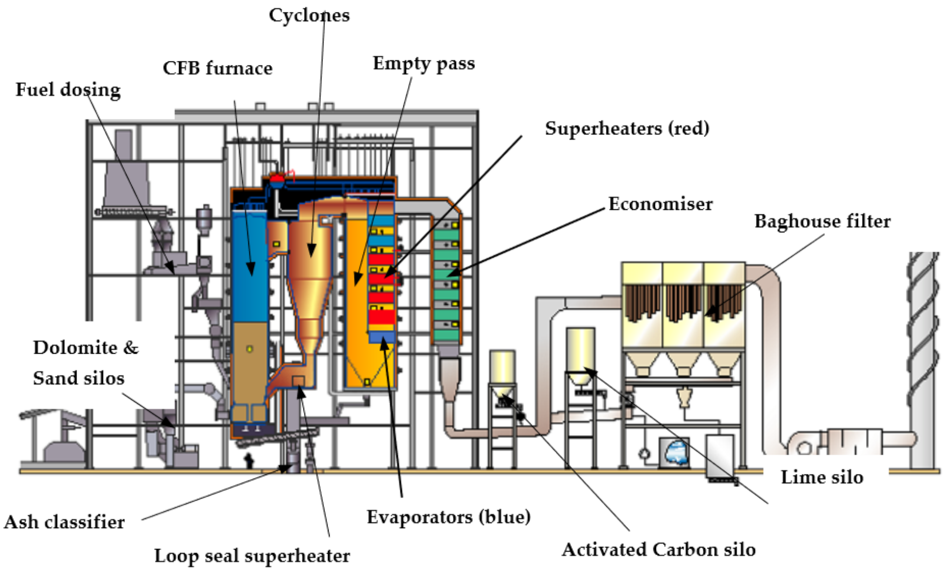


Figure 50 Händelö/Norrköping P14 CFB boiler

The boiler is designed for fuel flexibility, using a fuel mix of 30-50% combined household waste, 50-70% classified industrial waste and up to 20% sewage sludge.

The design of the Valmet CFB boiler used for combustion of MSW/RDF (Municipal Solid Waste, Refused Devised Fuels) fuels comprises some characteristic features to be outlined in the following text. The main parts in the boiler system are a water-cooled furnace with two integrated water-cooled cyclones and loop seals, containing the final superheaters, Figure 50. The cyclones are followed by a single pass radiation cavity (empty pass) and a convection pass with superheater banks, boiler banks and economizer banks. The boiler is equipped with a conventional steam soot blowing system cleaning the banks in the convection pass. Afterwards the empty pass has been equipped with two water cannons and the economizer with sonic cleaning, which is used together with the original installed steam soot blowers.

All four walls of the furnace are refractory lined, except for an area on the upper part of the sides and front wall. In 2021, a part of the refractory was replaced with overlay welded tubes (Inconel 625) to lower the temperature in the top of the furnace and in the following flue gas passes. The refractory and the overlay welded areas are made for erosion protection and to sustain furnace temperature above 850°C during 2 seconds after the last injection of air.

The boiler features two hot gas cyclones for separation of the bed material entrained by the flue gas and leaving the furnace at the furnace top. The separated material is returned to the lower part of the furnace via a loop seal. The loop seal contains a bubbling fluidized bed and is equipped with a number of air nozzles to ensure material transport. Moreover, it is designed to prevent flue gas from the furnace entering the cyclones through the bed material return leg.

The loop seal, which is a feature of the CFB process, offers a location of the final superheater (SH). Only the particles separated by the cyclone reach the loop seal.

The cyclones are constructed from water-cooled membrane walls, which form part of the water circulation system. The cyclone interior is fully refractory lined with a thin layer for erosion protection, which minimizes the amount/thickness of refractory and further reduces the maintenance costs and shortens the start-up time. An SNCR-system is installed, with ammonia injection in both cyclones.

The cyclones are followed by an empty pass for lowering the flue gas temperature to a temperature, which makes the ash ”dry” and non-sticky to the back pass tube banks. This will minimize deposit formation and corrosion attacks. The bottom of the empty pass is equipped with an ash extraction conveyor system.

A new evaporator bundle has been installed 2006 before the secondary superheater to reduce the flue gas temperature by 50°C. This bundle and four additional rows of boiler tubes protect the secondary superheater at the gas inlet side.

All superheater tubes in the first and last rows, near the soot blowers, are protected by tube shields.

Table 12 P14 operating data at MCR (Maximum Continues Rate).

Water/steam		
Feed water temp	°C	135
Steam flow	kg/s	27.5
Steam pressure	MPa	6.5
Steam temperature	°C	450
Miscellaneous		
Boiler efficiency	%	89.7
Exit flue gas temperature	°C	165-170
Unburned in bottom ash	%	<0,1
Unburned in fly ash	%	< 0,5

P15

The boiler, Figure 51, is a Circulating Fluidised Bed (CFB) boiler with a thermal capacity of 85 MW supplied by Foster Wheeler (today: Sumitomo). The boiler produces steam, primarily used for production of electricity, industrial process steam, and district heating. Some boiler data are shown in Table 13.

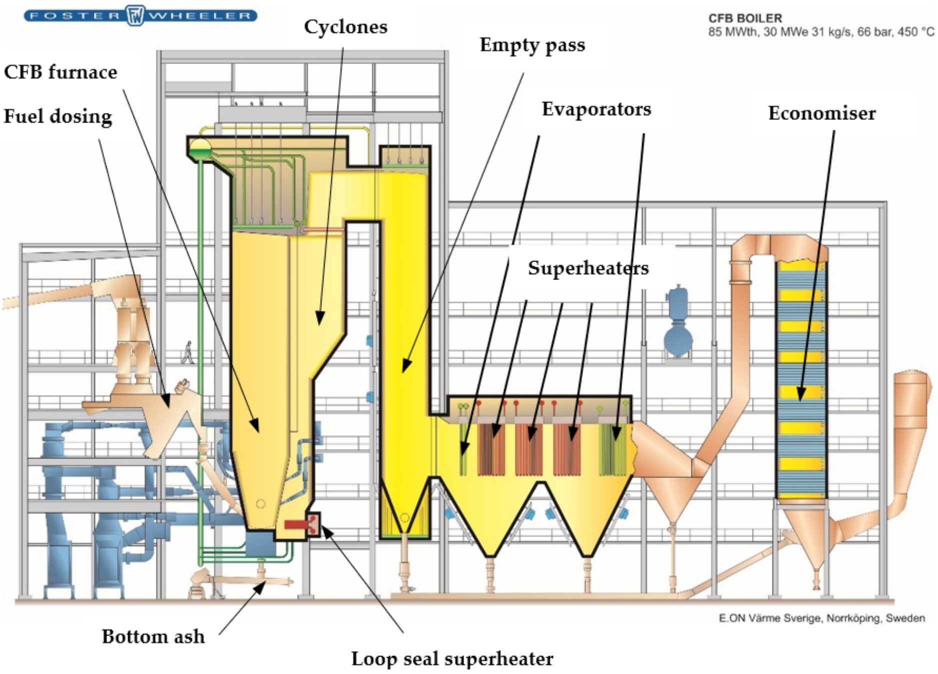


Figure 51 Händelö/Norrköping P15 CFB boiler.

The design of the Foster Wheeler CFB P15 boiler used for combustion of MSW/RDF (Municipal Solid Waste, Refused Devised Fuels) is similar to boiler P14 in many ways. In the following text, only the things that are different compared to P14 will be presented. The main parts in the boiler system are a water-cooled furnace with two integrated water-cooled cyclones and loop seals, containing the final superheaters, Figure 51. The main difference with P15 is that the single pass radiation cavity (empty pass) is followed by a *horizontal* convection pass with superheater banks and boiler banks.

All four walls of the furnace are refractory lined, unlike P14 where overlay welding on the tubes also is used as a shielding method.

The boiler features two hot gas cyclones for separation of the bed material entrained by the flue gas and leaving the furnace at the furnace top. The separated material is returned to the lower part of the furnace via a smaller loop seal, called wall seal, and a conventional loop seal (in P14 you can only find the conventional loop seal).

The bottom of the empty pass and the horizontal pass are equipped with an ash extraction conveyor system. In P15, there is no steam soot blowing system like in P14, instead, a rapping system is used regarding the superheater.

Table 13 P15 operating data at MCR (Maximum Continues Rate).

Water/steam		
Feed water temp	°C	135
Steam flow	kg/s	31
Steam pressure	bar	65
Steam temperature	°C	450
Miscellaneous		
Boiler efficiency	%	90
Exit flue gas temperature	°C	165–170
Unburned in bottom ash	%	<0,1
Unburned in fly ash	%	<0,5

5.2.2 Mälarenergi, Västerås

The boiler is designed by Metso Powers, now Valmet for Mälarenergi AB in Västerås, see Figure 52. The main part of fuel for combustion in CFB is a mixture of industrial waste and solid household waste called primary fuel. The secondary fuel system is the biofuels that are fed in via the return legs from the loop seals. Light oil is used as start-up and as support fuel.

The most important functions of the steam boiler are:

- Steam production: 58.2 kg/s
- Steam pressure at delivery limit: 74 bar(a)
- Steam temperature at delivery limit: 470°C
- Feed water temperature in feed water tank: 135°C

The Metso Powers (now Valmet’s) boiler type is of the circulating fluidized bed type with a steam drum and a furnace with a wall construction of a gas-tight membrane, two parallel cyclones and one empty pass with six sections. A rear draft, where the primary and secondary superheater and boiler bank are located and after that an economizer. Tertiary superheaters are located in the loop seals.

The boiler is equipped with a duct burner, as a start-up burner, placed in the primary air duct and two burners that are fired with light oil. Solid fuel can be fed from either the primary or secondary fuel supply system. Solid fuel is fed into the fluidized bed via six main feed lines – four for primary fuel (front wall of the boiler) and two for secondary fuel (back wall of the boiler). Four primary fuel feed lines each consist of a fuel silo with a screw in the bottom, a feeding master, and a rotary feeder.

There are two secondary fuel feed points in the return legs from the loop seals on the back wall of the boiler. Secondary fuel system consists of a fuel silo with a screw in the bottom, a scraper conveyor, two dosing screws and two rotary feeders. Coarse material from the bottom of the boiler is removed via four chutes and transferred by water-cooled screw feeders and a lamella conveyor to bottom ash sieves equipment to then return the fine ash back to the furnace.

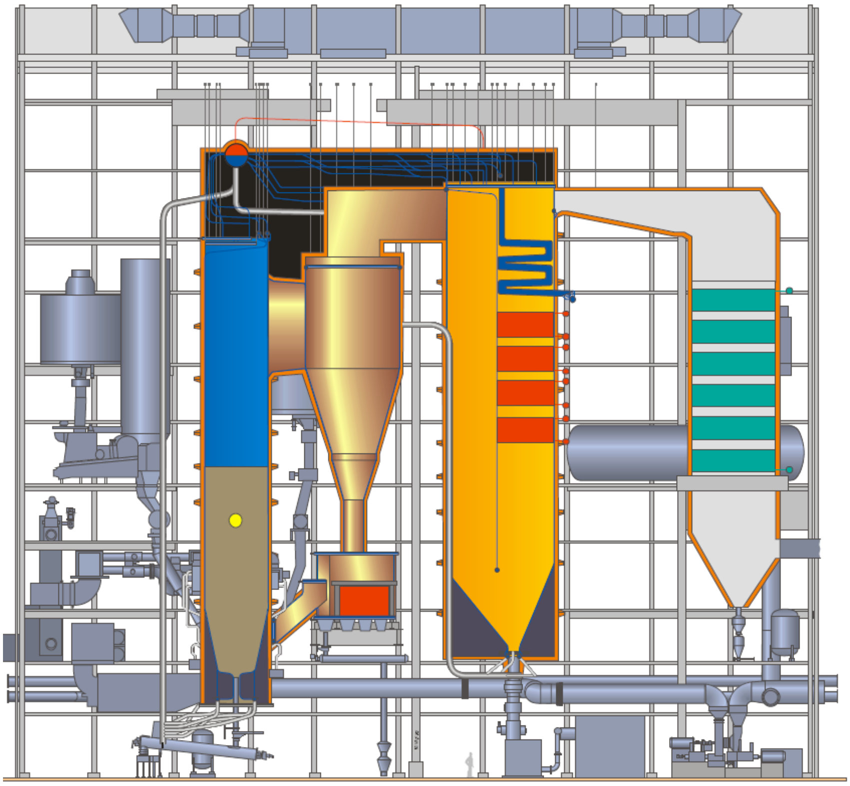


Figure 52 Valmet boiler no. 6 at Mälarenergi AB in Västerås.

The combustion air is heated by using heat from the cooling water of the bottom ash system through water batteries and the possibility of preheating with steam is also available. Combustion air is fed to the boiler with a primary air fan (fluidizing) and a secondary air fan. The flue gases are led after the boiler to flue gas treatment and then to the chimney. If necessary, flue gas can be recirculated after the flue gas fan with flue gas recirculation fans back to the lower part of the boiler in order to control the bed temperature by lowering the oxygen content of the bed.

5.3 REFRACTORY TYPES

Two types of refractory products were followed up in detail for this project. Both are low cement bonded types, castable, self-flowing, pumpable and spray-castable (i.e. installation using wet shot-creting). The two bulk types were alkali resistant mullite rich (the CALDE® FLOW LM 74 A and CALDE® CAST LM 74 A) as well as alkali resistant, high conductivity silicon carbide rich (the CALDE® SPRAYCAST SIC 70). Some areas were repaired with CALDE® STIX PB 85 C/G, a similar, high strength, high abrasion resistant product as the CALDE® FLOW LM 74 A, chosen for its ease to install in small areas. Hence, we did analysis on the formula refractory as well.

Both chosen products have a long history in boilers and incinerators as well as multiple other industries and are sold globally and produced in multiple countries.

The low cement bond system is tailor made to be as alkali resistant as possible. Tests have indicated that possibly a sol-gel bond system, found in e.g. CALDE® SOL SPRAYCAST SIC 70 (not part of this report), likely give an even higher alkali resistance. However, in most biofuel and municipal solid waste fuel situations this type of low cement bond by far exceeds expectations on performance. The low cement bond system is mainly consisting of Al_2O_3 and SiO_2 and small amounts of the high temperature resistant calcium-aluminate cement is providing some amounts of Calcium oxides.

The Mullite and other bulk components chosen for the recipe of CALDE® FLOW LM 74 A are produced in rotary kilns by fusing or sintering several alumina-silicate mineral raw materials, such as bauxite, into the preferred mullitized stabile crystalline phase consisting of Al_2O_3 and SiO_2. The main source of Mullite is via Imerys, since 1996 also the owner of Calderys.

The silicon carbide and other bulk components chosen for the recipe of CALDE® SPRAYCAST SIC 70 are synthetically produced in electric arc furnaces by Carbon and Silicon oxide raw materials into the preferred extremely hard crystalline phase called SiC or carborundum. The main sources of SiC comes globally and is expensive due to e.g. being electricity intensive. For refractories the very high thermal conductivity of SiC is preferred e.g. when municipal solid waste fuels tend to change to have higher calorific values, such as when food waste was omitted and the boilers needed to be "cooled". In really high temperatures Mullite is more favourable than SiC which then may oxidise.

Both types of products tested are mixed in special high intensity mixers using potable water and can be either casted direct into a mould, or "spray-casted", i.e. sprayed at high output speeds using the wet shot-creting technology where there is no need to neither spend time on moulding work nor waiting for the refractory to become hard. Both installation methods give the same high product characteristics.

All refractories in this report come from the Calderys production unit in Höganäs, Sweden.

5.4 STATUS EVALUATION OF REFRACTORIES IN BOILERS

Refractories are a type of wear lining with multiple functions, yet all types need to be monitored for fatigue or breakage that can happen due to many reasons. Normally, the condition of the refractory can only be checked physically during any outage of the boiler/incinerator being cool. The safest way to evaluate refractory condition is by a time-consuming procedure where the refractory condition is checked at all levels mainly via visible appearance as well as sound indication of any laminations, cracks, voids etc. by hammer testing.

Normally the refractory lining status is monitored and followed up via a collaboration by both the equipment owner and the refractory supplier/installer. This requires good expertise from both stakeholders to work well. Accessibility to all refractory areas is prone to requiring scaffolding or other platforms as access from manways only is not sufficient to evaluate via hammer-testing.

Predictability of the lining is sometimes difficult due to many factors such as temperature, abrasive medias, and fuel calorific, and other values may fluctuate. Apart from manual inspection, refractory samples may be taken to a suitable laboratory to check consistency, chemistry, and infiltrations etc.

On-site chemical analysis of the refractory is also possible and tested via handheld XRF analyser to some extent in this project, however it may be difficult to predict accurately for the lining condition due to that only the very surface, which may be having skin slag of different chemistry, is monitored.

Abrasion of the lining, especially in CFBs, may be difficult to monitor without unwanted drilling or chipping out of existing refractory to physically measure the remaining thickness down to the underlaying metal. There are other methods prone to be used for this, but not being part of this project. Calderys is exploring 3D laser scanning, where a full boiler/incinerator digital high accuracy point cloud is used to verify the lining surface location compared to e.g. full thickness as well as using sensors continuously measuring the lining properties giving feedback.

There are many new supportive methods for inspecting refractory conditions coming in a not too distant future. Among some e.g. ideas are developed on on-line characteristics monitoring during operation as well as digital twins etc targeted to give an enhanced predictability and maintenance support based on also using other input than physical inspections and hammer testing.

5.5 SAMPLING

The sampling done in this project is mainly to verify the refractory condition after some time in use compared to the original dried-out state.

First the unused refractories were tested against the main attack component, likely to be alkali attack by sodium or potassium compounds sticking to or migrating into the refractory. Please see below under "Cup tests" and "Ash analysis".

During a maintenance outage there was supplied fresh refractory and for several chosen target follow-up areas there was also handpicked a bag from each of the very same production pallet as was used for each installation area to be followed up. Whilst doing this was assured traceability including all raw material controls done prior to manufacture, as well as the opportunity to produce and test of "zero samples", i.e. test bars and tests done in a QC lab on the very same batch of refractory being monitored over time in the boiler.

These reference samples were casted into test bars in accordance with EN-standards and heat treated to 110°C, 800°C and 1000°C, all to reflect both standard- and boiler parameters. Then various characteristics were measured in a controlled and repeatable matter indicating various properties such as cold compressive strength, bulk density, dry weight, weight in fluid, wet weight, open porosity, and water absorption ratio. Also, a chemical and mineralogical analysis could be conducted hence giving valuable information on the levels of critical components such as Na, K, Pb etc being in the refractory from the installation day.

The installed areas in the boilers were carefully noted allowing traceability to each reference sample ("zero sample").

After some time periods in operation and after approval by each boiler owner, we mechanically removed good refractory trying to get as big pieces as possible. This may many times be difficult firstly because the refractory is designed to be very durable and thus difficult to break, and secondly because there need to be high attention put into not accidentally damaging the underlying tube metal pressure parts. Electrically powered hand-held designated wrecking machines were used to assure safe removal of the samples as well as lowest risk of vibration damaging hands or fingers of the machine operator.

The broken-out samples were carefully separated, put into sealed bags, and uniquely marked for traceability. The samples were then sent to the labs for analysis like the above to measure deviation compared to the original reference samples. The size of the samples was targeted to be maximum 20 cm height x 20 cm width and full thickness. Front versus back side of a sample is clear as one sees the tube area clearly identifying the "rear side".

The boiler areas where the broken-out samples were taken were, after no tube damage was seen, then carefully casted using the same product, see Figure 53. The area was marked on the refence drawings including production date, batch number etc should any follow-up be needed. The re-installed areas were given the standard dry-out needed as there were also other areas re-lined in the boiler.

Figure 53 Boiler area after break-out sample was taken, prior to re-casting.

5.5.1 Specimens

Table 14 shows the summary of reference and extracted materials from the different boilers that were studied in this project.

Table 14 Summary of studied specimens including information about boiler, sampling position, and estimated temperature.

	Sampling position	Temperature [°C]
CALDE LM74-REF	Calderys laboratory	RT
EON LM74-7m	E.ON. P15, furnace side wall	950
EON LM74-2y	E.ON. P14, lower furnace	950
ME LM74-7y	Mälarenergi P6, east wall in west channel/pipe	950
CALDE SiC-REF	Calderys laboratory	RT
EON SiC-6m	E.ON. P15, furnace front wall	950
EON SiC-1y	E.ON. P14, furnace center (cast 2019-10-17)	950
EON SiC-2y	E.ON. P14, upper furnace level 6	950
ME SiC-6y	Mälarenergi P6, furnace close to welded tubes	950
ME SiC-7y	Mälarenergi P6, south inlet back wall	950

5.5.2 Specimen preparation methods

XRF laboratory test samples

The samples taken from the boilers are delivered to the RISE laboratory in Mölndal. No specimen preparation is performed for these samples. XRF laboratory measurements are performed on the wall surface that has been exposed to the boiling mass inside the boilers.

Cross section specimens for microstructure analysis

For analysis of the microstructure and elemental composition, cross section specimens are prepared by cutting, vacuum impregnation and cold mounting in epoxy, mechanical grinding, and polishing. The last polishing step is performed using oxide polishing suspension (OPS). SEM and EDS analysis of cross section specimens are performed on refractory material approximately 1 – 2 cm below the wall surface.

5.6 ANALYSIS METHODS

5.6.1 X-Ray Fluorescence measurements

Several elements are expected to have detrimental effects on the refractory materials, which is why it would be of great value to measure their concentrations. Thus, the XRF technique is evaluated in this study as a fast and easy on-site measurement method. The equipment used is a Thermo Fisher Niton XL3t GOLDD+ and has a penetration depth of a few mm.

The elements of interest in this study are heavy metals such as Lead (Pb) and Zink (Zn), Sulphur (S), Calcium (Ca) and alkali (Sodium, Na, and Potassium, K). However, the detection limit of the XRF technique is atomic number 12 (Magnesium, Mg) or higher. Thus Na (with atomic number 11) is not detectable, which is typical for this technique.

Two on-site measurement tests were performed in the early part of the project (2019). However, due to the Covid-19 pandemic, access to the boilers during 2020-2021 was impeded and instead refractory material was extracted from the boilers during maintenance shut down and sent to the RISE laboratory for XRF (off-site) laboratory measurements.

5.6.2 Scanning Electron Microscopy

Imaging of the refractory material specimen microstructure is performed using Scanning Electron Microscopy (SEM). Two different scanning electron microscopes are used: a JEOL JSM-6610LV (Low Vacuum scanning electron microscope) and a JEOL JSM-7800F (Field Emission scanning electron microscope). Typical parameters used are 15 kV accelerating voltage and 10 mm working distance. Imaging is performed with secondary electrons (SE) that show topographic contrast and with backscattered electrons (BSE) to show atomic contrast (heavier material = brighter contrast). Two complementary techniques are evaluated:

Electron Backscattered Diffraction (EBSD) for crystallographic evaluation and Energy Dispersive X-ray Spectroscopy (EDS) for elemental analysis/composition.

Crystallographic analysis (Electron Backscattered Diffraction)

Electron Backscattered Diffraction (EBSD) gives information about the crystallographic phases present, crystal orientations and texture in crystalline materials. This technique has been used for analysis of many different metallic materials (such as steels, titanium alloys, aluminium alloys, etc.). Ceramic materials have been analysed in a smaller extent, but one important field using this technique is geology. In the present project, the EBSD technique is tested and evaluated for characterisation of refractory materials.

EBSD method evaluation was performed early in the project and compared to EDS analysis in refractory material CALDE® STIX PB 85 CG. At the time of this evaluation, it was still not decided that the full evaluation of materials as a function of exposure time was going to be concentrated on only one mullite based material (CALDE® CAST LM74A). EBSD analysis is performed using a detector from Bruker, model e-Flash HR, operated with the software Esprit 2.3.

Elemental analysis (Energy Dispersive X-ray Spectroscopy)

Elemental analysis in the SEM is performed using detectors from Bruker, model XFlash 5010 and the software Esprit versions 2.1 – 2.3. EDS spectra acquisition, line scans and mapping of areas of interest are performed. From mapping data, the element distribution is examined. Also, EDS spectra are extracted from the binding phase to study the diffusion/enrichment of foreign and/or detrimental elements in the refractory materials with increasing exposure time.

5.6.3 3D scanning

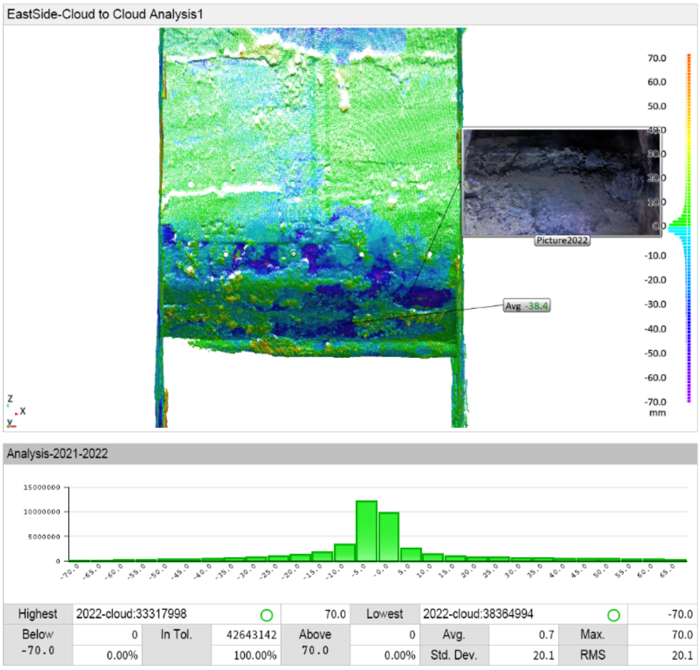
Calderys is exploring for example 3D laser scanning services ("CALDE 360"), tested under this project as well, where a full boiler/incinerator digital high accuracy point cloud is used to verify the lining surface location compared to e.g. full thickness. Mobility to scan confined spaces and difficult-to-reach areas all merged in one end file is achieved. Quick, non-destructive documentation of refractory surface status of + 1 mm up to 70 meters is possible. The Scan, software preparation, launch into the Cloud with designated accessibility was tested successful to facilitate the Maintenance Process. Furnace needed to be cool. 3D Scan was done using a Tripod, scan at min. 3-4 + locations (@10 mins each) was done. Data saved in the scanner and in the Cloud - sharable to customer to view and monitor in 3D at any place and any time.

Access anywhere, anytime through Cloud system, was confirmed. Virtual walks through of the furnace, 360° view and other features possible. Ability to take measurements on 3D images tested. Comparison with previous 3D scans from any previous years to monitor change was used in e.g. Norrköping. See Figure 54.

Figure 54 3D cloud image from multiple scan positions giving a 360 degree image fully measurable.

In Figure 55 there is a wall image where the 3D scan cloud has been used to indicate varying lining thickness due to spalling, slag build-up etc.

Customer view cloud data accessible as panoramic, 3D or point views to help investigation and decision making. Possibilities to view 3D photo like images and capture on-screen real-life distance/area measuring and wear depth indications may also be useful. Please see Figure 56 and Figure 57 below where examples from Norrköping are shown.



Highest	2022-cloud:33317998 ○		70.0	Lowest	2022-cloud:38364994 ○				-70.0
Below -70.0	0	In Tol.	42643142	Above 70.0	0	Avg.	0.7	Max.	70.0
	0.00%		100.00%		0.00%	Std. Dev.	20.1	RMS	20.1

Figure 55 3D scan cloud has been used to indicate varying lining thickness due to spalling, slag build-up etc.

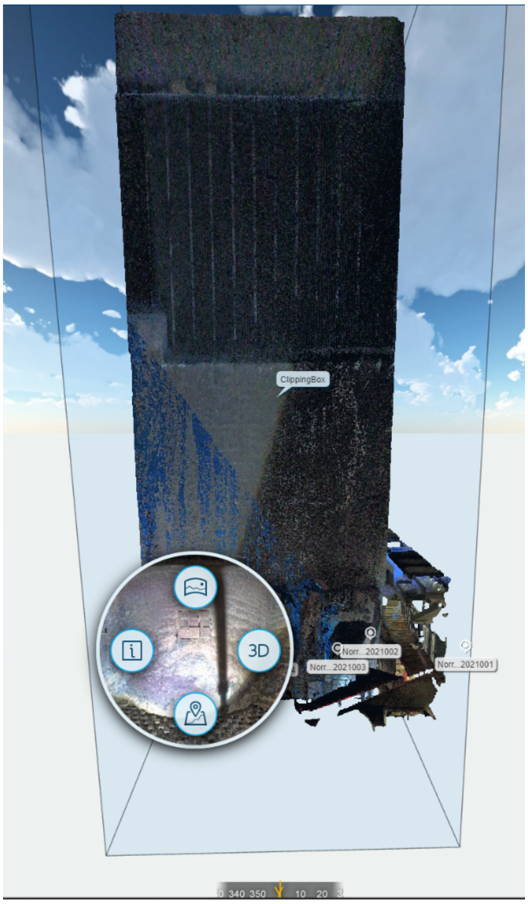


Figure 56 Use of the 3D scan cloud to orient and check detailed areas in various views such as panoramic.

Figure 57 From the image seen in Figure 56 it is one click to get a 3D view fully measurable for surface analysis.

5.6.4 Cup tests

A cup test is a test where you pour ash or similar into a cup of refractory material and expose it at different temperatures to see how the refractory material is affected by the ash. Corrosion cup-test of CALDE® SPRAYCAST SIC 70 are performed where two corrosive elements are tested.

Firstly, a standard K2CO3 powder – always much more aggressive than any boiler slag known was used. Then an ash sample received from a boiler WtE CFB P15, E.ON. Händelöverket, Norrköping was used.

Two temperatures were tested in the lab; 950°C considered being a normal CFB temperature as well as 1400°C considered to really give effect on alkali corrosion risks. One test was done with the K_2CO_3 powder, and two samples were prepared for each temperature using the ash sample as a corrosive element.

CALDE® LM 74 A was not cup tested for this project, but is prone to perform better than CALDE® SPRAYCAST SIC 70, especially at temperatures above 1500°C and when moisture is present e.g. via additives being fed to reduce emissions.

5.6.5 Ash analysis

In connection with this project an Imerys lab in Austria received a bottom ash from Waste to Energy CFB P15, E.ON, Händelöverket. The sample was characterized regarding the chemical (XRF) and mineralogical composition (XRD / Rietveld) as well as regarding the behavior during a thermal treatment (using heating microscopy). Additionally, the viscosity of the slag at higher temperatures was calculated using FactSage. The ash used for this test is extracted from E.ON. Händelö P15 and analysed by Calderys.

5.7 RESULTS

5.7.1 X-Ray Fluorescence measurements

The early XRF tests performed on-site at E.ON, Händelö, showed the potential of the method as an easy on-site evaluation method. The equipment used did only have rather general methods (Test All Mode, General metals and Electronic metals) that were not ideal for measurement of ceramic refractory materials. Therefore, later XRF laboratory measurements were performed using another equipment (same model) containing a more suitable method (Test All Geo).

XRF laboratory measurement results are given in Table 15 and Table 16 below for CALDE® CAST LM74A and CALDE® SPRAYCAST SIC 70 materials, respectively. To resemble on site measurements, the laboratory measurements are performed on the outer wall surface that has been exposed to the boiling mass during service. Thus, slag products or a mixture of refractory material and slag is expected to be analysed.

Table 15 XRF results from laboratory measurements of CALDE® CAST LM74A (normalised weight%).

Specimen	Exp.time [years]	Pb [wt%]	Zn [wt%]	Cu [wt%]	Fe [wt%]	Ti [wt%]	K [wt%]	Ca [wt%]	S [wt%]	Al [wt%]	Cl [wt%]	Si [wt%]	Bal. [wt%]
CALDE LM74-REF	0	0,0	0,0	-	0,1	0,2	0,2	2,7	0,0	22,2	-	13,3	61,2
EON LM74-7m	0,6	0,1	1,4	38,9	2,9	0,7	0,1	13,8	8,1	16,1	0,4	12,2	5,4
EON LM74-2y	2	0,0	0,5	0,1	1,2	1,3	0,2	26,7	21,5	1,4	0,1	2,3	44,8
ME LM74-7y	7	0,0	1,3	0,3	3,0	1,1	0,8	14,3	6,8	2,6	7,4	3,6	58,8

Notice that the material extracted from Mälarenergi (specimen ME LM74-7y) is from a different material batch compared to the CALDE and EON materials (specimens CALDE LM74-REF and EON LM74-7m/2y). This needs to be kept in mind when comparing element concentrations and searching for trends.

No elevated concentrations of heavy metals such as Pb and Zn are detected in the CALDE® CAST LM74A material after exposure times up to 7 years. Notice that the measurement performed after 7 months (EON LM74-7m) shows high concentration of Copper (Cu) and low balance (where Oxygen, O is included), indicating that the area measured probably contains high amount of metallic Cu.

Table 16 XRF results from laboratory measurements of CALDE® SPRAYCAST SIC 70 (normalised weight%).

Specimen	Exp.time [years]	Pb [wt%]	Zn [wt%]	Cu [wt%]	Fe [wt%]	Ti [wt%]	K [wt%]	Ca [wt%]	S [wt%]	Al [wt%]	Si [wt%]	Bal. [wt%]
CALDE SiC-REF	0	-	0,0	0,0	0,1	0,0	0,2	2,9	0,1	20,7	23,8	52,0
EON SiC-6m	0,5	0,0	22,1	0,5	1,8	1,1	0,1	18,9	16,5	2,0	3,5	29,5
EON SiC-1y	1	-	0,3	0,6	0,7	0,6	0,8	10,2	6,8	1,4	7,5	70,0
EON SiC-2y	2	0,0	0,3	0,4	0,5	0,7	2,0	11,6	4,2	2,7	8,7	57,6
ME SiC-6y	6	0,0	1,3	0,6	4,0	1,0	1,6	8,8	4,9	1,7	7,5	53,7
ME SiC-7y	7	0,2	0,3	12,4	1,2	0,0	1,3	1,2	2,9	4,6	11,5	62,0

As seen in Tables 5.4 and 5.5, the concentrations of K, Ca, S increase with exposure time in both materials (CALDE® CAST LM74A and CALDE® SPRAYCAST SIC 70). Furthermore, the concentrations of Ca and S are significantly higher than the concentration of K. No elevated concentration of Pb is detected in the SiC-based material. The Zn concentration is also generally very low, except for the measurement performed after 6 months (EON SIC-6m) where high concentration of Zn and low balance (where O is included), indicating that the measured area probably contains an elevated amount of metallic Zn.

When performing XRF laboratory measurements on extracted material from the boilers, the specimens were limited to small sizes. As is seen, in both tables (5.4 and 5.5) there was one measurement showing presence of high metallic content (Cu in CALDE® CAST LM74A and Zn in CALDE® SPRAYCAST SIC), which most probably is not representative of the whole slag/wall composition. To minimise this effect, it is suggested that future on-site XRF measurements are performed on several points over an area on each sampling position.

5.7.2 Scanning Electron Microscopy

Crystallographic analysis (Electron backscattered diffraction)

Analysis of refractory material (CALDE® STIX PB 85 CG) shows that the Al_2O_3-phase gives diffraction patterns and can be indexed, see Figure 58. No other crystalline phases are identified and/or indexed in the material (in the binding phase and/or other crystals), even after several attempts at varying magnifications and using different diffraction pattern resolution.

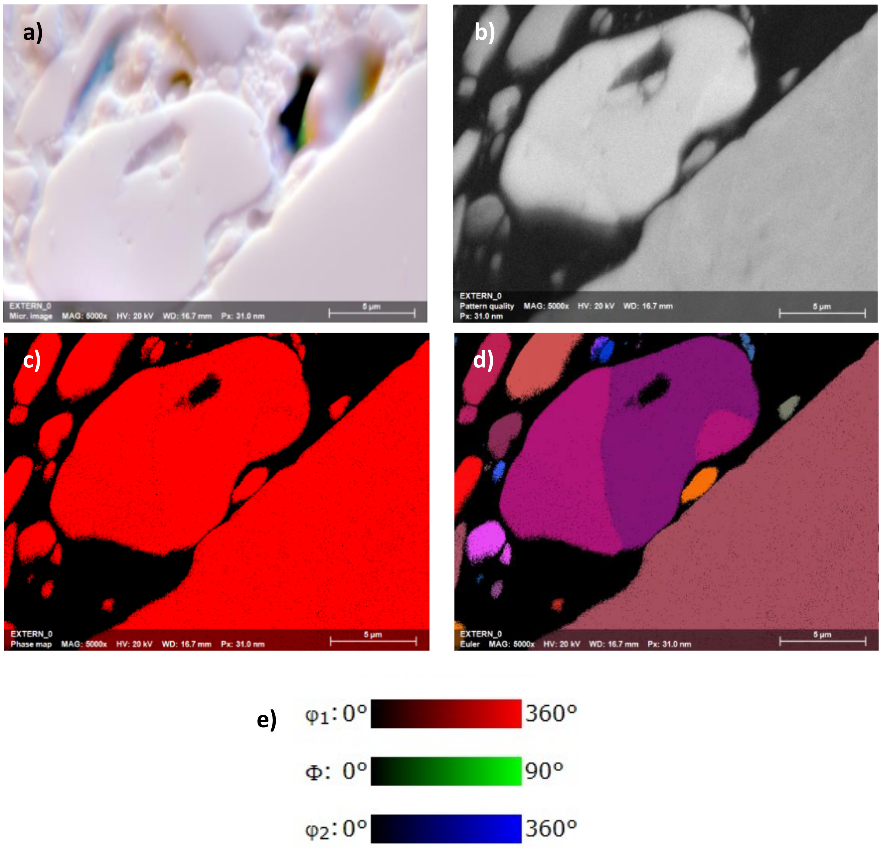


Figure 58 ***a) Forward scattered electron (FSE) image of CALDE® STIX PB 85 CG reference (0 years) taken at x5000, with corresponding EBSD maps: b) pattern quality map, c) phase map (red = Al_2O_3), d) Euler angle orientation map, and e) corresponding Euler angle legend.***

The main interest in this project is studying the change in composition and enrichment of diffusing elements into the refractories, which is expected to occur preferentially in the binding phase. As seen, the EBSD technique only gave indexing of the mullite-crystals, and no other crystalline phases are detected. Therefore, elemental analysis by EDS is chosen as the main SEM-based analysis technique for detailed analysis of the refractory materials.

Elemental analysis (Energy dispersive X-ray spectroscopy)

SEM and EDS images of the studied refractory material microstructures are given in this section. The microstructures at different magnifications are shown in Figure 59 and Figure 60 for the CALDE® CAST LM74A and CALDE® SPRAYCAST SIC 70 materials, respectively. The corresponding EDS measurement results are shown in Figure 61 - Figure 65 and Table 17 - Table 18.

The microstructures of CALDE® CAST LM74A and CALDE® SPRAYCAST SIC 70 consist of crystals, both large (hundreds of micrometres) and smaller (tens of micrometres), dispersed in a binding phase, see Figure 59 and Figure 60.

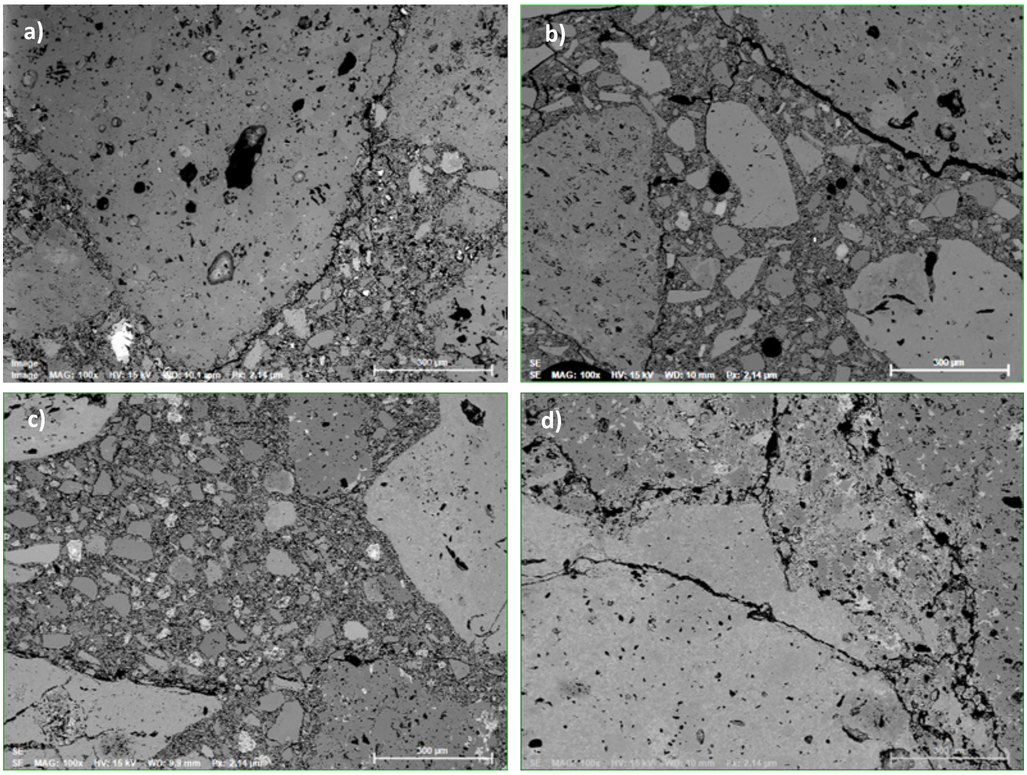


Figure 59 ***SEM-images of CALDE® CAST LM74A after different exposure times: a) reference, 0 years (specimen CALDE LM74-REF); b) 7 months, 0.6 years (specimen EON LM74-7m); c) 2 years (specimen EON LM74-2y); and d) 7 years (specimen ME LM74-7y). Notice that the material extracted from Mälarenergi (specimen ME*) is from a different material batch compared to the CALDE and EON materials (specimens CALDE* and EON*).***

Diffusion of foreign and/or detrimental elements into the refractory materials is expected to mainly occur in the binding phase. Therefore, analysis of the element composition in the binding phase with increasing exposure time is of great interest. Cross section specimens of refractory materials extracted from the boilers are prepared and analysed 1 – 2 cm below the wall surface.

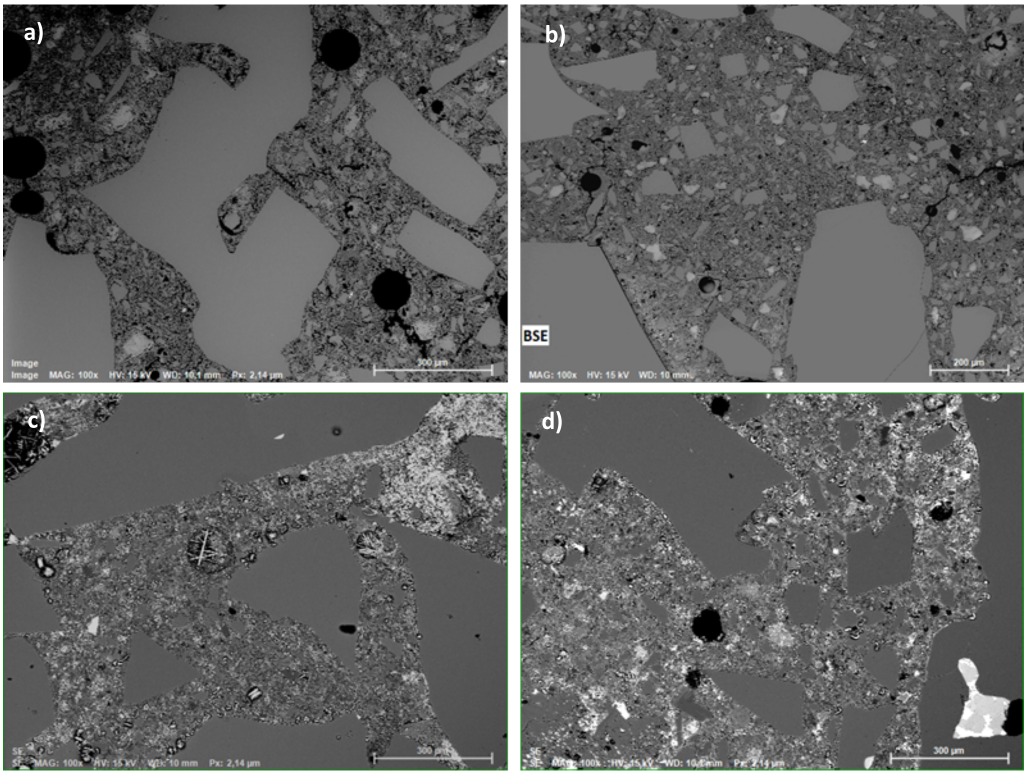


Figure 60 ***SEM-images of CALDE® SPRAYCAST SIC 70 after different exposure times: a) reference, 0 years (specimen CALDE SIC-REF); b) 6 months, 0.5 years (specimen EON SIC-6m); c) 2 years (specimen EON SIC-2y); and d) 7 years (specimen ME SIC-7y). Notice that the material extracted from Mälarenergi (specimen ME*) is from a different material batch compared to the CALDE and EON materials (specimens CALDE* and EON*).***

EDS mapping of the reference microstructures of CALDE® CAST LM74A and CALDE® SPRAYCAST SIC 70 are shown in Figure 61 and Figure 62 below. In the EDS maps it is possible to see the distribution and relative concentration of the main constituents of the refractory materials studied. Notice that the element concentration scale is colored from 0 to 50 wt% (normalized).

CALDE® CAST LM74A is a mullite based material with the main constituents O, Al, Si, Ca and Fe. As seen in the EDS maps shown in Figure 61 b-f, all these elements are present in the binding phase, the largest crystals in the microstructure are rich in Al and O (Al_2O_3), and the smaller consist of Si and O (SiO_2), Ca and O (CaO) and Fe and O (Fe_3O_4, very small amounts).

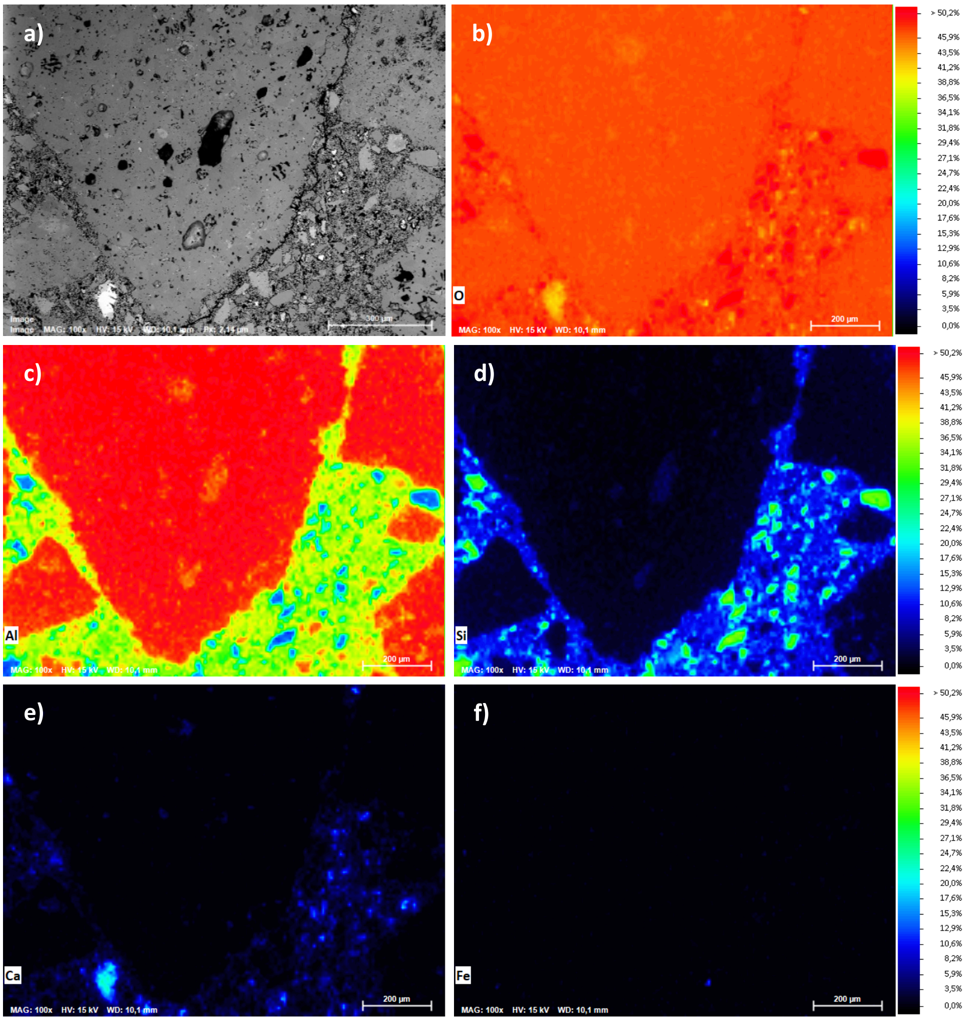


Figure 61 a) SEM-image of CALDE LM74-REF (exposure time 0 years), and corresponding EDS maps for main constituent elements (colour scale with maximum 50 weight%): b) O; c) Al; d) Si; e) Ca; and f) Iron (Fe).

CALDE® SPRAYCAST SIC 70 is a silicon carbide material with the main constituents C, O, Al, Si, Ca and Fe. As seen in the EDS maps shown in Figure 62 b-f, all these elements are present in the binding phase, the largest crystals in the microstructure are rich in Si and C (SiC), and the smaller consist of Si and O (SiO2), Al and O (Al2O3), and Ca and O (CaO).

Analysis of the binding phase is performed as shown in Figure 63, and results are presented in Table 17 and Table 18 and diagrams in Figure 64 and Figure 65.

When comparing the results after as a function of exposure time, it is important to keep in mind that the materials extracted from Mälarenergi (exposed 6-7 years) are from different material batches compared to the CALDE reference materials and the exposed materials from E.ON, Händelö. Also, the environments inside the boilers are most probably not identical to each other, i.e. there may be differences in chemistry of the waste, operating parameters, etc.

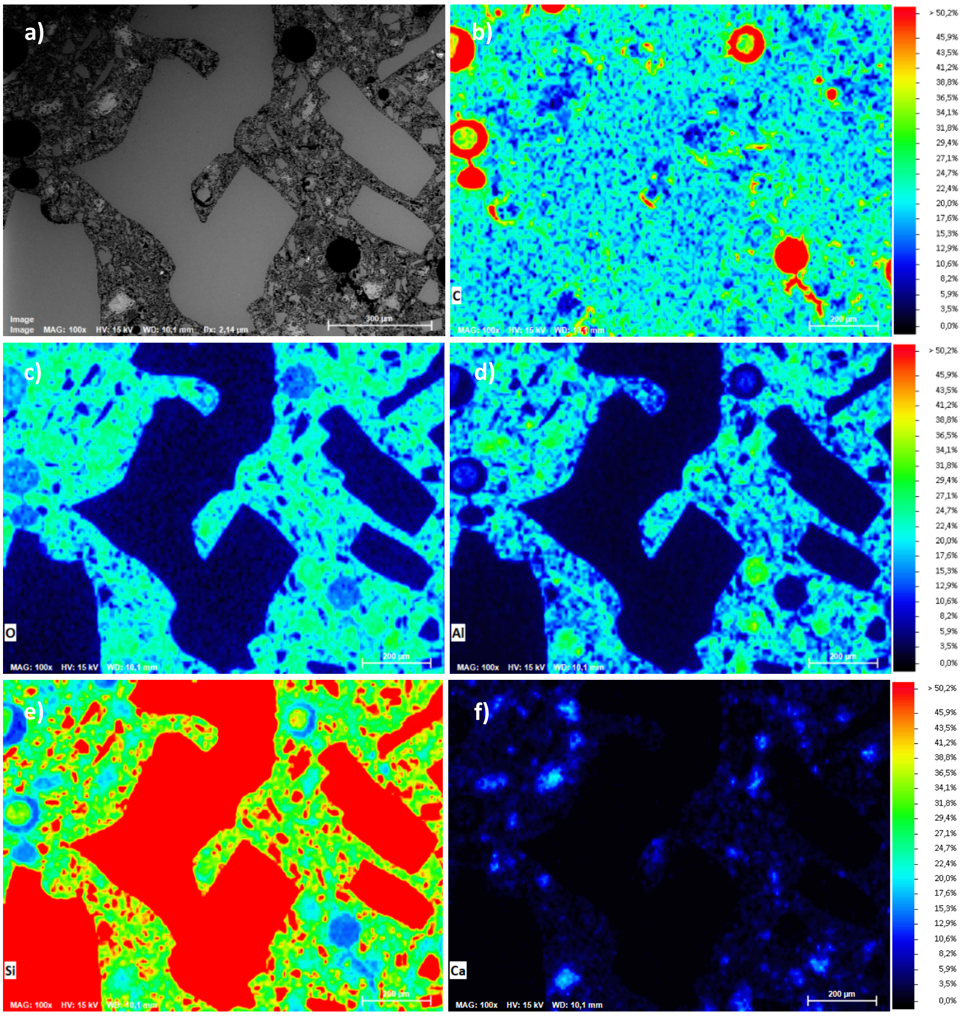


Figure 62 a) SEM-image of CALDE SIC-REF (exposure time 0 years), and corresponding EDS maps for main constituent elements (colour scale with maximum 50 weight%): b) C; c) O; d) Al; e) Si; and f) Ca.

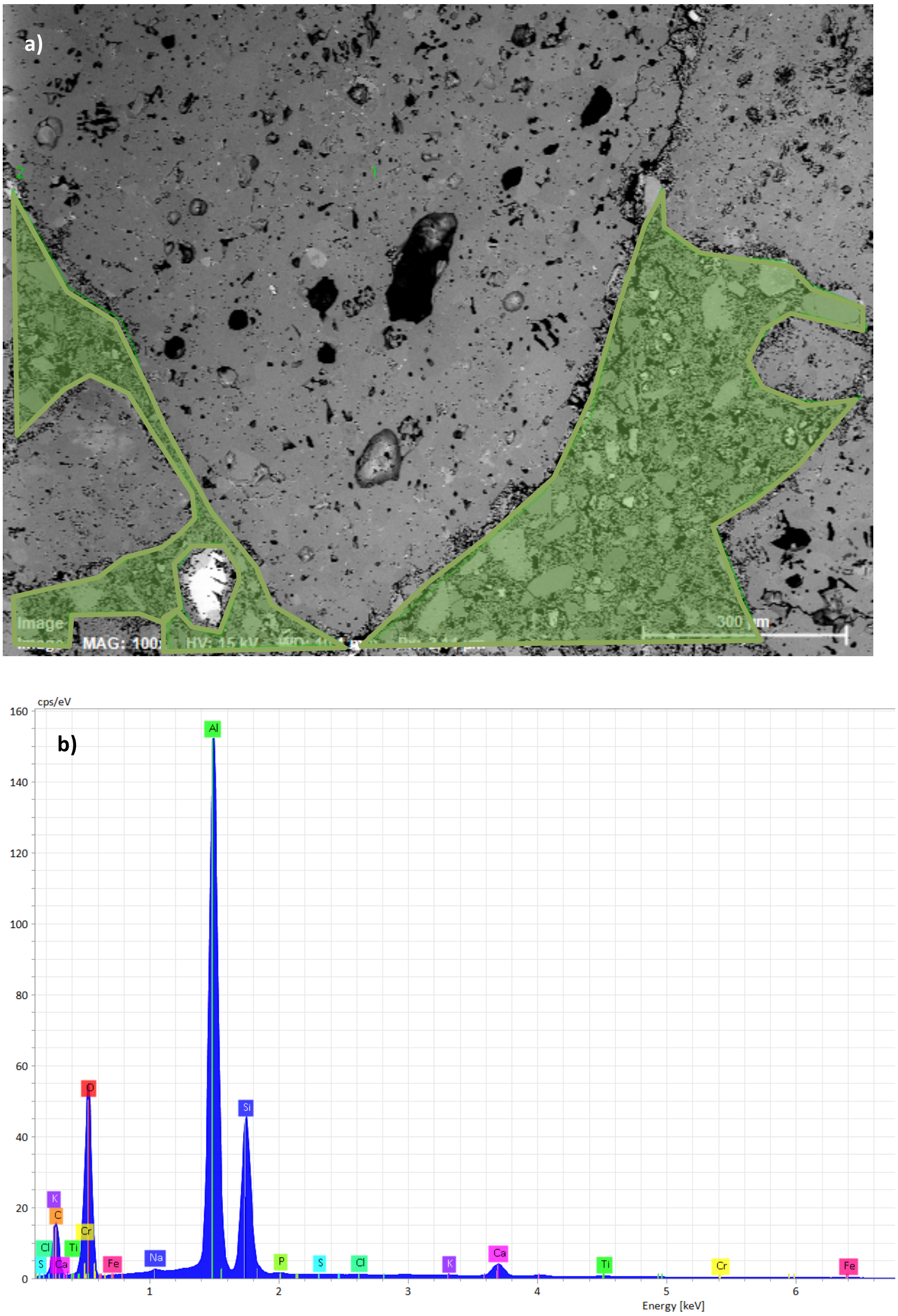


Figure 63 a) SEM image of refractory microstructure; b) EDS spectrum from binding phase (corresponding to green area marked in figure a).

Table 17 Semi quantitative EDS analysis results: composition of binding phase in CALDE® CAST LM74A (normalized weight %).

	Exp time	O	Na	Al	Si	P	S	Cl	K	Ca	Ti	Fe
	[years]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]
CALDE LM74-REF	0	48,1	**0,2**	34,2	14,1	0,2	**0,0**	0,1	**0,1**	**2,4**	0,3	0,2
EON LM74-7m	0,6	48,5	**1,1**	28,9	18,1	0,2	**0,3**	0,0	**0,3**	**2,0**	0,3	0,2
EON LM74-2y	2	48,0	**0,6**	29,5	17,3	0,1	**0,0**	0,1	**0,5**	**3,3**	0,3	0,3
ME LM74-7y	7	46,7	**2,8**	28,9	14,8	0,2	**0,7**	0,4	**2,0**	**2,7**	0,3	0,5

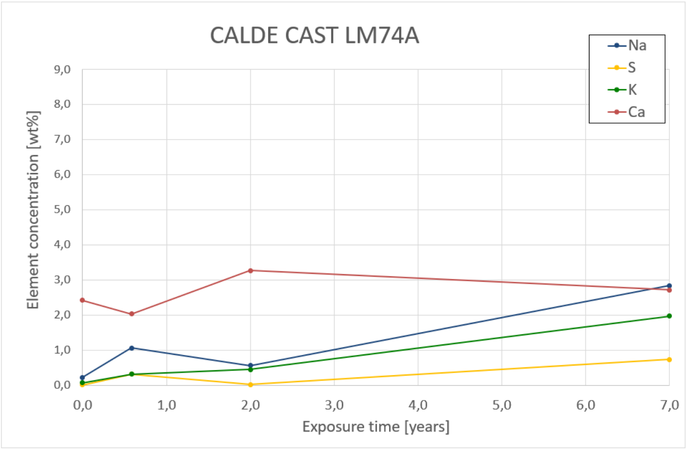


Figure 64 Element concentration as a function of exposure time in CALDE® CAST LM74A. Notice that the material exposed for 7 years is from a different material batch compared to the other materials.

For the CALDE® CAST LM74A material, there is a good correlation between the material extracted from E.ON. and Mälarenergi. In general, the amounts of Ca, S and alkali (Na, K) increase somewhat with exposure time in the binding phase, but the levels are very low. No Pb and/or Zn is detected by EDS analysis in the binding phase (1-2 cm under the surface) after exposure.

Table 18 Semi quantitative EDS analysis results: composition of binding phase in CALDE® SPRAYCAST SIC 70 (normalized weight %).

	Exp time	C	O	Na	Al	Si	S	Cl	K	Ca	Ti	V	Fe	Cu	Zr
	[years]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]
CALDE SiC-REF	0	27,3	22,8	**0,1**	15,5	29,8	**-**	0,1	**0,2**	**3,7**	-	-	0,1	-	0,3
EON SiC-6m	0,5	23,6	26,3	**0,2**	18,2	27,0	**0,1**	0,1	**0,2**	**4,0**	-	-	0,1	-	0,2
EON SiC-2y	2	8,7	27,4	**8,3**	16,0	19,7	**3,5**	7,9	**3,0**	**4,4**	0,1	-	0,2	-	0,2
ME SiC-7y	7	9,5	26,1	**5,6**	16,7	21,3	**2,6**	8,1	**3,6**	**3,8**	0,1	0,1	0,6	1,7	0,2

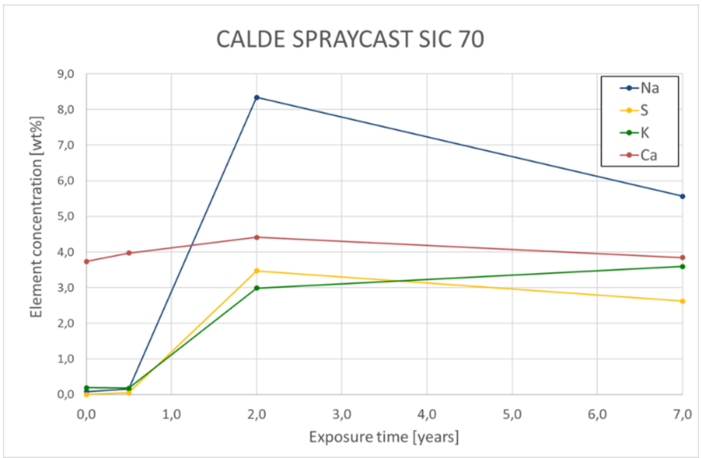
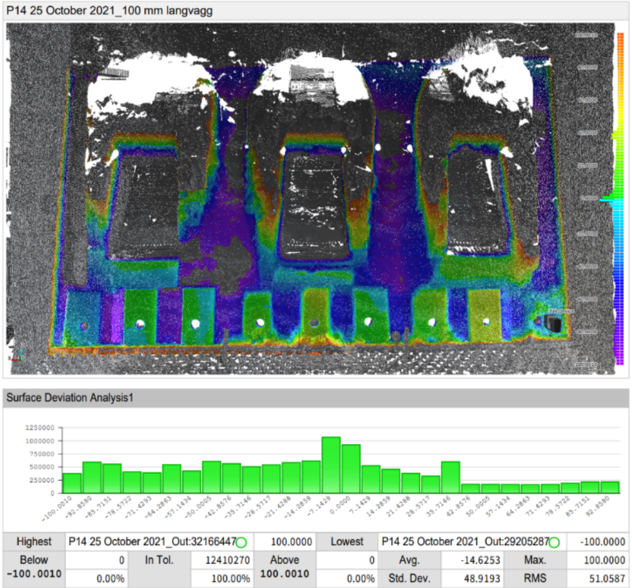


Figure 65 Element concentration as a function of exposure time in CALDE® SPRAYCAST SIC 70. Notice that the material exposed for 7 years is from a different material batch compared to the other materials.

For CALDE® SPRAYCAST SIC 70, the measured concentrations of elements in the binding phase are not increasing gradually with exposure time: the concentrations of S and alkali (Na, K) are somewhat higher after 2 years at E.ON. compared to after 7 years at Mälarenergi. This may be due to differences in the waste chemistry, operating parameters, etc used in the different boilers. The general trend seems to be that the concentration of S and alkali (Na, K) in the binding phase starts increasing after 0,5 years and stabilizes after 2 years exposure time. The concentration of Ca however seems to stay rather constant. Like for the mullite based refractory material, no Pb and/or Zn is detected in the binding phase after exposure (1-2 cm under the surface).

5.7.3 3D scanning

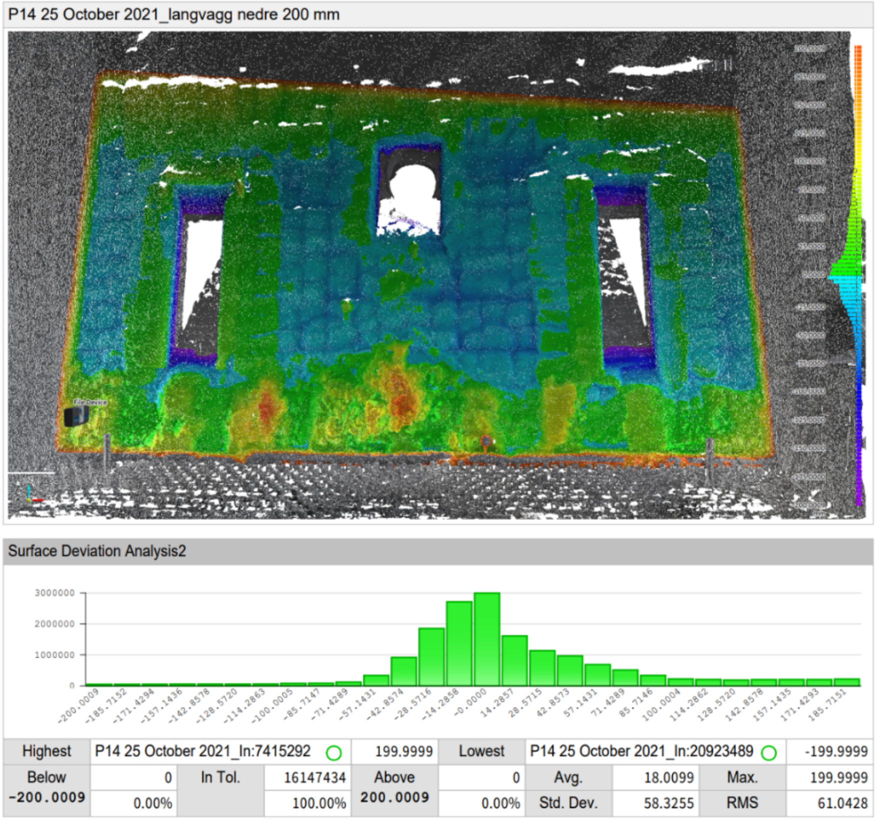
Examples used in this project can be seen in Figure 66– Figure 69 below.



Highest	P14 25 October 2021_Out:32166447○			100.0000	Lowest	P14 25 October 2021_Out:29205287○			-100.0000
Below -100.0010	0	In Tol.	12410270	Above 100.0010	0	Avg.	-14.6253	Max.	100.0000
	0.00%		100.00%		0.00%	Std. Dev.	48.9193	RMS	51.0587

Figure 66 3D software used to show refractory lining surface deviations in a rainbow scale.

Figure 67 The same 3D cloud instead shown as a 3D view to help increase the ease of understanding.

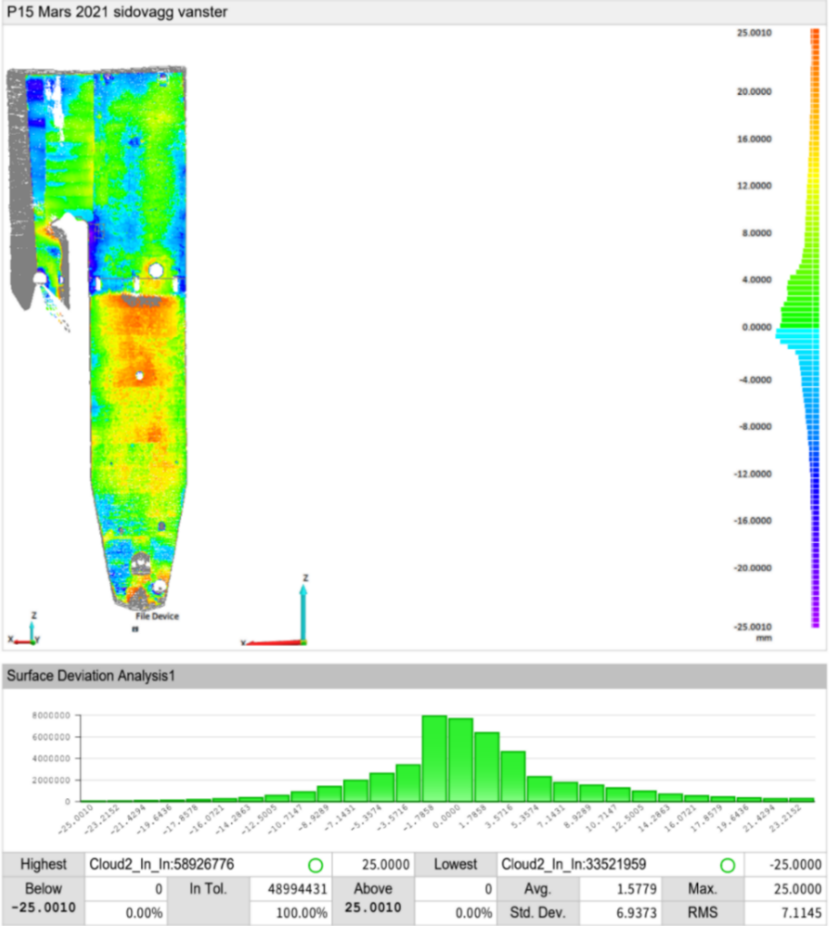


P14 25 October 2021_langvagg nedre 200 mm

Surface Deviation Analysis2

Highest	P14 25 October 2021_In:7415292 ○			199.9999	Lowest	P14 25 October 2021_In:20923489 ○			-199.9999
Below -200.0009	0	In Tol.	16147434	Above 200.0009	0	Avg.	18.0099	Max.	199.9999
	0.00%		100.00%		0.00%	Std. Dev.	58.3255	RMS	61.0428

Figure 68 Refractory lining surface deviations in a rainbow scale on the opposite wall.



<table>
<tr><td>Highest</td><td colspan="3">Cloud2_In_In:58926776 ○</td><td>25.0000</td><td>Lowest</td><td colspan="3">Cloud2_In_In:33521959 ○</td><td>-25.0000</td></tr>
<tr><td rowspan="2">Below
-25.0010</td><td>0</td><td rowspan="2">In Tol.</td><td>48994431</td><td rowspan="2">Above
25.0010</td><td>0</td><td>Avg.</td><td>1.5779</td><td>Max.</td><td>25.0000</td></tr>
<tr><td>0.00%</td><td>100.00%</td><td>0.00%</td><td>Std. Dev.</td><td>6.9373</td><td>RMS</td><td>7.1145</td></tr>
</table>

Figure 69 Full boiler side wall indicating lining surface deviation using the rainbow scale.

Results on the 3D scanning method was that is working well and with high accuracy giving output on the surface compared to either a best fit flat surface or compared to previous historic 3D scan cloud images.

5.7.4 Cup tests

Photos of the CALDE® SPRAYCAST SIC 70 cup-test specimens are shown in Figs. Figure 70 - Figure 72 for the three different corrosive environments: K_2CO_3, ash sample (1) and ash sample (2), respectively.

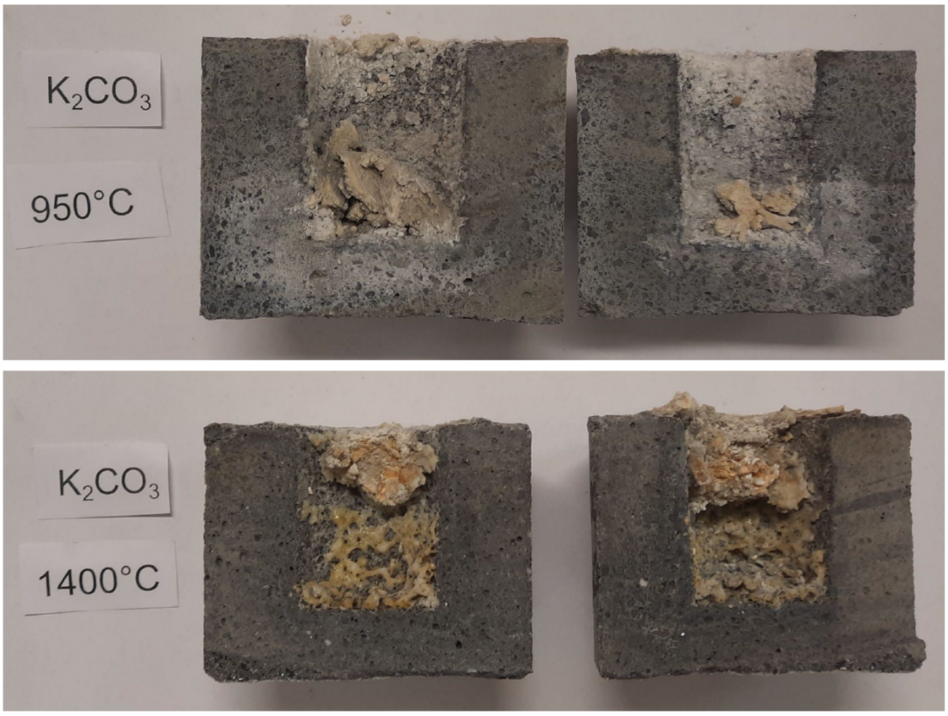


Figure 70 Photos of CALDE® SPRAYCAST SIC 70 cup-test specimens tested with K_2CO_3.

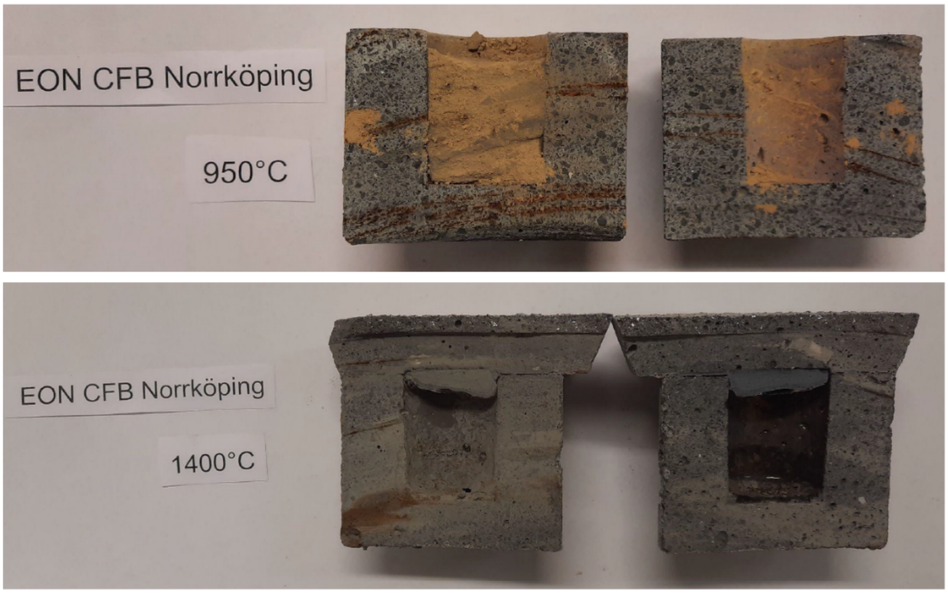


Figure 71 Photos of CALDE® SPRAYCAST SIC 70 cup-test specimens tested with ash sample (1).

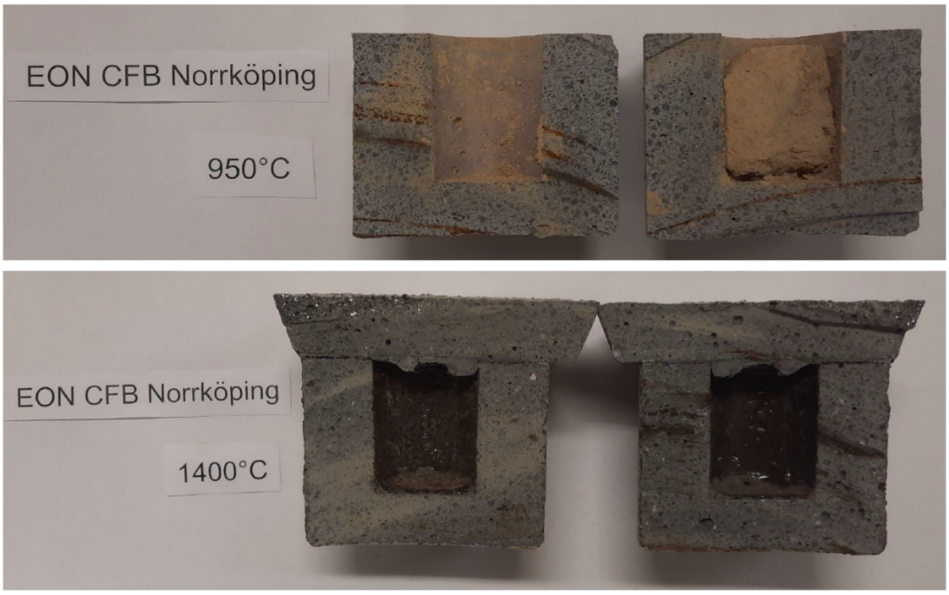


Figure 72 Photos of CALDE® SPRAYCAST SIC 70 cup-test specimens tested with ash sample (2).

CALDE® SPRAYCAST SIC 70 is a very corrosive resistant material against alkali (K_2CO_3) attack at both 950°C and 1400°C. Virtually no infiltration into the material of the potassium powder can be observed. Some traces of white powder in the picture at 950°C is something that has happened during the sawing of the samples after the test.

CALDE® SPRAYCAST SIC 70 also has not suffered any degradation from the ash sample at either of the two temperatures tested. At 1400°C we can see that the ash sample has melted. Some of the material is glued to the surface of the refractory material but without infiltration or generation of cracks. Most of the ash at 1400°C seems to have recondensed on the top cover of the sample resulting in the fact that the cover has got stuck on top of the cup sample.

To see what could happen if wrongly choosing a non-alkali resistant product we used an historic example of an 80% Al_2O_3 product (mullite/tab alumina based low cement castable) not suitable for the alkali rich combustion condition. This can be seen in Figure 73 below where a photo of another refractory (not from present study) is used only to exemplify what can happen. The “A” type products, i.e. alkali resistant, have been developed and improved during more than 20 years.

5.7.5 Ash analysis

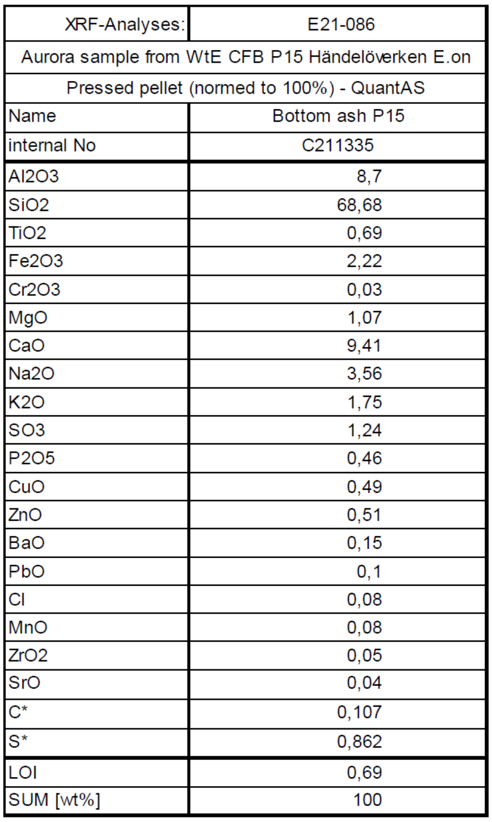
The results from ash analysis performed on ash extracted from E.ON, Händelö P15 and analysed by Calderys are given in Table 19 and Table 20.

Figure 73 Photos of a high-quality refractory without the proper alkali resistance needed.

Table 19 Mineralogical composition (XRD) of the bottom ash.

XRD-Analyses:	E21-086
Aurora sample from WtE CFB P15 Händelöverken E.on	
Rietveld Analysis	
Name	Bottom ash P15
internal No	C211335
Albite	6,3
Anorthite	8,4
Orthoclase	2,7
Andesine	0,8
Akermanite	0,3
Gehlenite	3,2
Diopside	7,1
Larnite	trace
Wollastonite	1
Mullite	1,8
Quartz	40
Spinel	0,3
Rutile	1
Hematite	trace
Corundum	1
Apatite	1
Al-Phosphate	trace
Anhydrite	1,3
Amorphous	23
SUM [wt%]	**99,2**

Table 20 Chemical analysis (XRD) of the sample.



XRF-Analyses:	E21-086
Aurora sample from WtE CFB P15 Händelöverken E.on	
Pressed pellet (normed to 100%) - QuantAS	
Name	Bottom ash P15
internal No	C211335
Al2O3	8,7
SiO2	68,68
TiO2	0,69
Fe2O3	2,22
Cr2O3	0,03
MgO	1,07
CaO	9,41
Na2O	3,56
K2O	1,75
SO3	1,24
P2O5	0,46
CuO	0,49
ZnO	0,51
BaO	0,15
PbO	0,1
Cl	0,08
MnO	0,08
ZrO2	0,05
SrO	0,04
C*	0,107
S*	0,862
LOI	0,69
SUM [wt%]	100

* LECO analysis

From the results shown it becomes clear that the composition of the sample regarding the chemical as well as the mineralogical constituents is very complex.

The bottom ash consists mainly of lime and silica with quartz and several Ca compounds as dominant phases. Additionally, the sample contains a high amount of amorphous material. In addition to the main elements, the sample also contains some trace components, partly obviously different metal oxides as well as a small number of volatile elements (P, S, Cl).

The total amount of alkalis is with 5 – 6% within an intermediate range. The Na level is significantly higher than the potassium content. These components are obviously mainly bonded in silicates like the detected feldspars but to a certain amount probably also within the amorphous phase.

Besides the chemical and mineralogical composition, the softening and melting behaviour of the samples in dependence on temperature was also investigated. For this a heating microscope from Hesse Instruments GmbH / Germany was used, see result diagram in Figure 74.

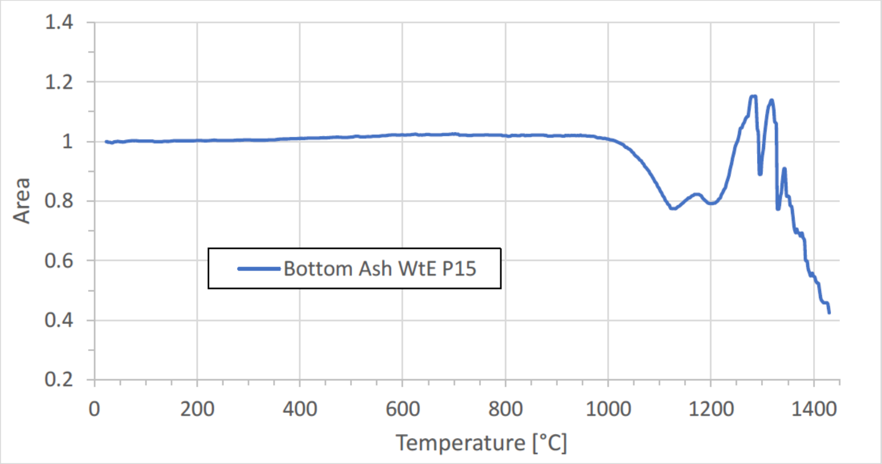


Figure 74 Heating microscopy course for the sample area.

The softening and melting temperatures are given in Table 21. The softening temperature is determined as the temperature at which the test piece has rounded corners and its height corresponds to the length of its baseline (DIN 51730:2007). The melting temperature is determined according to DIN 53710:1984 (the sample height has attained one third of its initial height).

Table 21 Characteristic temperatures of the sample.

Sample	Softening [°C]	Melting [°C]
Bottom Ash	1153	1430

In Figure 75 the result of a viscosity calculation by using FactSage is shown.

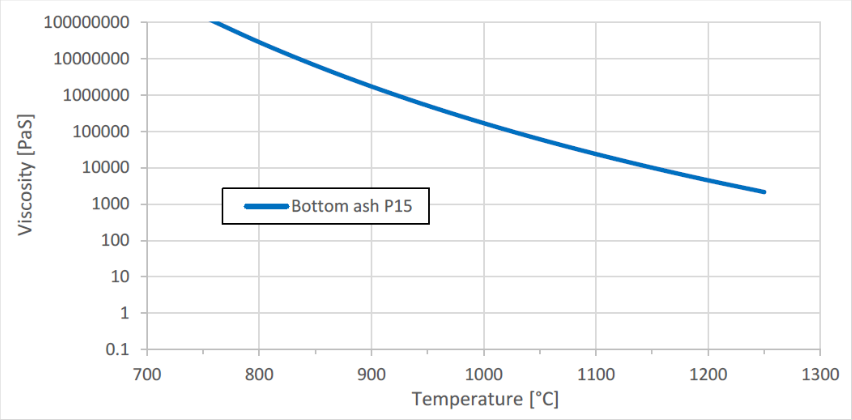


Figure 75 Slag viscosity calculation using the FactSage.

Since the content of volatiles and other special impurities is relatively low, for this calculation 97% of the total composition are considered (e.g. P_2O_5, BaO, CuO, S, C, Cl are not included). Therefore, the calculated data seem to be quite reliable.

From the graph in Figure 75 it can be seen that the viscosity is relatively high which can be directly related to the relatively high amount of silica.

5.8 DISCUSSION

The presence of heavy metals and/or alkali that can deteriorate refractory materials has been studied through advanced analysis of exposed material with respect to changes in structure or chemistry. Both on-site experimental methods (XRF) and laboratory methods (SEM-based techniques) have been tested and evaluated.

The XRF technique is evaluated in this study as a fast and easy on-site measurement method. Two early test measurements were performed at E.ON, Händelö during 2019. However, due to the Covid-19 pandemic, access to the boilers during 2020-2021 was impeded and instead extracted refractory material were analysed off-site. These measurements were conducted to resemble on-site measurements as much as possible. The method is found fast and simple and can give a good indication of what is present on the outer surface of the slag, but to obtain representative data it is suggested that several measurements are performed over an area. However, a limitation of this method is that very little can be said about the detrimental element concentration inside the refractory materials.

On mullite based refractories tested no significant accumulation of alkali (Na, K) and/or S is observed over time, neither in the bulk nor in the binding phase. The alkali resistant products from Calderys have a name suffix "A" (Alkali resistant). This feature is designed in the refractory formulations by assuring alkali resistance of both the bond system and the grain/bulk system as well as minimising refractory in-situ porosity.

On high amount SiC based materials there is only a small accumulation of K, Na, S over time. This product type is chosen solely due to its higher heat conductivity, suitable in various places as the fuel has higher calorific values today due to e.g. less organic fractions present than historically.

We also can conclude that any unwanted accumulation of heavy metals, e.g. Pb, inside the refractories over time was not seen either, as a result of the refractory formulation.

When evaluating elemental analysis results from the different techniques used in this project, it is important to consider that XRF measurements are performed on the wall surface (where mostly slag is analysed) while EDS measurements are performed in the binding phase of the refractories approximately 1 – 2 cm under the wall surface. Thus, the concentrations of elements obtained with the two techniques are not directly comparable.

A great effort is made in finding improved ways of inspecting refractories within the power plant industry, both in general and in particular as a part of this project, in order to prolong reliable operation without unnecessary replacement or unexpected failures. Results from 3D scanning and cup tests show that these are useful complementary methods that can be employed to analyse and predict alkali resistance.

There is a need for flexibility within the refractory materials available, due to changes in waste fuel over time. Thus, continuous monitoring of waste fuel and refractories used is needed. For example, as more biowastes are separated from the municipal solid waste leads to a higher calorific value of the general solid waste fuel. Thus, there is a need of "cooling" the boilers via e.g. the use of SiC containing products. When the future encouragements to separate more fractions, by e.g. excluding also plastics from the municipal solid waste, a fuel with relatively lower calorific values is obtained and boiler adjustment will be needed accordingly (not become too "cool").

5.9 CONCLUSIONS WP4

Refractory materials evaluated in this study are shown to be very resistant against alkali compounds. Diffusion of heavy metals and alkali species is very limited during service, and there are no signs of significant wear or chemical attack (corrosion) on the refractories during exposure (up to 6-7 years).

The work within this project has contributed to an increased understanding about new supportive methods for inspecting refractory condition in boilers, such as on-site XRF analysis, 3D scanning, ash analysis and cup tests.

6 WP5 – Excellence in performance

6.1 OPPORTUNITIES TO ACHIEVE EXCELLENCE IN PERFORMANCE

An overarching aim of this project has been to understand which material challenges are most critical towards increased fuel flexibility and operational performance of boilers with challenging fuels. It has also been aimed to find ways to handles these. From collection of experiences from seven different boilers, five types of important challenges have been identified: studding materials for attachment of refractory materials in the furnace, erosion patterns of refractory materials in cyclone, erosion and corrosion of tube and tubes shields in superheater, sooting strategies and changing in the waste fuel composition and humidity which affects the incineration of the fuel. These findings and opportunities, including any more detailed information that could be retrieved with respect to each of them, were tried to be incorporated into the research work of this project as far as feasible within the scope and plan that were set for the project. Yet, they still provide for a number of possible topics for future work. In particular, sooting strategies and fuel humidity were not addressed specifically in this work. More details of the identified opportunities for future work are given in Section 2.3.

The possibility of overcoming several of the challenges requires materials with improved capabilities to withstand erosion-corrosion. Field tests with new coating materials have been made for both positions where the test materials have been cooled from the underside and where it was left uncooled at position with a high flue gas temperature. The field test with cooled materials did not show an improved performance of the newly developed FeCrAl coating materials compared to the state-of-the-art alloy 625 coating. However, the tests showed that there is good potential in the material type. On the other hand, the field test performed with uncooled specimens showed that the coating Amdry 510 applied by HVOF had the best behaviour of all the tested materials. This test was done in a boiler inside the manifold duct just before the vertical empty pass where the temperature was approximately 900 °C and could reach temporarily a maximum of 950 °C, and the flue gas flow was considered somewhat erosive. Amongst the surpassed tested materials was solid 253 MA, which is a state-of-the-art material for these conditions, as well as alloy 625. Thus, it can be concluded that HVOF applied Amdry 510 coating, which is new to this application, has potential to improve material performance significantly for uncooled parts.

Refractory materials evaluated in this study are shown to be very resistant against alkali compounds. Diffusion of heavy metals and alkali species is very limited during service, and there are no signs of significant wear or chemical attack (corrosion) on the refractories during exposure (up to 6-7 years).

The work within this project has contributed to an increased understanding about new supportive methods for inspecting refractory condition in boilers, such as on-site XRF analysis, 3D scanning, ash analysis and cup tests.

An important design question in boilers is whether to put refractory or not on the upper parts of the water walls of the furnace and some following flue gas paths with high gas temperature. Two factors are at play here. One is the amount of cooling of the flue gas that is wanted at the top of the furnace. The other is the life expectancy of the materials. A change in cooling can be desired to allow the boiler to operate with another or more flexible fuel mixture, depending on the heat value (also known as calorific value) of the new mixture. However, adding or removing refractory to encompass this comes with material challenges. This work has provided insight to what can be promising materials for both cases, with evaluation of alkali resistant refractory materials as well as of coating materials capable of withstanding high temperatures and erosive environment. For cases where a choice is required that needs both good heat transfer and refractory, a SiC containing refractory can be chosen.

6.2 PROJECT GOAL FULFILMENT

The overarching long-term aim of the project was to aid the change of combined heat and power production to become completely renewable with high fuel flexibility and reliable operation. It shall allow for environmentally friendly energy recovery with high efficiency from recycled fuels containing heavy metals that would be difficult to reuse by other means.

> *It is considered that the project has supported this aim by identifying and investigating boiler parts that was found to be prone to failure under these conditions, and by evaluating materials performance regarding both refractory and metallic materials, as well as investigating new inspection methods for refractories.*

The project goals were that for boilers operating with challenging fuels:

- To achieve a generalised understanding of which are the most important challenges with respect to operational parameters, without being boiler specific and with the purpose of facilitating increased fuel flexibility and performance.

  > *It is considered that the project has fulfilled this goal by finding similarities in challenges from seven different boilers.*

- To obtain new knowledge on how heavy metals in deposits influence corrosion of cooled parts in boilers, that is when exposed to a heat flux causing a temperature gradient.

  > *It is considered that the project has fulfilled this goal by performing in-depth metallographic investigation of materials from a field exposure with cooled materials in a boiler where heavy metals are abundant.*

- To gain an understanding of the corrosion performance and processes related to the use of new or improved coating materials with the purpose of allowing implementation or further improvements.

  > *It is considered that the project has fulfilled this goal by performing in-depth metallographic investigation of materials from two field exposures with coating materials in boilers where heavy metals are abundant.*

- To identify, if possible, 1-2 coating candidates that appear to have the potential to improve the life performance by 20 %.

  > *It is considered that the project has fulfilled this goal by identifying at least one coating material that during particularly challenging exposure conditions was behaving significantly better than today's state-of-the-art materials.*

- To find targeted solutions for the challenges experienced by mostly uncooled components.

  > *It is considered that the project has fulfilled this goal by identifying at least one coating material together with a coating application procedure which resulted in that during particularly challenging exposure conditions the coating was behaving significantly better than today's state-of-the-art materials.*

- To obtain new knowledge on how corrosive fuel components degrade refractories with the purpose of allowing further improvements.

  > *It is considered that the project has fulfilled this goal by performing in-depth microstructural investigation of materials from several field exposures with refractory materials in boilers where heavy metals are abundant.*

- To find improved ways of inspecting refractories allowing prolonged reliable operation without unnecessary replacement or unexpected failures.

  > *It is considered that the project has fulfilled this goal by investigating several new techniques of inspection of refractories, whereof at least one 3D field inspection technique appears promising.*

- To identify, if possible, 1-2 refractory material candidates that appear to have the potential to improve the life performance by 20 % or decrease the need of replacements correspondingly.

  > *It is considered that the project has fulfilled this goal by performing several field exposures with refractory materials in boilers, where heavy metals are abundant and where local refractory failures have occurred, which have revealed materials that appear resistant for long usage periods.*

- To gain knowledge of combinations of operational conditions which are particularly beneficial or detrimental for certain material selections.

  > *It is considered that the project has fulfilled this goal by performing several field exposures with both metallic and refractory materials in boilers, where heavy metals are abundant, resulting in that material selections have been found that have performed well during the operational conditions of the exposures.*

- To achieve an understanding for when refractories are particularly beneficial to be used for protection of underlying metal and when other corrosion prevention methods may be attractive.

  > *It is considered that the project has fulfilled this goal by performing several field exposures with both metallic and refractory materials in boilers, where heavy metals are abundant, resulting in that material selections of both types have been found that have performed well during the operational conditions of the exposures, which provides opportunities to meeting different fuel dependent needs of desired cooling conditions.*

- The project aims at publishing 2-3 scientific journal articles and to present the results at 1-2 international conferences.

  > *It is considered that the project has partially fulfilled this goal by preparing one manuscript based on the in-depth metallographic investigation of materials from one field exposure which is to be submitted to a scientific journal, and by presenting project-related results at two international conferences.*

7 WP6 – Co-operation and communication

7.1 EFFICIENT CO-OPERATION AND COMMUNICATION

A vital part of the project has been the communication of industrial needs to the academic researchers and the dissemination of results from the researchers back to industry. This procedure was facilitated by Energiforsk who was responsible for efficient co-operation and being a link between researchers, research projects, Swedish Energy Agency and the industry stakeholders.

Energiforsk has been responsible for results dissemination, collaboration and continuous knowledge exchange between the academia and institutes and the industry stakeholders, in different stages of the value chain. The project results have been reported regularly at research symposiums within the field.

The researchers at RISE have been responsible for the new knowledge gained within the project being disseminated to the international research community.

7.2 PUBLICATIONS

Håkan Kassman, Tomas Leffler, Christer Forsberg, and Jinying Yan (2021), *Operational challenges in a BFB boiler firing demolition wood with addition of ammonium sulphate to reduce superheater corrosion*, presented at CFB-13 (13th International Conference on Fluidized Bed Technology

Håkan Kassman, Tomas Leffler, Rikard Norling, Alice Moya Núñez (2022), *Experiences from eight years of firing demolition wood using ammonium sulphate to mitigate superheater corrosion*, presented at Impacts of Fuel Quality 2022 (IFQ 2022).

M.A. Valiente Bermejo, A. Moya Núñez, R. Norling (2022), *Metal loss and corrosion attack of FeCrAl overlay welds on evaporator tube shields of a waste-fired power plant*, to be submitted for publication in a scientific journal.

8 Concluding remarks

This project has set out an ambitious overarching long term aim to aid the change of combined heat and power production to become completely renewable with high fuel flexibility and reliable operation. It shall allow for environmentally friendly energy recovery with high efficiency from recycled fuels containing heavy metals that would be difficult to reuse by other means.

It is considered that the project has made significant steps towards this by fulfilling a number of challenging project goals. Some of the more important of these are:

- To obtain new knowledge on how heavy metals in deposits influence corrosion of cooled parts in boilers, that is when exposed to a heat flux causing a temperature gradient.
- To gain an understanding of the corrosion performance and processes related to the use of new or improved coating materials with the purpose of allowing implementation or further improvements.
- To identify, if possible, 1-2 coating candidates that appear to have the potential to improve the life performance by 20 %.
- To identify, if possible, 1-2 refractory material candidates that appear to have the potential to improve the life performance by 20 % or decrease the need of replacements correspondingly.

In particular it is worth highlighting, the field test performed with uncooled specimens, which were done in a boiler inside the manifold duct just before the vertical empty pass where the temperature was approximately 900 °C and the flue gas flow was considered somewhat erosive. It showed that the coating Amdry 510 applied by HVOF had the best behaviour of all the tested materials. Amongst the surpassed tested materials was solid 253 MA, which is a state-of-the-art material for these conditions, as well as alloy 625. Thus, it can be concluded that HVOF applied Amdry 510 coating, which is a new material for this application, has the potential to improve material performance significantly for uncooled parts.

INCREASED FUEL FLEXIBILITY AND PERFORMANCE FOR BOILERS WITH CHALLENGING FUELS

The project Increased fuel flexibility and performance for boilers with challenging fuels has aimed to understand which material challenges are most critical for the operational performance of boilers. To achieve this objective, the corrosion performance of cooled and uncooled metallic parts has been investigated, as well as the deterioration and corrosion of refractory materials.

Results of particular interest were achieved by a field test performed with uncooled specimens, which were done in a boiler inside the manifold duct just before the vertical empty pass where the temperature was approximately 900 °C and the flue gas flow was considered somewhat erosive. It identified a coating material applied by HVOF which had the best behaviour of all the tested materials. Amongst the surpassed tested materials was solid 253 MA, which is a state-of-the-art material for these conditions, as well as the well-known alloy 625. Thus, it was concluded that this coating material has the potential to improve material performance for uncooled parts.

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