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CONSORTIUM MATERIALS TECHNOLOGY for demonstration and development of thermal energy processes

Correlation between deposit chemistry and initial corrosion of superheaters

Annika Talus, Rikard Norling, Peter Viklund, Pamela Henderson, Annika Stålenheim, Peter Sjövall, Bertil Magnusson, Håkan Kassman

KME-504

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KME-504

Preface

The project has been performed within the framework the fifth stage of the material technology research programme KME.

KME, Consortium Materials technology for demonstration and development of thermal Energy processes, was established 1997 on the initiative of the Swedish Energy Agency. In the consortium, the Swedish Energy Agency, seven industrial companies and 18 energy companies participate. The programme stage has been financed with 60.2 % by participating industrial companies and with 39.8 % by Swedish Energy Agency. The consortium is managed by Elforsk.

The programme shall contribute to increasing knowledge to forward the development of thermal energy processes for various energy applications through improved expertise, refined methods and new tools. The programme shall through material technology and process technology developments contribute to making electricity production using thermal processes with renewable fuel more effective. This is achieved by

- Forward the industrial development of thermal processes through strengthen collaboration between industry, academy and institutes.
- Build new knowledge and strengthen existing knowledge base at academy and institutes
- Coordinate ongoing activities within academy, institutes and industry

KME's activities are characterised by long term industry relevant research and constitutes an important part of the effort to promote the development of new energy technology with the aim to create an economic, environmentally friendly and sustainable energy system.

Abstract

It was found that ammonium sulphate is more effective compared to mono ammonium phosphate in reducing the chloride content in deposits. When adding ammonium sulphate it is concluded that the oxygen level in the boiler is more important than the dosage of additive in order to decrease the chloride content efficiently. This information is highly valuable since the excess air ratio is typically decided from other criteria than corrosion, such as economic.

Sammanfattning

Biomassa innehåller i allmänhet höga halter av kalium och klor, medan halten av svavel normalt är relativt låg. Vid förbränning frigörs dessa element till rökgasen och bildar olika aggressiva ämnen som kan leda till ökad risk för korrosion. En strategi för att undvika dessa korrosionsproblem är att ändra miljön i pannan. Det har visats att bildandet av avlagringar och överhettar-korrosion kan motverkas genom samtidig förbränning av svavelrika bränslen eller tillsatser. Slam är en produkt som ofta innehåller höga halter av fosfater som också tros ha en liknande effekt på gasfasreaktionerna som sulfater. Omfattande forskning på laboratorieskala har under de senaste åren bidragit till ökad förståelse för korrosionsproblem hos överhettarrör. Laboratorie-exponeringar tar dock inte hänsyn till den komplexa miljö som råder i pannan.

I detta projekt har komplexa men ändå kontrollerade pilotskaleförsök utförts för att ytterligare öka kunskapen om överhettarkorrosion. Fokus i projektet har varit att analysera avlagringar och material från pilotskaletester, med kontrollerad dosering av S och P. Försöken i pilotskala har också jämförts med prover från fullskaliga test. Målet med projektet har varit att öka kunskapen och förståelsen gällande effekten av ökad ångtemperatur och användningen av additiv på avlagringskemi och initial korrosion i överhettare. Ett sekundärt syfte har varit att etablera riktlinjer för analysmetoder för att studera avlagringskemin och den initiala korrosionen.

Arbetet har utförts av Vattenfall AB, Swerea KIMAB och SP Tekniska Forskningsinstitut under perioden 2010-2013.

Resultatet från projektet visade att genom att öka doseringen av både svavel- och fosforinnehållande additiv kunde alkalikloridhalten i rökgasen minskas. Det visade sig även att fosforinnehållande additiv hade bättre effekt (mätt i kg, P eller S/h/MW) jämfört med det svavelhaltiga additivet. För fosfatadditivet krävdes dock en högre dosering jämfört med sulfatadditivet i avseende att minska kloridinnehållet i avlagringen. En annan faktor som påverkade både kaliumkloridhalten i rökgasen och klorhalten i avlagringen var syretillgången i pannan (λ). En bättre sulfatering av rökgasen uppnåddes med hjälp av både ökad sulfatinjektion och ökat syretillgång. När prover och avlagring studerades i tvärsnitt kunde det ses att båda tillsatser minskade klor nära gränsskiktet metall/oxid. Istället kunde små mängder svavel identifieras som visar att den deponerade kaliumkloriden är sulfaterad innan klor kan diffunderar genom oxidskiktet eller att tillräckligt sulfatering också skett nära gränsskiktet.

Den initiala korrosionen visade sig öka med högre kaliumkloridhalt i rökgasen men genom att öka svavelinjektion och syretillgången minskades risken för korrosion. Genom att använda sulfatadditiv minskades också risken för inre korrosion vid högre temperaturer. Undersökningen visade generellt att båda additiven såg ut att minska den initiala korrosionen. Det visades dock att de lokala korrosionsangreppen som noterades för alla testade fall spelade en viktig roll i utvärderingen.

Att fastställa lämpliga halter för kontrollerad dosering av tillsatser visade sig vara svårt, i synnerhet för ammoniumsulfat. I själva verket visade sig den exakta dosen av additiv sig vara av mindre betydelse än luftöverskottet. Denna information är mycket värdefull eftersom förhållandet för

luftöverskottet vanligtvis bestäms utifrån andra kriterier än korrosion, såsom ekonomiska.

Projektets mål har uppfyllts och ökade kunskaper och förståelse för avlagringskemi och initial korrosion i olika miljöer har erhållits. Det sekundära syftet, att etablera riktlinjer för analys av avlagringa och initial korrosion har också uppfyllts. Alla undersökta analystekniker har visat sig vara användbara och kunskap om tid och kostnad för olika tekniker har erhållits.

Nyckelord: Returträ, biomassa, korrosion, klor, svavel, fosfor, analysmetoder, rostfritt stål

Summary

Biomass generally contains high amounts of potassium and chlorine, while the content of sulphur is normally relatively low. During combustion these elements are released to the flue gas forming various aggressive species that can severely accelerate the corrosion attack. One strategy to avoid corrosion problems is to change the atmosphere in the boiler. It has been proven that deposit formation and superheater corrosion can be counteracted by co-combustion with sulphur-rich fuels or additives. Sludge often contain high amount of phosphates, which are believed to have a similar effect on the gas phase reactions as sulphates. Extensive research on laboratory scale in recent years has surely contributed to an increased understanding of the corrosion problem of superheater tubes. However, laboratory exposures do not take the complex environment with numerous competing reactions in to account.

In this project, complex, yet controlled, pilotscale exposures have been performed to further increase the knowledge regarding superheater corrosion. The main focus in the project has been to analyse deposits and materials from pilot-scale tests, using controlled dosage of S and P. Tests have also been performed and compared with samples from full scale testing. The goal with the project was to increase the detailed knowledge and understanding regarding the effect of increased steam temperatures and the controlled use of additives on deposit formation and initial corrosion of superheater tubes. A secondary objective was to establish a guideline for deposit and corrosion analysis method.

The work has been carried out by Vattenfall AB, Swerea KIMAB and SP Technical Research Institute of Sweden during the period 2010-2013.

The result from the project showed that by increasing the dosage of both sulphur and phosphor containing additives the alkali chloride content in the flue gas could be decreases and it was also shown that phosphorous containing additive have the best effect (measured in kg, P or S/h/MW) compared to the sulphur containing additive. However, for MAP a higher addition was needed compared to AS in order to decrease the chloride content in the deposit, while for AS lesser amount of additive was required to do this effectively. Another factor that also showed to affect both the KCl (g) in the flue gas and the chlorine content in the deposit in a positive way was the oxygen content (λ). A better sulphation of the flue gas could consequently be achieved by using both increased sulphate injection rates and increased excess air ratios.

When studying the samples and deposits in cross section it could be seen that both additives decreased the chlorine close to the metal/oxide interface. Instead low amounts of sulphur could be detected which indicates that the deposited KCl (s) is sulphated before the chlorine can diffuse through the oxide scale or that sufficient sulphation also is occurring close to the interface.

The initial corrosion was shown to increase with higher KCl (g) in the flue gas. However, an increase in sulphur addition and oxygen level seemed to decrease the risk of corrosion. The investigation showed that the used additives seemed to have a slight effect of the initial corrosion although it was not very pronounced. It was shown that the local corrosion attacks occurring for all samples played an important role in the evaluation. Sulphate addition

was also shown to decrease the risk for internal corrosion at the higher temperatures.

To establish schemes for controlled dosage of additives proved to be difficult in particular for ammonium sulphate. In fact, during injection the exact dosage was shown to be of lesser importance than the excess air ratio for the studied conditions. This information is highly valuable though, since the excess air ratio is typically decided from other criteria than corrosion, such as economic.

The project goals have been fulfilled and increased knowledge and understanding regarding the deposit formation and initial corrosion in different atmospheres has been achieved. The secondary objective, to establish a guideline for deposit and corrosion analysis has also been fulfilled. All investigated analysis techniques were shown to be useful and knowledge about time and cost for the different techniques has been achieved.

Keywords: Waste wood, biomass, corrosion, chlorine, sulphur, phosphor, analysis methods, stainless steel

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1 Introduction

1.1 Background

Rapid corrosion attack on critical components is a common problem during power generation in biomass-fired boilers. As a consequence, maintenance costs are high and the steam temperature is kept low to mitigate subsequent breakdown. Biomass generally contains high amounts of potassium and chlorine, while the content of sulphur is normally relatively low. During combustion these elements are released to the flue gas forming various aggressive species that can severely accelerate the corrosion attack. The highest temperature and fastest degradation is often seen on the superheater tubes components which are facing a highly complex atmosphere with a number of gaseous and solid compounds present. In particular, significant amounts of alkali chlorides may condense on the tubes forming a chloride-rich deposit.

The corrosion problem has not yet been solved by appropriate alloy selection, although improved corrosion resistance has been observed for higher alloyed steels. Another possible strategy to avoid corrosion problems is to change the atmosphere, in particular this means to avoid the build-up of deposits rich in alkali chlorides. It has been proven that deposit formation and superheater corrosion can be counteracted by co-combustion with sulphur-rich fuels or additives. With a sufficient concentration of sulphur in the fuel the alkali chloride can be converted into a less corrosive alkali sulphate. Coal, peat and sludge are examples of fuels which can be used for co-combustion with biomass, while elemental sulphur and ammonium sulphate are commonly used sulphur-based additives. Theoretically, a molar ratio of 0.5 is sufficient to produce K_2SO_4. In practice, an excess of S is needed to prevent the formation of KCl and according to Salmenoja et al [12] a S/Cl-ratio of 4 in the fuel is needed to prevent severe corrosion problems.

The sulphation can be both homogeneous (occur in the gas phase) and heterogeneous (occur by the gas phase interacting with a liquid or solid phase). From a corrosion point of view an interesting question is if materials performance is affected by whether a heterogeneous or homogeneous sulphation takes place.

Sludge often contain high amount of phosphates, which are believed to have a similar effect on the gas phase reactions as sulphates. The effect of pure phosphate additives on KCl conversion has been little studied.

1.2 Description of the research field

Corrosion is a central issue if power production from biomass and waste is to be increased. Gaseous chlorine and solid or liquid chloride-containing compounds are considered the main reason for severe corrosion attack. In

laboratory investigations, the detrimental effect of HCl [1, 2], KCl [3, 4], K_2CO_3 [4] and molten chlorides [5, 6, 7] have been studied and their ability to prevent the formation of a protective oxide scale has been revealed. In these detailed studies, the main objectives have been to elucidate how individual components, present in the boiler, interact with the metal or the metal oxide. Investigations of superheater corrosion in full-scale boilers have confirmed the aggressive nature of the chlorides and in some cases confirmed the behavior observed in the laboratory. However, the environment in full-scale boilers is highly complex, including a number of simultaneous competing reactions, and predicting the magnitude or even the type of corrosion attack is very difficult.

Several different strategies are being developed in order to handle the corrosion problems. Laboratory investigations within HTC [4] have shown that alkali chlorides are far more corrosive than the corresponding sulphates. It is also well-known that a deposit, containing only sulphates, has a higher first melting point than deposits containing alkali chlorides [9]. A promising approach to mitigate superheater corrosion is therefore the addition of sulphur containing compounds to the fuel [8,10,11,12,13,14]. With a sufficient concentration of sulphur in the fuel [15] or the flue gas, alkali sulphates rather than alkali chlorides are stable on the superheater tubes. Tests in full-scale boilers with different types of sulphur-containing additives have lowered corrosion rates and the effect has been correlated to the decrease in alkali chlorides in the deposit. In KME-135 [16], it was shown that the "ChlorOut" additive, developed by Vattenfall AB, containing ammonium sulphate could reduce the corrosion rate in biomass-fired boilers by up to 50%. Later in the KME-408 project [17], ammonium sulphate was tested in a number of different waste-fired boilers. In this study, corrosion rate measurements indicated a possibility for significantly higher steam temperatures if sufficient sulphation could be achieved. In the parallel project KME 411 [19], different additives, including sewage sludge, were tested in the Händelö-boiler P14 with a similar positive effect. Recently promising results have also been obtained with a phosphorous-rich additive [20].

1.3 Research task

Extensive research on laboratory scale in recent years has surely contributed to an increased understanding of the corrosion problem of superheater tubes. However, laboratory exposures do not take the complex environment with numerous competing reactions in to account. At the same time, full-scale exposures may be difficult to control and large variations in exposure conditions can render accurate analysis difficult. In this project, complex, yet controlled, pilotscale exposures have been performed to further increase the knowledge regarding superheater corrosion and the strategies to handle these problems. The pilot-scale exposures have also been compared with full-scale investigations.

The main focus in the project has been to analyse deposits and materials from pilot-scale tests, using controlled dosage of S and P. Tests have also been performed and compared with samples from full scale testing.

The overall objectives of the project have been to improve the description of the chemistry of a deposit and link it to the initial corrosion. The investigations have been focusing on not only the amount of Cl, S and P in the deposit, also the form of which these elements are present in the deposit have been studied.

Also different analysis methods have been studied and evaluated. Historically samples covered with deposit have been weighed and then chemically analysed in a scanning electron microscope (SEM). This gives an average amount of various elements in the deposit but no information on the compounds present. Generally it is assumed that more Cl means a more corrosive deposit, but this is a very simplified conclusion. For a long time also same analysis techniques have been used even though several new techniques are available. In order to improve the analysis of the deposits and understand how different analysis techniques can be used some chosen techniques have been evaluated within the project. The objective with this has been to establish recommendations on how and when different analysis methods can be useful.

1.4 Goal

The project shall increase the detailed knowledge and understanding regarding the effect of increased steam temperatures and the controlled use of additives, e.g. sulphur-containing, on deposit formation and initial corrosion of superheater tubes.

A secondary objective is to establish a guideline for deposit and corrosion analysis.

1.5 Project organisation

The work has been carried out by Vattenfall AB, Swerea KIMAB and SP Technical Research Institute of Sweden during the period 2010-2013.

The total project budget was 3094 kSEK of which 2000 kSEK were industrial contributions from Vattenfall AB and 1094 kSEK was a cash contribution from KME.

Swerea KIMAB has been responsible for the project leadership. The chemical analysis and evaluation has mainly been performed by the Peter Viklund and Annika Talus (Swerea KIMAB). Peter finished his PhD studies in April 2013 within the project and Annika started hers in February 2013.

Peter Sjövall (SP), specialist on the TOF-SIMS analytical technique has been responsible for the analysis contribution from SP.

The project reference group, monitoring the work, has also included Lars-Gunnar Johansson and Jesper Liske at Chalmers University of Technology.

2 Experimental

2.1 Boiler description

Two boilers have been used in the project, a 12 MW CFB boiler at Chalmers University of Technology (Göteborg) and a 63 MW BFB boiler in Jordbro. Further plant descriptions are to be found below.

2.1.1 12 MW CFB boiler at Chalmers University of technology

The CFB boiler at Chalmers University of technology is a research boiler in which exposures, while maintaining control over operation parameters such as load, air supply and fuel mix composition, can be performed. In Figure 1 a schematic picture of the boiler are shown. [21]

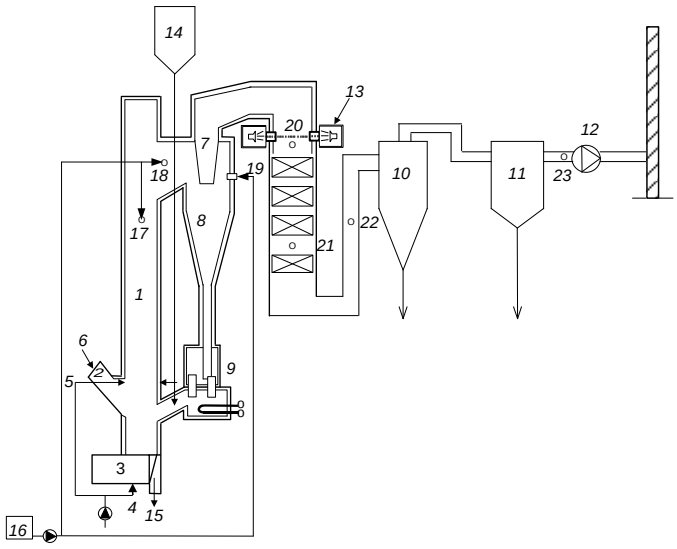


Figure 1. **The 12 MW CFB boiler. 1. furnace; 2. fuel chute; 3. air plenum; 4. primary air; 5. secondary air; 6. fuel feed and sand; 7. cyclone outlet; 8. primary cyclone; 9. particle seal; 10. secondary cyclone; 11: bag house filter; 12. flue gas fan; 13. IACM (*In-situ* Alkali Chloride Monitor); 14. Kaolin; 15. bed material; 16. ammonium sulphate (AS); 17-19. injection of AS and measurement positions; 17. upper part of the combustion chamber; 18 cyclone inlet; 19. in the cyclone; 20-23. measurement positions; 20. before the convection pass; 21. in the convection pass, 22. after the convection pass; 23. before the stack. [21]**

2.1.2 63 MW BFB boiler in Jordbro

The BFB boiler in Jordbro is a full scale boiler in which exposures in field atmosphere has been performed. In Figure 2, a schematic picture of the boiler is shown.

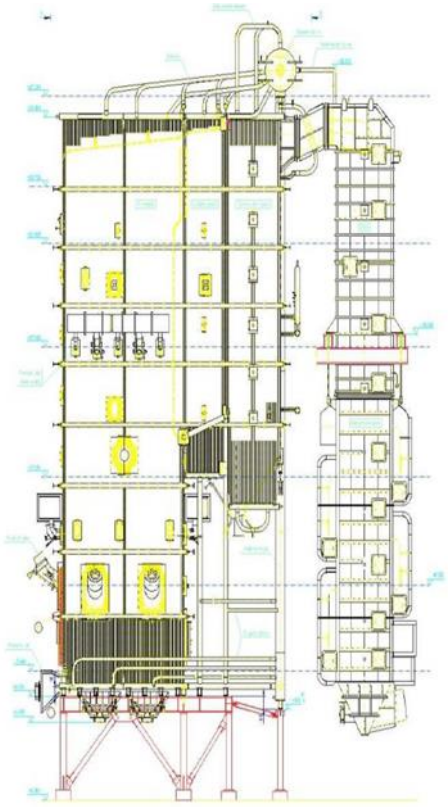


Figure 2. Illustration of the 63 MW BFB boiler in Jordbro.

2.2 Corrosion ring specimens

Ring specimens of the tested alloys have been exposed on air-cooled probes, placed close to the superheaters, in the two different boilers. The probes have been temperature controlled in order to achieve wanted metal temperature for the ring specimens given in each exposure. For all exposure the exposure time has been 3 hours. Example of a probe with mounted ring specimen can be seen in Figure 3.

Figure 3. Appearance of an air cooled probe prior to exposure. [17]

2.3 Exposure details

2.3.1 Influence of excess air and sulphate injection

In this campaign the 12 MW boiler was running on a base fuel of wood chips (from stem wood) and addition of straw pellets (from wheat straw) in order to increase the KCl content in the flue gas. Three different excess air ratios was tested (λ=1.1, 1.2 and 1.4) in combination with different injection rates of ammonium sulphate (REF, ASL, ASH). The temperature of the exposure was controlled to 500°C. Ring specimens machined from compound tubing, having an inner carbon steel core and an outer part made of Sanicro 28, with composition according to Table 1, was exposed on air-cooled probes. Duplicate ring samples were mounted on the probes and exposed for 3h at positions corresponding to that of the superheater tubes in the boiler.

Table 1. Composition (wt%) of the investigated alloy Sanicro 28

Alloy:	Fe	Cr	Ni	Mo	Mn	Si	C
Sanicro 28	Bal.	27	30	3.5	1.6	0.4	0.02

During exposure the flue gas composition was monitored using In-Situ Alkali Chloride Monitor (IACM) and Fourier Transform Infra-red Spectroscopy (FTIR) instruments. The IACM-instrument measures the sum of gaseous NaCl and KCl, giving instantaneous feedback regarding sulphation of the flue gas.

2.3.2 Effects of sulphate and phosphate injection

In this campaign ring specimens of 10CrMo9-10 (2218) and 304L (2352) with chemical composition according to Table 2 were exposed in the 12 MW boiler running on a fuel mixture of wood chips, wood pellets and PVC to control the potassium chloride levels to approximately 35-40 ppm.

Table 2. Composition (wt-%) of the investigated alloys.

Alloy:	Fe	Cr	Ni	Mo	Mn	Si	C
10CrMo9-10	Bal.	2.0	-	0.9	0.4	0.5	0.08
304L	Bal.	18.2	10.1	-	-	-	0.02

Tests were performed in different conditions where the chloride levels were varied between 5-40ppm either by lowering the PVC-level or by adding ammonium sulphate (AS) or mono ammonium phosphate (MAP) to the flue gas. The additives were injected before the primary cyclone at two different flue gas temperatures, 865°C and 790°C. The ring specimens were mounted on an air cooled probe controlled to 500, 550 and 600°C and each test was performed during 3 hours. In Table 3 and Table 4 the test parameters are presented.

Table 3. Test parameters for samples exposed in a flue gas temperature of 865°C.

Additive	KCl level [ppm]	Gas temp [°C]	Ring ID	Material	T, °C
MAP	20, 10, 5	865	A1, C1, B1	2352	600
			A2, C2, B2	2218	600
			A3, C3, B3	2352	550
			A4, C4, B4	2218	550
			A5, C5, B5	2352	500
			A6, C6, B6	2352	500
No additive	20, 40	865	D1, E1	2352	600
			D2, E2	2218	600
			D3, E3	2352	550
			D4, E4	2218	550
			D5, E5	2352	500
			D6, E6	2352	500
AS	5, 10, 20	865	J1, K1, N1	2352	600
			J2, K2, N2	2218	600
			J3, K3, N3	2352	550
			J4, K4, N4	2218	550
			J5, K5, N5	2352	500
			J6, K6, N6	2352	500

Table 4. Test parameters for samples exposed in a flue gas temperature of 790°C.

Additive	KCl level [ppm]	Gas temp [°C]	Ring ID	Material	T, °C
MAP	10	790	H1	2352	600
			H2	2218	600
			H3	2352	550
			H4	2218	550
			H5	2352	500
			H6	2352	500
No additive	40	790	I1	2352	600
			I2	2218	600
			I3	2352	550
			I4	2218	550
			I5	2352	500
			I6	2352	500

During exposure the flue gas composition was monitored using In-Situ Alkali Chloride Monitor (IACM) and Fourier Transform Infra-red Spectroscopy (FTIR) instruments. The IACM-instrument measures the sum of gaseous NaCl and KCl, giving instantaneous feedback regarding sulphation of the flue gas.

2.3.3 Effect of ChlorOut at temperatures above 560°C

In order to study the effect of ammonium sulphate injection at temperatures over 560° and also verify the results from previous studies performed in the pilot plane, exposures were performed in the 63 MW boiler in Jordbro. Exposures were performed with injection of ammonium sulphate at high (ASH) and low (ASL) rate, as well as without for reference (REF). The high injection rate was 120 l/h and the low was 60 l/h, for test parameters see Table 5.

Ring specimens were exposed for 3 hours and during the test, IACM measurements were performed in order to monitor the flue gas composition. Each probe had three temperature zones, which were controlled to ring metal temperatures of 560, 600 and 640 °C. This corresponds to steam temperature interval of about 530-610°C. Two alloys were exposed 304L (2352) and 13CrMo44 (2216), see Table 6 for chemical composition.

Table 5. Test parameters for samples exposed.

Duration of test [hh:mm]	Ring ID	Injection rate [l/h AS]	Material	Material Temp [°C]
09.40 – 12.40	1	60 (ASL)	2352	640
	2		2352	640
	3		2352	600
	4		2216	600
	5		2352	560
	6		2216	560
13.20 – 16.20	7	120 (ASH)	2352	640
	8		2352	640
	9		2352	600
	10		2216	600
	11		2352	560
	12		2216	560
17.35 – 20.35	13	Ref (No injection)	2352	640
	14		2352	640
	15		2352	600
	16		2216	600
	17		2352	560
	18		2216	560

Table 6. Composition (wt-%) of the investigated alloy.

Alloy:	**Fe**	**Cr**	**Ni**	**Mo**	**Mn**	**Si**	**C**
13CrMo44	Bal.	0.4	-	0.4	0.4	0.2	0.09
304L	Bal.	18.2	10.1	-	-	-	0.02

During exposure the flue gas composition was monitored using In-Situ Alkali Chloride Monitor (IACM) and Fourier Transform Infra-red Spectroscopy (FTIR) instruments. The IACM-instrument measures the sum of gaseous NaCl and KCl, giving instantaneous feedback regarding sulphation of the flue gas.

2.4 Post exposure analysis

After exposure the ring specimens were analysed in order to study the deposit chemistry and the initial corrosion. Post-exposure analyses of the deposit have mainly been focusing on the windward side of the ring specimens. Most often thicker deposits are encountered at this region and the windward side is usually regarded more prone to rapid corrosion. However, for some studies also the leeward side was investigated for comparison.

In order to fulfil one of the goals several analysis methods were used and compared within the project. All used techniques with settings and parameters are presented below.

2.4.1 SEM

This technique is based on that electrons from an ion beam are interacting with atoms at the sample surface. The atoms at the surface emit new electrons which are specific for each element and these can be detected and analysed by a detector in the instrument. The atoms are not only giving away electron as emission, also X-ray-photons are emitted and by analysing the energy of the photon (energy dispersive spectroscopy, EDS) or the wavelength of the photon (wavelength dispersive spectroscopy, WDS) the elemental information of the analysed species can be achieved.

The analyses performed with Scanning Electron Microscopy (SEM) have been performed at Swerea KIMAB. For the analyses a Jeol JSM-7000F analytical FEG-SEM equipped with Energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS) spectrometers was used. In this project only EDS was used in order to study the elemental composition.

The ring specimens have been analysed both in order to study the deposit composition at the surface and also in cross section in order to study initial corrosion. The deposit analysis at the surfaces has been 6-10 areas of 2*2.5 mm^2. Cross-sections of the windward side of the samples have been dry-polished with SiC 4000 mesh paper to avoid dissolution of chlorides, for illustration of analysed areas see Figure 4.

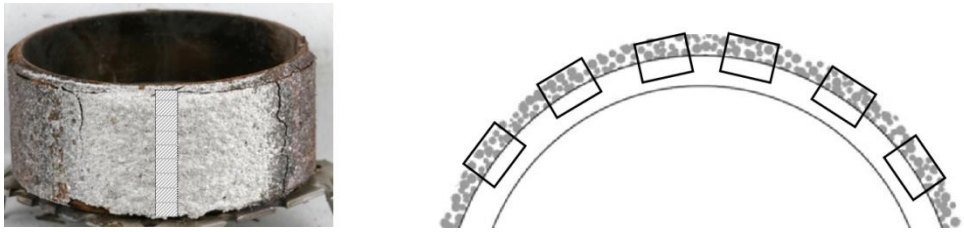


Figure 4. Illustration of anlaysed areas in SEM/EDS for deposit composition and cross section.

2.4.2 XRD

Also X-Ray Diffraction (XRD) using a Bruker D8 with CuK_α-radiation has been used in order to analyse the deposits. These analyses were performed at Swerea KIMAB. This technique makes it possible to study crystalline compounds by analysing the X-ray diffraction pattern given from each compound when hit by an electron source. In Figure 5 an illustration of the analysed are of the samples are shown.

Figure 5. Illustration of anlaysed area in XRD for deposit composition.

2.4.3 IC/ICP-OES

The deposits were also analysed with ion chromatography (IC) and inductively coupled plasma optical emission spectrometry (ICP-OES) at SP. For these analyses the whole sample has been investigated since the deposit needs to be dissolved in solution for the analysis.

For the ion chromatography the samples have been leached in water in order to dissolve chloride (Cl^-) and sulphate (SO_4^-) in the deposit. The theoretical sulphur content possible in the deposit based on the SO_4^- content was calculated.

To further analyse the samples using ICP-OES the samples have been leached in as second step in an acid blend consisting of nitric acid (HNO_3), hydrochloric acid (HCl) and hydrofluoric acid (HF) in order to dissolve the rest of the deposit. This analysis was performed in order to analyse Al, Ca, Fe, K, Mg, Mn, Na, P, Si and Ti.

2.4.4 XRF

XRF (X-ray Fluorescence) is a method that is based on that a sample surface is hit with a primary X-ray source. When the atoms at the surface are hit with this primary X-ray source, secondary X-ray emission is leaving the sample due to instability in the atom and this emission can be detected in order to analyse the composition.

The analysis in this project has been carried out according to method SP 4343, using a Thermo Advant-X XRF instrument and UniQuant® software. The analysed areas have been approximately 15*20mm^2 and are illustrated in Figure 6.

Figure 6. Illustration of analysed area in XRF for deposit composition.

2.4.5 TOF SIMS

Time of flight Secondary Ion Mass Spectroscopy (TOF-SIMS) is a method based on that the sample surface is sputtered by high ions. In this process secondary ions are emitted and analysed by the instrument. During analysis, the primary ion beam is scanned over a selected area on the sample surface and data is recorded separately from a selected number of raster points within the analysis area (typically 128x128 or 256x256 pixels). The recorded data can then be used to produce (i) ion images showing the signal intensity of a selected ion within the analysis area, (ii) total area mass spectra and (iii) mass spectra from selected regions of interest within the analysis area. The technique is somewhat destructive but since a very small amount of the sample is destroyed (approximately 10 nm depth) the surface will not change remarkable after the analysis.

The TOF-SIMS data was acquired using a TOF-SIMS IV instrument (IONTOF GmbH) with a 25 keV Bi_3^+ primary ion beam and a low energy electron beam for charge neutralization of the sample surface. The pulsed primary ion current was 0.10 pA in the bunched mode and 0.05 pA in the burst alignment mode. The area of analyse has been 500*500 μm^2 and in Figure 7 an illustration of the analysed are of the samples are shown. Note that the marked areas in not to scale.

For a more detailed description of the method and performance, see Appendix II.

Figure 7. Illustration of analysed areas in TOF-SIMS.

3 Results

3.1 Influence of excess air and sulphate injection

3.1.1 Gas atmosphere

IACM-measurements of the alkali chloride content in the flue gas show that the concentrations are lowered when injecting a sulphate additive. Also higher excess air seems to decrease the alkali chloride content. As a consequence the hydrogen chloride is increasing in the gas with injection of additive and by using a higher excess air ratio. The gas atmospheres during the exposures are shown in Figure 8.

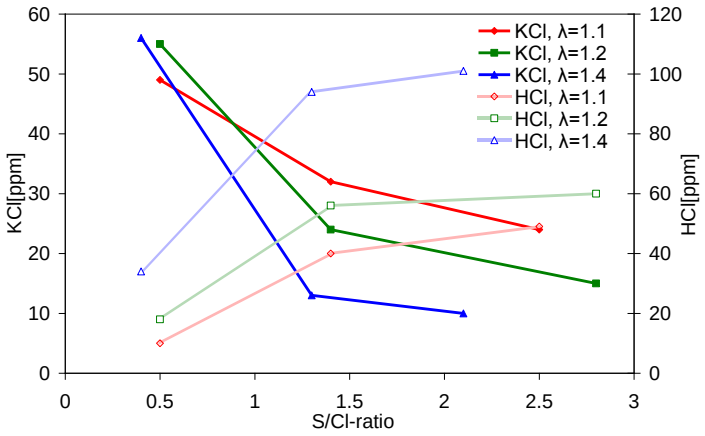


Figure 8. Concentration of KCl and HCl in the flue gas during exposures.

3.1.2 Deposit characterisation

Three different analysis methods described in chapter 2.4 were chosen for evaluation of the samples; SEM/EDS, XRD and IC/ICP-OES.

Figure 9 shows the windward side elemental composition of the deposit measured with EDS during the different test conditions. As evident, the major changes are observed in terms of chlorine and sulphur concentrations. Increasing the sulphate injection rates leads to increased sulphur content and a corresponding decrease in chlorine content. These trends are further reinforced by increased excess air ratios. At λ=1.2 and 1.4 no chlorine is found at the surface for the high injection rate of ammonium sulphate. The concentrations of alkali (Na+K) remain fairly unaffected during all the tests. The results indicate a change from KCl to K_2SO_4 in the deposit when injecting ammonium sulphate and especially when running the boiler at higher λ-values.

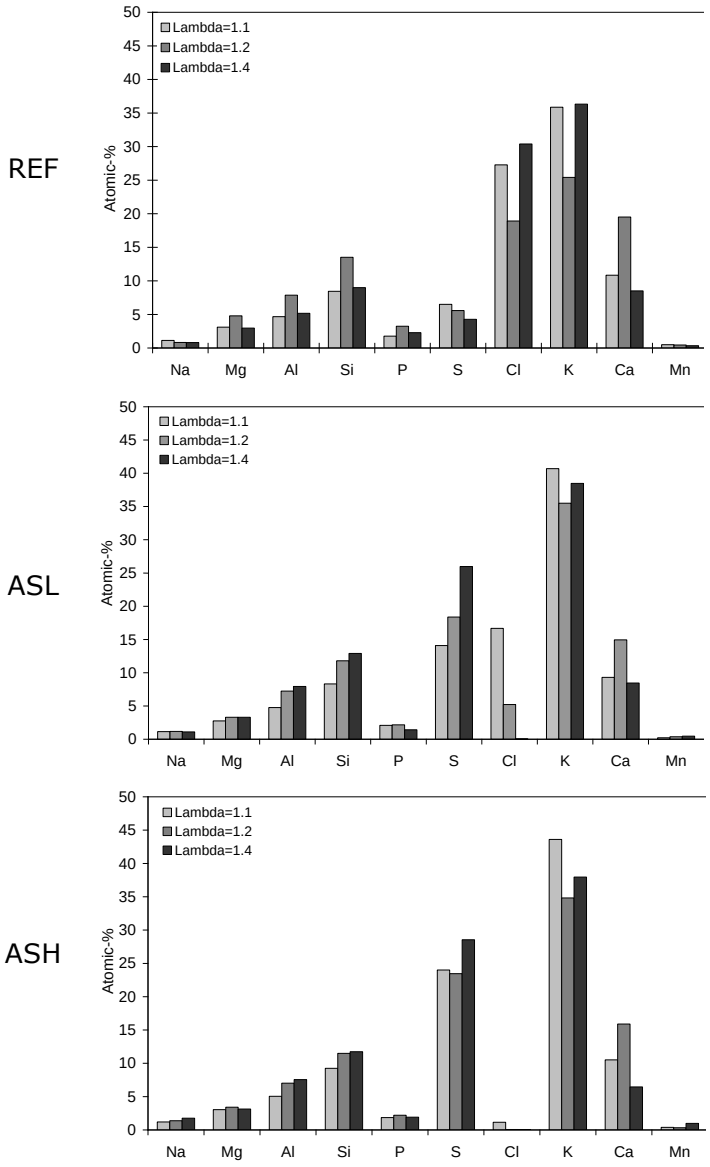


Figure 9. EDS-analyses of the deposit showing the windward side elemental composition for the different test conditions. Oxygen is excluded from the analysis.

The XRD-measurements showed that the deposit in the different exposures mainly consists of KCl, K_2SO_4 and austenite (γ), with small quantities of $K_2Ca_2(SO_4)_3$ also present. In Figure 10 it can be seen that both KCl and K_2SO_4 in the deposit are decreasing with increasing excess air when no ammonium sulphate is used (REF case). When using ammonium sulphate addition KCl is dramatically decreased in the deposit and also in this case a higher excess air ratio is further decreasing the KCl content. For the low ammonium sulphate addition a slight decrease of the K_2SO_4 is seen but seems not to be dependent on the excess air. With a higher ammonium sulphate addition the K_2SO_4 are increasing but only for the case were the excess air ratio is 1:1.

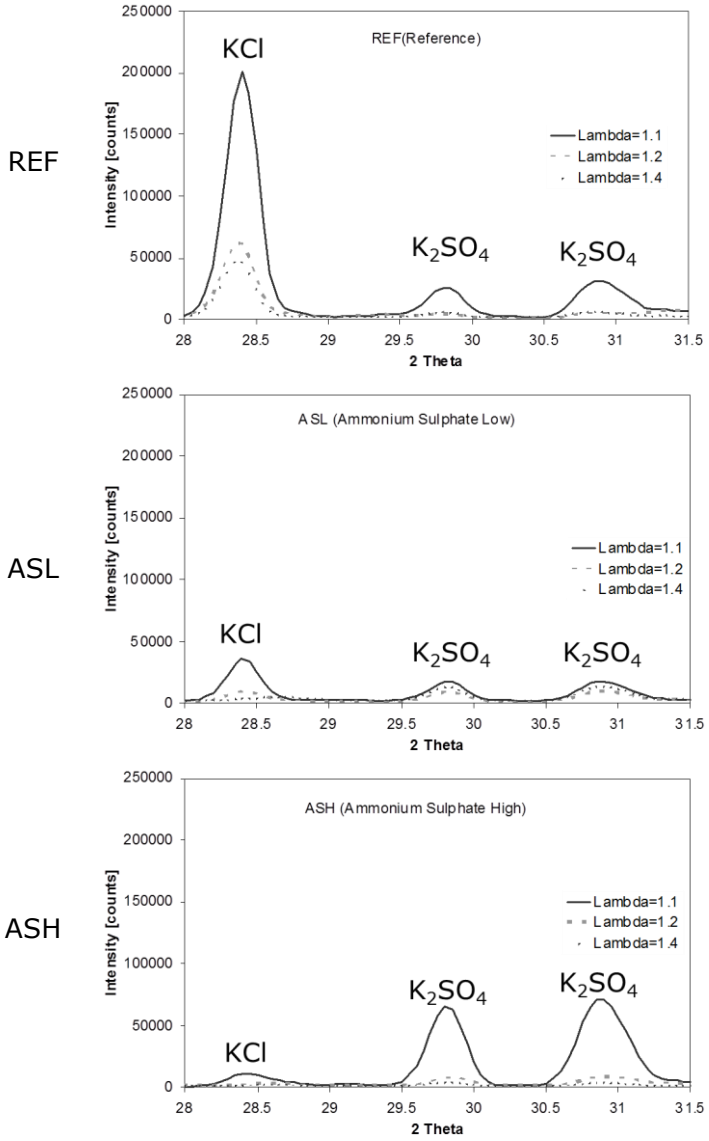


Figure 10. XRD-analyses of the deposit showing the detected phases for the different test conditions.

In Figure 11 the measured chlorine concentrations in the deposits are summarised for all the tests. In Figure 11a, the windward side chlorine concentration measured with SEM/EDS is given. It is evident that the deposit composition reflects the KCl-concentrations in Figure 8 very well with decreased alkali chloride-concentrations when increasing the sulphur injection rates. In accordance to the alkali chloride measurements a beneficial effect of oxygen level can also be seen. During operation at λ=1.4 the chlorine content in the deposit is negligible also during injection of low ammonium sulphate concentrations. At both λ=1.1 and λ=1.2 higher sulphur injection rates are required to prevent the build-up of a chlorine-rich deposit, although the

chlorine concentration is always very low when injecting high ammonium sulphate rates. Comparing the EDS-results with the ICP-OES results, Figure 11b, it can be seen that the chloride content in the deposit follows a similar trend with ICP-OES even though the absolute values are not the same.

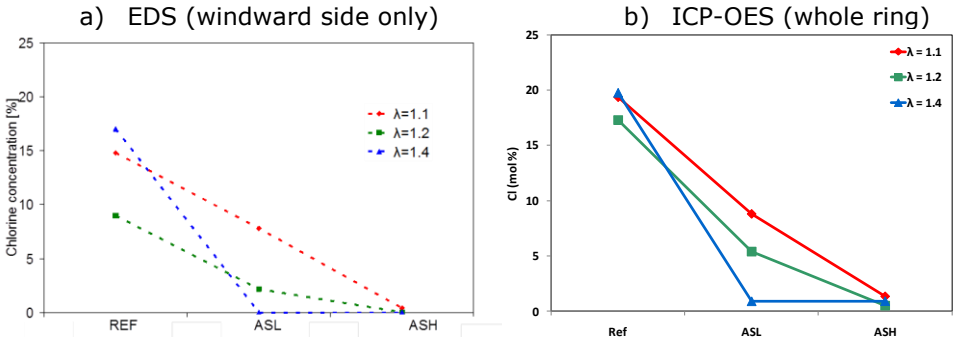


Figure 11. Comparison between chloride concentration results achieved from EDS and ICP-OES.

Using tabulated correction factors (I_o/I_{corr}) for each detected phase in the XRD measurement it is possible to obtain a semi-quantitative result of the KCl-concentration in the deposit, see Figure 12b. The results correspond well with the elemental composition measured with EDS, Figure 12a. At λ=1.1 a linear decrease in chlorine/KCl content in the deposit is evident when injecting ammonium sulphate. At higher λ-values the decrease in chlorine/KCl content is significantly faster.

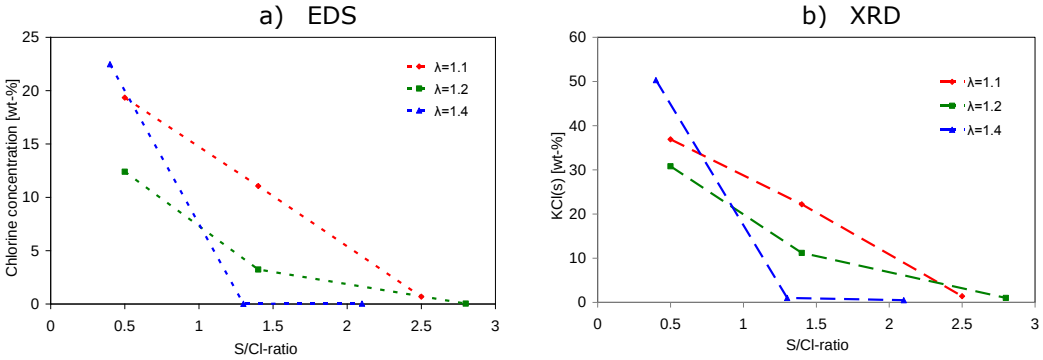


Figure 12. *EDS-analyses (a) and semi-quantitative XRD-analyses (b) of the deposits showing the chlorine-concentration.*

3.1.3 Initial corrosion

Three hours of exposure showed to be a too short period of time to evaluate the corrosion rate of high alloyed chromia-forming steel such as Sanicro 28. Still, it has been possible to study the appearance of the initial corrosion attack and relate it to the change in deposit composition achieved by controlling the ammonium sulphate injection and excess air in the flue gas. After removal of the outer deposits all specimens exhibited interference coloured oxides indicating very thin oxide scales. Cross-sectional analyses

were not considered useful for characterising and quantifying the attack. Instead SEM surface analyses were made on the windward side of all samples. The position of analysis is the same as that previously analysed in terms of deposit composition with XRD and SEM/EDS. Although not quantitative, the surface analyses confirm the hypothesis of a less aggressive atmosphere when sulphur injection is combined with increased excess air during firing. During the reference tests (REF), as well as during the exposures with low excess air (λ=1.1) a rougher surface as well as significant oxide spallation could be observed.

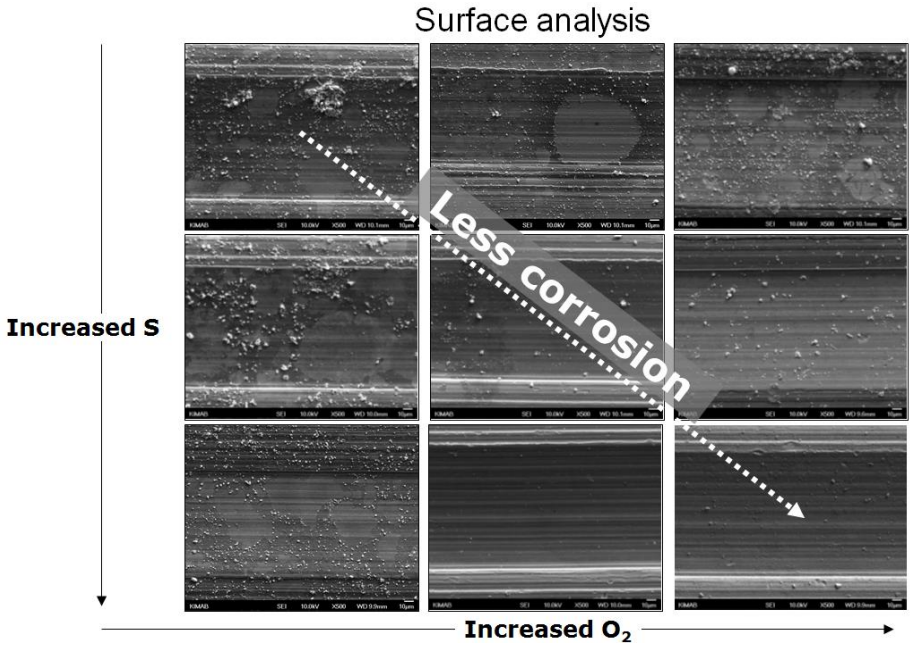


Figure 13. SEM images at 500X magnification showing the surface appearance of different ring specimens after removal of deposit.

Figure 14 show the spallation for the reference sample at λ=1.1 at higher magnification.

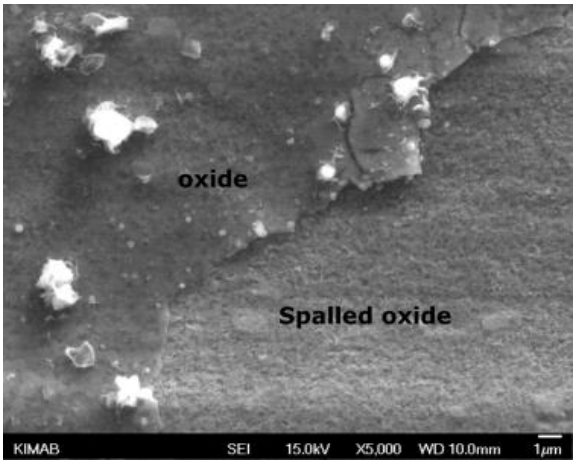


Figure 14. SEM image showing spallation of reference sample at λ=1.1.

From a corrosion point of view it is important to understand which factor(s) that govern an accelerated attack. In Figure 15 the flue gas and deposit analyses are given with the specimens exhibiting the fastest initial corrosion attack highlighted. It is evident that the most severe corrosion attack (in this case a rough surface morphology, oxide spallation and metal chloride formation) is not taking place on specimens facing the highest chlorine concentration in the deposit, but rather the specimens facing the highest KCl(g) concentrations in the flue gas. The finding indicates that deposit analyses may not be sufficient to predict an accelerated chloride-induced initial corrosion attack.

(a) KCl in flue gas (IACM) (b) Cl concentration in deposit (EDS)

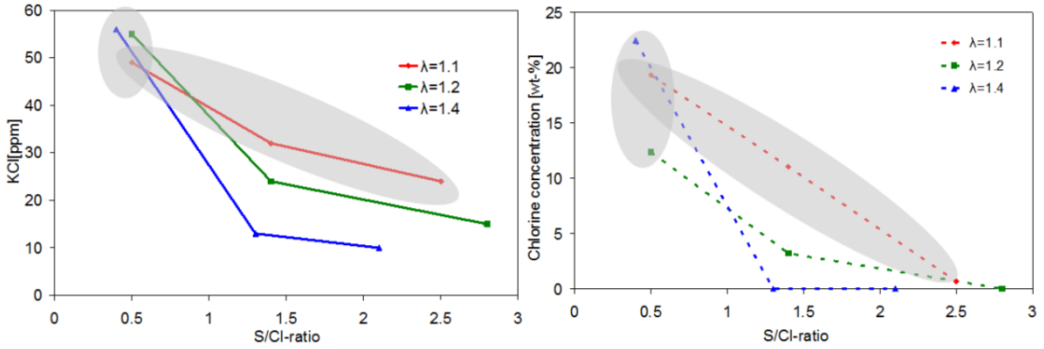


Figure 15. KCl-concentration in the flue gas (a) and chlorine-concentration in the deposit measured with EDS (b). Specimens exhibiting an accelerated initial attack, in terms of rough surface morphology or spalled oxide, are highlighted.

In cases when ammonium sulphate was injected during conditions with low λ-values a pronounced corrosion attack was observed although no or little chlorine was observed in the deposit. This behaviour is explained by an initial deposition of KCl(s) on the tube surface and a subsequent sulphation by a heterogeneous reaction. During the initial residence time of KCl(s) it may react with the alloy forming poorly protective corrosion products. During the heterogeneous sulphation release of HCl(g) is expected, which may also be a cause for accelerated corrosion attack.

3.2 Effects of sulphate and phosphate injection

3.2.1 Gas atmosphere

In Figure 16 the variations in KCl- and SO_2-concentrations in the flue gas (T=865°C) close to the deposit probe are shown, when injecting various amounts of ammonium sulphate and mono ammonium phosphate to a flue gas that originally contains about 35 ppm of KCl(g). The behaviour is similar for both additives and increased injection rates give lower chloride content in the flue gas. Increased injection rates of ammonium sulphate leads to a dramatic increase of SO_2 in the flue gas while the effect of MAP is almost negligible, as could be expected. In the figure the added AS and MAP (5, 10, 20 ppm) has been recalculated to added mass of S and P per hour and MW. The results show that a lower amount of phosphorous containing additive are needed in order to reduce the KCl (g) in the flue gas (measured in kg,P or S/h/MW) compared to the sulphur containing additive.

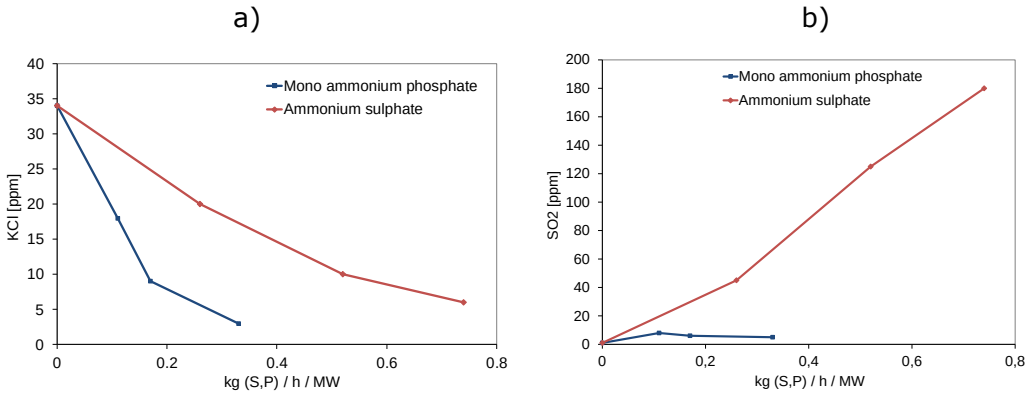


Figure 16. Flue gas analyses showing a) KCl- and b) SO_2-concentrations in the flue gas during injection of various rates of ammonium sulphate and mono ammonium phosphate.

3.2.2 Deposit characterisations

Three different analysis methods described in chapter 2.4 were chosen for evaluation of the samples; SEM/EDS, XRD and IC/ICP-OES.

Figure 17 shows the elemental composition, measured with IC/ICP, of the deposit formed during different test conditions for a flue gas temperature of 865°C and at a metal temperature of 500°C. The results show minor differences for most elements, with the exception of chlorine, sulphur and phosphorus which are significantly affected by the two tested additives.

For mono ammonium phosphate (MAP), the chlorine concentration in the deposit decreases with injected amount of the additive in a similar manner as the KCl (g) concentration (Figure 16a). A relation between increased injection of MAP and decrease in chloride content in the deposit is seen. Injection of MAP also clearly increases the phosphorus content in the deposit.

The changes in deposit chemistry when using ammonium sulphate (AS) are different. During all test conditions, despite appreciable KCl(g)-concentrations in the flue gas, very low chlorine concentrations are observed in the deposit when injecting ammonium sulphate independently of added amount of the additive. A dramatically increased sulphur-content in the flue gas can be observed during sulphate injection but the sulphur content in the deposit does not mirror the amount of injected ammonium sulphate, but instead remains at a high level in all cases. The results indicate that sulphation of the chloride-containing deposit is taking place when ammonium sulphate is injected.

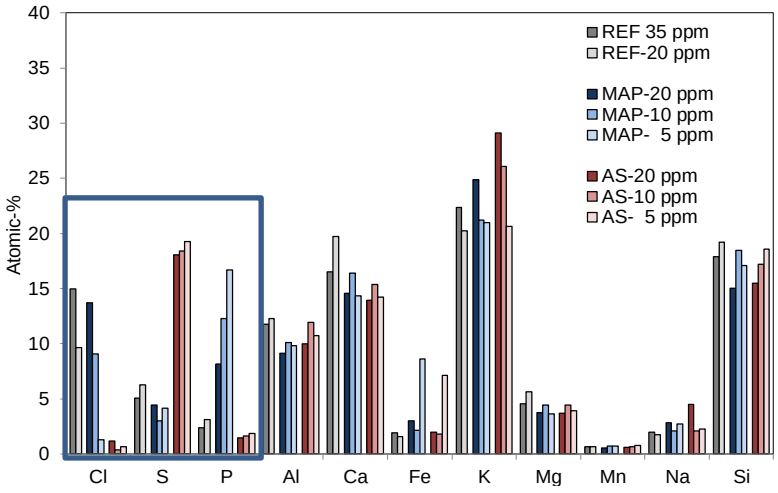
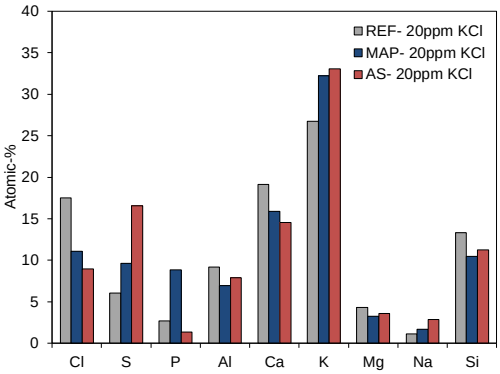


Figure 17. Deposit composition measured with IC/ICP-OES.

In Figure 18 the localised deposit composition measured with EDS is shown for three conditions having the same KCl(g) concentration in the fuel gas, flue gas temperature (865°C) and metal temperature (500°C). As expected, the results are fairly similar to those of the IC/ICP analyses, with increased sulphur concentrations when using AS and increased phosphorus concentrations when injecting MAP. However, differences are observed comparing the windward and leeward sides. First of all, more K is for all cases present on the windward side, while calcium, silicon and aluminium are higher on the leeward side.

a) Windward side



b) Leeward side

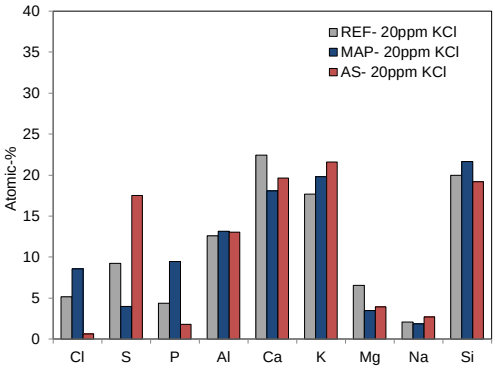


Figure 18. Deposit composition measured with EDS.

Most interesting is the variation in chlorine-concentration. Although the IC/ICP-OES analyses showed that AS is efficient in removing chlorine from the deposit, there seems to be a difference comparing the windward and leeward sides of the ring. The chlorine-concentration remains high on the windward side but is almost negligible on the leeward side during the AS 20 ppm test. The windward side is a position known to have the fastest deposit build-up, which is easily observed visually. In this case it seems that that reaction kinetics limits the sulphation of the windward side deposit when conducting short-term exposures. That is alkali chlorides are deposited on the windward side at such a rate that a complete sulphation cannot occur. The difference in chlorine-content between windward and leeward sides is much less during the MAP 20 ppm test. This is in agreement with the previous conclusion that the conversion of KCl during mono ammonium phosphate injection primarily takes place in the gas phase.

From XRD measurements performed, see Figure 19, it can be seen that the results reflects what is seen also with SEM. The AS is slightly more effective for reducing the KCl content in the deposit compared to the MAP. One difference between the two additives is the $K_3Na(SO_4)_2$ that is seen for the AS but not for the MAP. However, no phosphorous containing products are seen which indicates that these compounds have poor crystallinity.

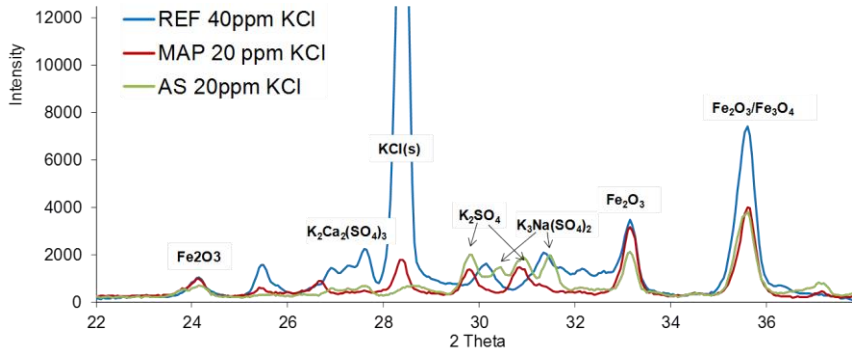


Figure 19. XRD-analyses of the deposit showing the detected phases for the different test conditions.

The summarised results from IACM-measurements and the results achieved from ICP-OES analysis in Figure 20 are showing that the KCl (g) content in the flue gas show a clear connection to the Cl-content in the deposit when injecting MAP. However, when injecting AS this connection is not seen to the same extent. Theoretically, similar amount of KCl (g) in the flue gas should give similar levels of condensed KCl (s) at the tube surfaces but this does not seems to be right for this case. This behaviour could be explained by the fact that sulphation reactions not only occur in the gas phase but also in the deposits at the tube surface.

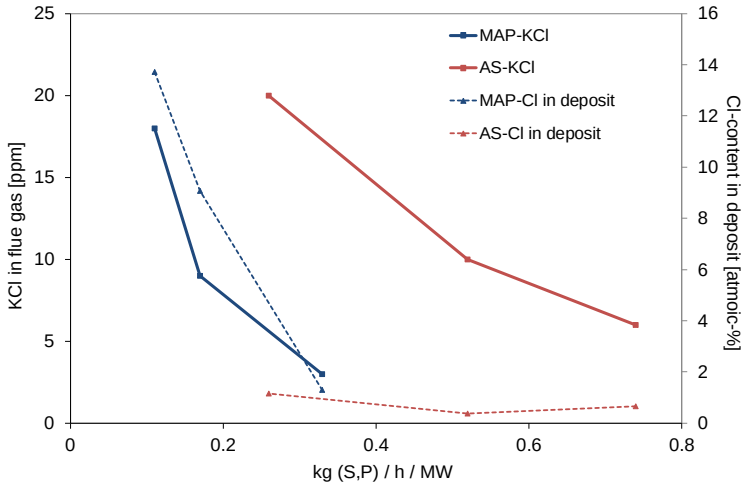


Figure 20. KCl content in the flue gas measured with IACM and Cl content in the deposit measured with IC/ICP-OES for different injecting levels of AS and MAP.

Other effects that were observed was the temperature dependence for the chloride content in the deposit for some selected cases where the additive addition was kept constant, see Figure 21. For the reference case with 40 ppm KCl in the flue gas the chloride content seems to increase with temperature. For mono ammonium phosphate a similar trend is noticed while for the ammonium sulphate the chloride content in the deposit is decreasing with increased temperature. Only the high alloyed steel is presented but similar trends were noticed also for the low alloyed steel in 550 and 600°C.

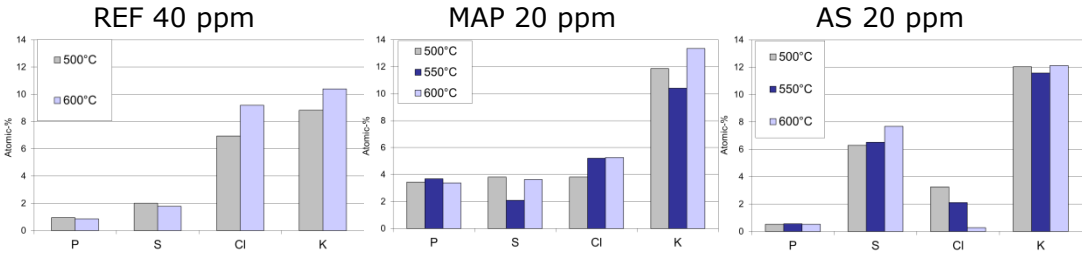


Figure 21. Metal temperature dependence for chloride content in deposit (SEM/EDS) for REF 40, MAP 20 and AS 20, flue gas temp 865°C.

Tests were also performed in order to study the influence of the flue gas temperature upon change in deposit chemistry at constant metal temperature of 500°C. The ICP-OES results from some chosen samples from these tests are presented in Figure 22. For none of the cases a very pronounced effect depending on the flue gas temperature. However, differences can be seen for aluminium, silicon and iron which are decreased in the deposit with increased flue gas temperature.

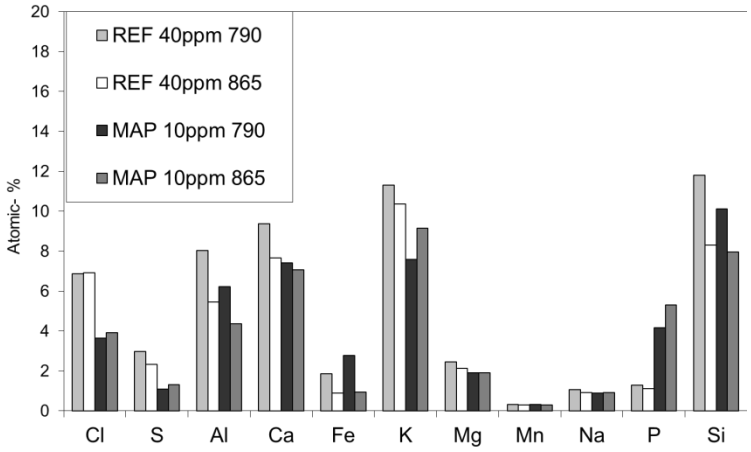


Figure 22. Flue gas temperature dependence for chloride content in deposit for REF 40 and MAP 10, metal temperature and additive constant 500°C and 40/10ppm respectively.

3.2.3 Initial corrosion

The initial corrosion was studied in cross section of the windward side by measuring the oxide thicknesses in SEM. Six areas of each cross section were studied for average and maximum oxide thickness.

The initial corrosion was studied for alloy 10CrMo9-10 (2218) at 550°C and 600°C. Both mean and maximum values of the corrosion attack were measured. For 550°C no clear difference could be seen for the reference sample compared to the samples with injection of AS or MAP. For 600°C a slight improvement can be seen although it is not very pronounced and more measuring points would have been needed in order to draw conclusions.

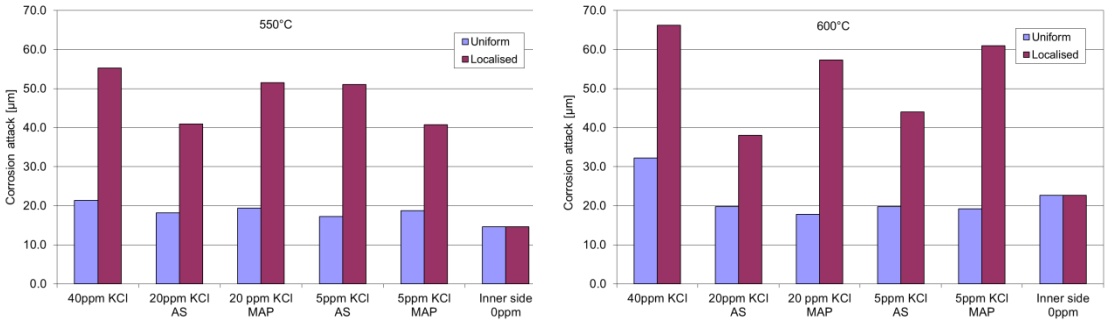


Figure 23. Uniform corrosion rates and localized corrosion attack at 550 and 600°C for different conditions

Several corrosion attacks were studied in cross sections of 2218, see example in Figure 24. The results show that chlorine is observed within the deposit close to the metal/oxide interface for both temperatures. In 550°C the chlorine is found together with iron and oxygen, probably $FeCl_2$ (s) while at

600°C potassium is found together with the chlorine, probably KCl (s). When injecting ammonium sulphate and mono ammonium phosphate resulting in as low concentrations of 5 ppm KCl (g) in the flue gas chlorine is no longer found at the metal/oxide interface, see Figure 25. Small amounts of sulphur are however seen. The oxides seen in both figures, one lighter and one darker, is probably Fe_2O_3(darker) and Fe_3O_4 (lighter).

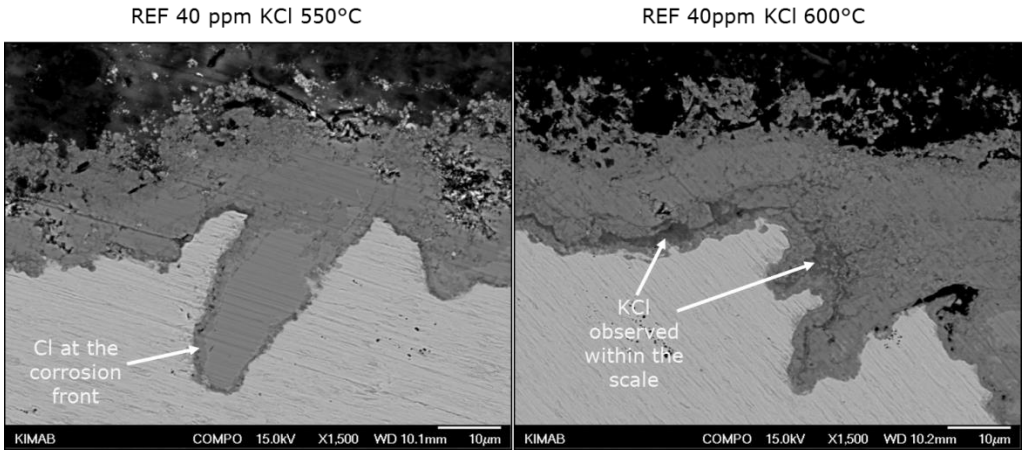


Figure 24. Cross section of corrosion attack in 2218 for samples without injection of additive at metal temperatures of 550 and 600°C.

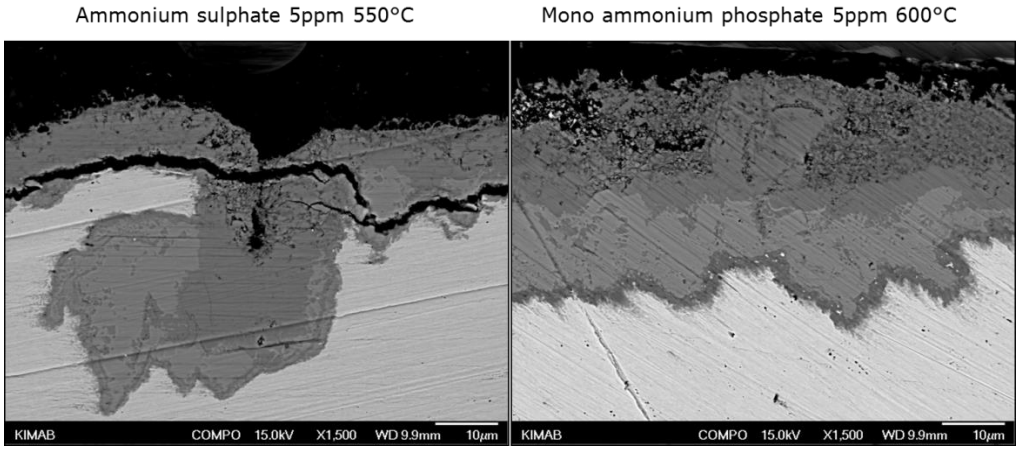


Figure 25. Cross section of corrosion attack in 2218 for samples with injection of additive at metal temperatures of 550 and 600°C

It was not possible to see any positive effect of increasing the additive and lower the KCl content in the flue gas for any of the temperatures. The results points towards that the corrosion rate is greatly affected by the local corrosion attacks seen for the samples. These corrosion attacks are seen also when using the highest levels of additives which possibly could be explained by the fact that this material is not aimed to be used in these temperatures. The corrosion for 2352 was not measured.

3.3 Effect of ChlorOut at temperatures above 560°C

3.3.1 Gas atmosphere

In Figure 26 the KCl content in the flue gas measured using the IACM-measurement is presented. The results show that the concentrations are lowered when injecting ammonium sulphate. It can also be seen that the efficiency varies slightly depending on injection rates.

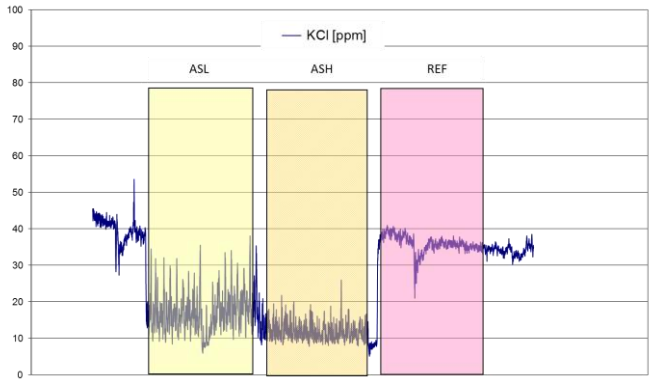


Figure 26. IACM measurements during exposure.

3.3.2 Weight gain measurements

In Figure 27 results from the weight increase for all ring specimens are shown. It can be seen that the ammonium sulphate injection results in a lower weight increase compared to the reference case. A low alloyed steel show also higher weight increase compared to a high alloyed.

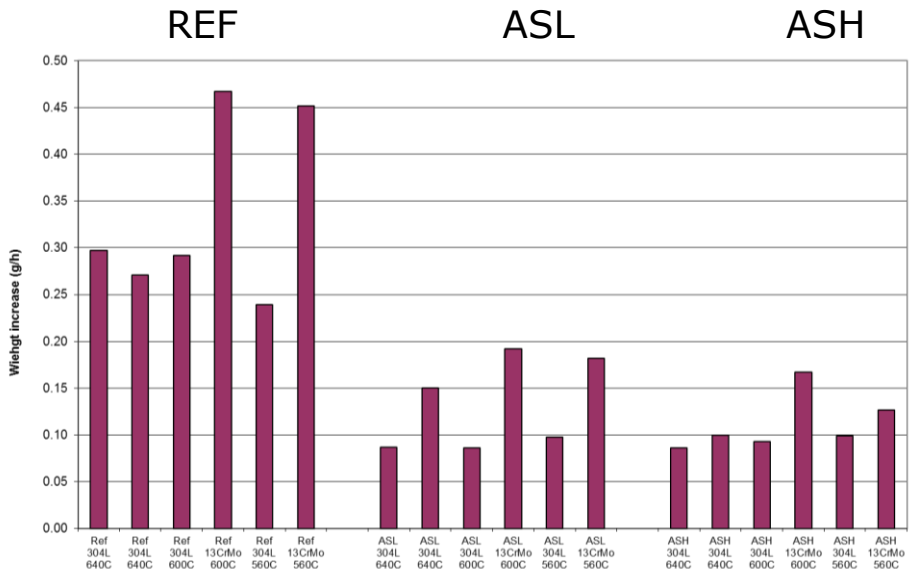


Figure 27. Weight increase for exposed ring specimen.

3.3.3 Deposit characterisation

The samples were analysed by using SEM/EDS (described in chapter 2.4) in order to study the composition of the deposits and mainly the chlorine content.

From the surface analysis of the deposit it can be seen that the ammonium sulphate has a clear effect in decreasing the chlorine content in the deposit, see Figure 28. A minor decrease is seen from ASL to ASH but the difference is very low and can more or less be neglected. This indicates that there is not a big difference between injecting 60 or 120l/h for the chloride content in the deposit. No clear temperature dependence is seen either although an indication of a decreased chlorine content in the deposit for the reference samples are seen with increasing temperature.

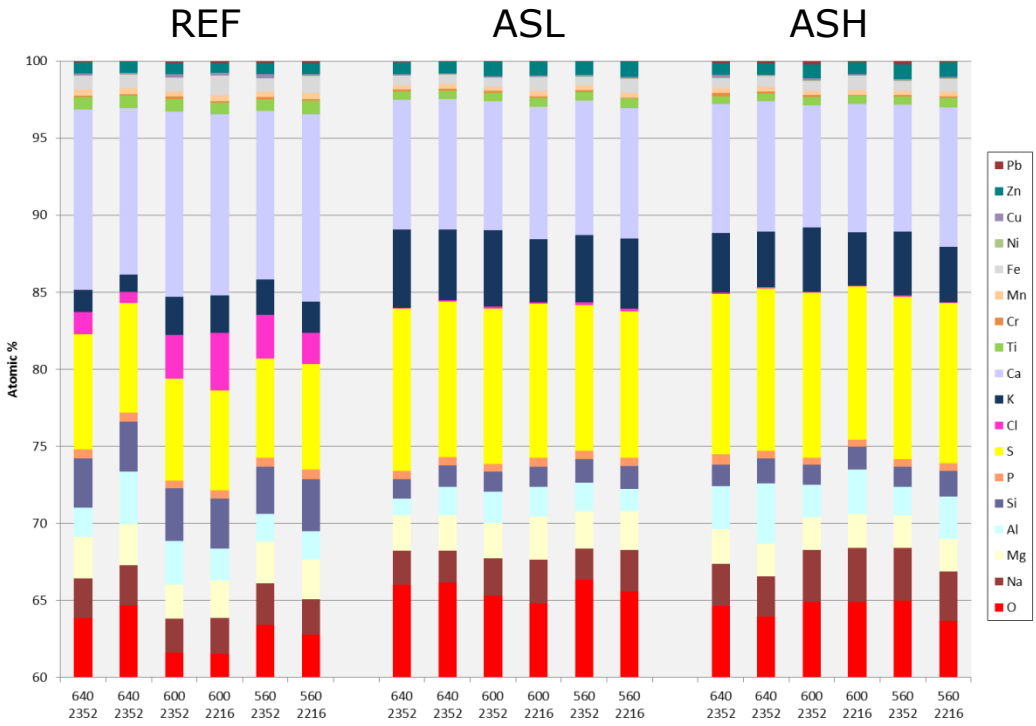


Figure 28. SEM/EDS analysis of the deposit after exposure, results in at%.

3.3.4 Initial corrosion

The initial corrosion was studied visually in cross section using SEM for material 2352 at 560°C and 640°C. Ten areas of 2*2.5 mm^2 at each cross section were studied. The other samples were not analysed within the project.

The result from both temperatures shows that the deposit for the reference case is thicker than for the cases when adding ammonium sulphate, see Figure 29 (a) and (b). This is well in accordance with the weight gain measured for the ring specimens. For the reference sample exposed at 640°C internal corrosion is also seen.

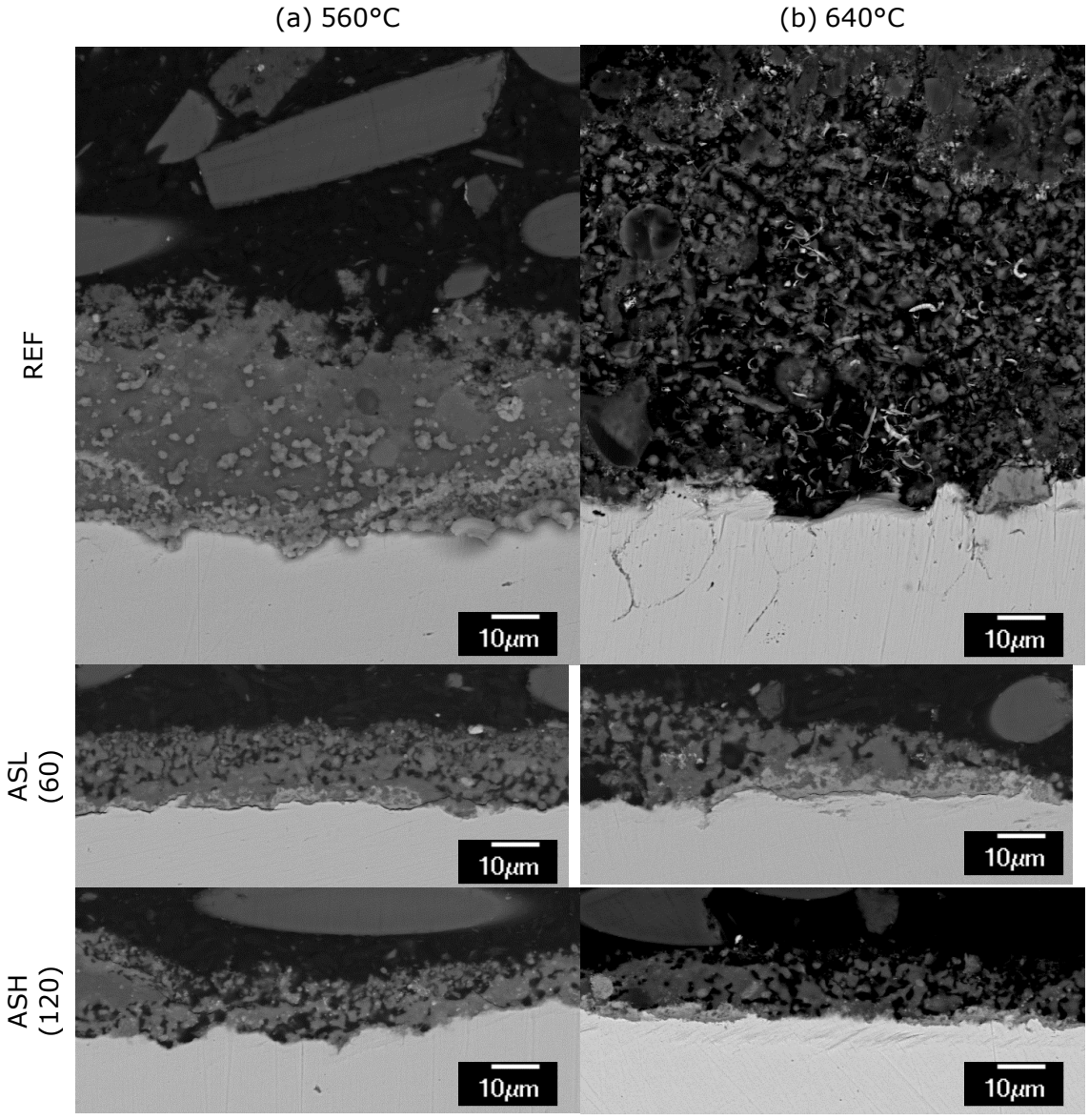


Figure 29. Cross sections of samples exposed at 640°C.

The deposit for the reference case exposed at 640°C is also shown to be thicker than for the 560°C-exposure. It can also be seen that the deposit looks somewhat different for the two cases. For the lower temperature it looks like more chlorine is seen close to the interface and in the deposit. This can also be seen in the surface analysis with SEM where a higher chlorine signal is seen for 560°C case. However, no dramatic change is seen for the cases with ammonium sulphate comparing 560 and 640°C but a slight indication of decreased chlorine content in the deposit with increasing temperature can be seen.

From the EDS measurements it can also be seen that for the reference cases chlorine is seen close to the interface while when using the additive no or very low chlorine contents are seen instead sulphur is seen at the interface. It can also be seen that the internal corrosion observed for the 640°C-reference case are inhibited for the cases when ammonium sulphate is added.

3.4 Comparison of analysis methods

As a final activity it was intended to establish a guideline for deposit and corrosion analysis based on the experiences from the different analysis methods used within the project. Different analysis methods were evaluated in order to find out the best suitable way to use each analyse method. In Table 7 chosen samples of 2352 from the exposure with ammonium sulphate and mono ammonium phosphate, chapter 2.3.2 are analysed with different methods in order to study the outcome.

Table 7. Samples chosen for analysis method comparison.

Additive	KCl level [ppm]	Gas T [°C]	Ring ID	Material	T, °C	EDS	XRD	IC/ ICP-OES	TOF SIMS	XRF
MAP	20	865	A1	2352	600	X			X	X
			A3	2352	550	X			X	X
			A5	2352	500			X		
			A6	2352	500	X	X		X	X
Reference, no additive	20	865	D3	2352	550	X			X	X
			D5	2352	500			X		
			D6	2352	500	X			X	X
Reference, no additive	40	865	E1	2352	600	X			X	X
			E5	2352	500			X		
			E6	2352	500	X	X		X	X
AS	20	865	N1	2352	600	X			X	X
			N3	2352	550	X			X	X
			N5	2352	500			X		
			N6	2352	500	X	X		X	X

In Figure 30 results from SEM/EDS and ICP-OES are shown. Evaluating the deposits in SEM gives the opportunity to study both windward and leeward sides while the whole ring is dissolved in the analysis with ICP-OES.

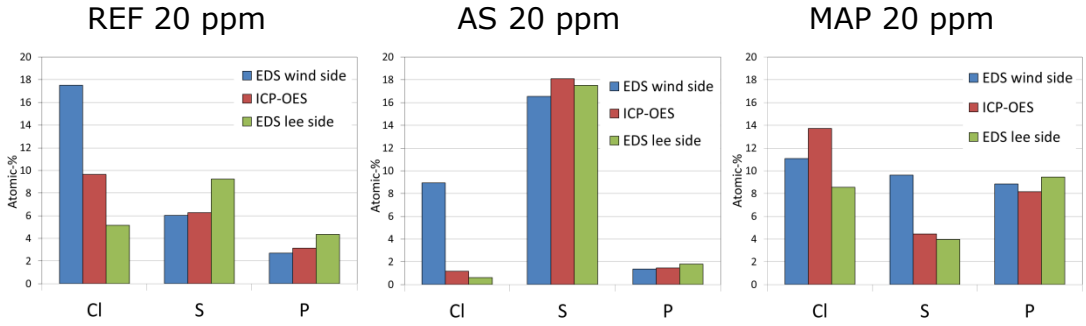


Figure 30. Comparison between analysis in SEM/EDS and ICP-OES regarding Cl, S and P content in deposit.

As shown in the figure, most often lower chloride content is seen in the deposit at the leeward side. This is most pronounced for the reference case and the ammonium sulphate case. When analysing the whole ring using ICP-OES for the mentioned cases the chloride content is more or less in between

the leeward and windward side values measured with SEM/EDS. Both methods give the same conclusion regarding the efficiency of reducing chloride content in the deposit for the two additives which is that AS seems to be more efficient compared to MAP. However, in SEM/EDS the difference between the additives is not that pronounced if only the windward side is studied. Evaluating the ICP-OES result the efficiency seems to be much greater for AS. This is a result which can be derived to the difference in analysed area. In SEM the analysed area is smaller and several areas need to be analysed in order to get good statistics. It could also be difficult to analyse the exact same area for each sample which also leads to deviations in the results. In ICP-OES the results are easier to compare for different samples since the whole sample is analysed every time but the results will represent a mean value of the specimen and differences between different locations at the sample cannot be evaluated.

The results in Figure 31 show how the samples is evaluated using XRD. With this technique local variations of the crystalline products at the surface of the deposit can be studied. Also this technique conclude that AS is more efficient in reducing chloride containing products in the deposit compared to MAP at the windward side. By using this technique information regarding which type of chloride present at the surface is given. The main factor that the conclusion is based on in this case is that the KCl peak is decreasing when adding the different additives. Other products like iron oxide (Fe_2O_3 in figure) and potassium sulphate (K_2SO_4 in figure) can be studied in order to strengthen the conclusions. However, this technique is only analysing products that are crystalline. In this investigation no phosphorus containing phases was found, see chapter 3.2.2, which results in that additional effects of phosphorus cannot be studied.

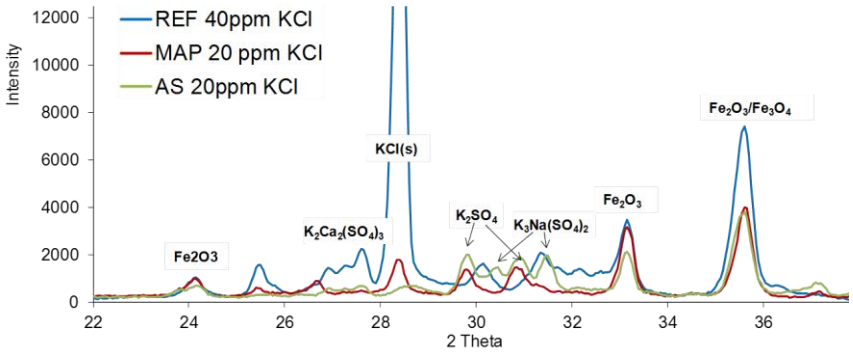


Figure 31. Results from XRD-evaluation showing crystalline products present in the deposit.

In Figure 32, the results from XRF-measurements are shown. The elements Cl, S and P have been selected for evaluation in this summary report. For the full report from these analyses see APPENDIX I. It can be seen that also this analysis method give the same conclusion as previous presented analysis with AS showing the best efficiency to decrease chlorine in the deposit. Comparing this with Figure 21 it can be seen that also with XRF a temperature dependence with metal temperature for the chloride content in the deposit is seen for AS but not for the other cases.

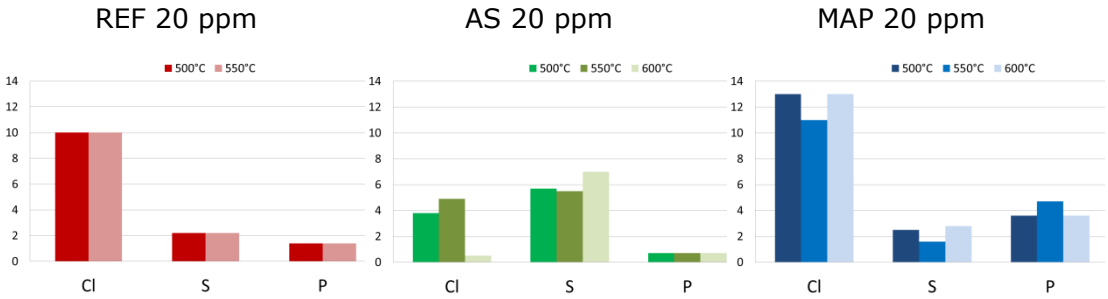


Figure 32. Results given from XRF analysis of deposit showing the amount of Cl, S and P in the deposit.

The last technique used was the TOF-SIMS analysis and selected results can be seen in Figure 33-34. For the full report from these analyses see APPENDIX II. This analysis method is giving the results in form of positive and negative ions from compounds at the deposit surface.

In Figure 33 (a) it can be seen that the intensity for KCl is strongly reduced in the cases with additives compared to the reference case. Comparing the two additives the KCl content is significantly lower for AS compared to MAP which is well in accordance with results from previous presented analysis techniques. As expected, the signal from potassium sulphate show a considerable increase in the AS samples but surprisingly also in the MAP samples. This is however believed to be caused by a signal contribution from potassium phosphate ($K_3PO_3H^+$) and should be considered as a highly uncertain result. Comparing KCl and NaCl the results show that the NaCl content in the samples is slightly decreased when using additive but not to the same extent as for KCl. However, the initial levels of NaCl are much lower making a direct comparison difficult. It is also shown that sodium sulphate is increasing in the AS samples while it stay rather similar in the REF and MAP case, see Figure 33b.

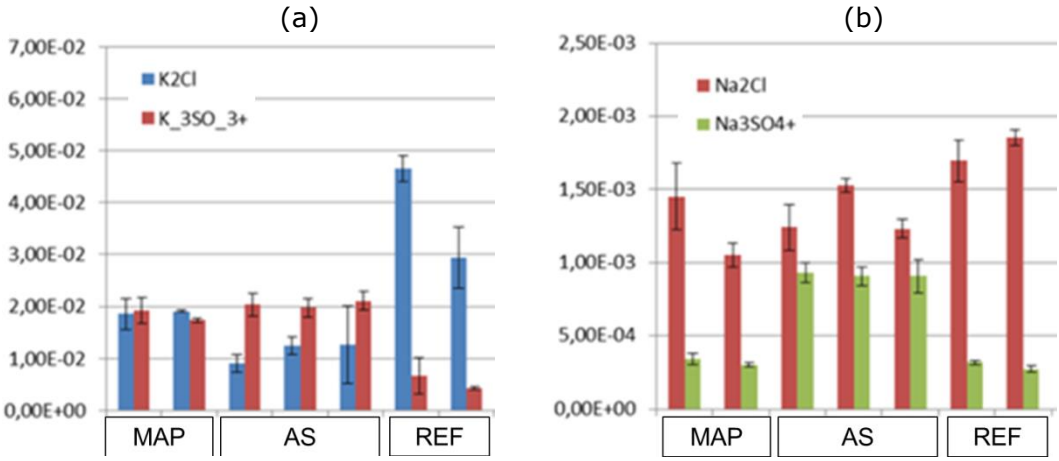


Figure 33. Results given from TOF-SIMS analysis of deposits showing the amount of phases in the deposit.

For this technique also the phosphorus containing compounds in the deposit can be detected and in Figure 34 these are presented. It is only for the MAP case it is possible to see any significant difference regarding the phosphorus containing compounds where potassium and calcium phosphate is increased.

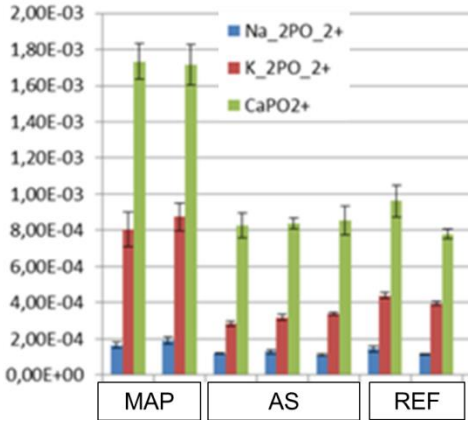


Figure 34. Results given from TOF-SIMS analysis of deposits showing the amount of phosphorous containing compounds.

An additional feature that can be used for TOF-SIMS is to study the distribution of the compounds at the analysed surface. The results strengthen the conclusions drawn from previous analysis methods that both additives work well for decreasing the potassium chloride at the surface and also that AS seems to be the most efficient additive. Additional information from this study is also that the particles of potassium chloride seem to be larger than the ones for potassium sulphate. It can also be seen that the particles appear to be separated at the surface and not in a mixed form since they then should have been yellow.

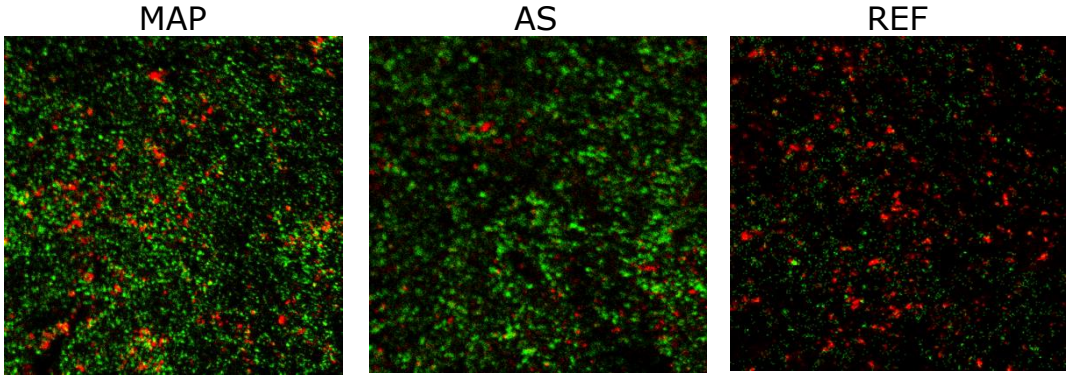


Figure 35. Results given from TOF-SIMS analysis of deposits showing the distribution of phases at the surface. Green: potassium sulphate, Red: potassium chloride. Area of analyse: 200*200µm^2.

4 Analysis of the results

4.1 Deposit chemistry depending on atmosphere

The main focus of this project has been to study KCl as the major corrosive species. Elements like lead and zinc, which are believed to behave in a corrosive manner together with Cl, have also been found in the deposits. These elements have not shown to be affected by the additive as the alkali chloride though and thereby have not been further studied within the project.

Three different approaches for changing the atmospheres in the test have been conducted; addition of sulphur containing additives (ammonium sulphate, AS), addition of phosphorous containing additives (mono ammonium phosphate, MAP) and also change of excess air (λ).

Increasing the dosage of both additives has shown to decrease the chloride content in the flue gas and it has also been shown that phosphorous containing additive have the best effect (measured in kg, P or S/h/MW) compared to the sulphur containing additive. However, this is not reflecting the deposit composition regarding chlorine content. For MAP the chlorine content in the deposit decreases with addition but does not show as low chlorine content as the AS until the KCl (g) content in the flue gas is as low as 5 ppm. However, for AS the chlorine content in the deposit is low for all cases regardless of KCl (g) content in the flue gas. This means that for MAP a higher addition is needed compared to AS in order to decrease the chloride content in the deposit, while for AS lesser amount of additive is required to do this effectively.

As commented in the background, sulphation can occur both in the gas phase (homogenous) and by the gas phase interacting with a liquid or solid phase (heterogeneous). From the results where ammonium sulphate and mono ammonium phosphate are compared it is believed that different mechanisms are active for the two cases. Both additives clearly showed to work for decreasing the KCl (g) content in the flue gas. However, for MAP mainly the homogenous sulphation is seen since the chloride content in the deposit is clearly following the measured KCl (g) in the flue gas. For AS on the other hand it seems as also heterogonous sulphation is occurring since very low or absent chlorine signal is measured in the deposits while the KCl in the flue gas shows a higher value.

If chlorine in the deposits is the major cause to corrosion these results show that for AS a higher KCl (g) content can be accepted in the flue gas compared with the MAP-case since much low chlorine contents in the deposit is measured.

When studying the deposit in cross section it could be seen that for both the cases when additives is added to reduce the KCl (g) in the flue gas to 5 ppm

no chlorine was detected close to the metal/oxide interface. Instead low amounts of sulphur could be detected which indicates that the deposited KCl (s) is sulphated before the chlorine can diffuse through the oxide scale or that sufficient sulphation also is occurring close to the interface. This is strengthening by the fact that very low chlorine contents are seen in the deposits for these samples. The same result was also seen for the full scale exposure in Jordbro where no or very low chloride content was measured at the metal/oxide interface with AS injection.

Another factor that also has shown to affect both the KCl (g) in the flue gas and the chlorine content in the deposit in a positive way is the oxygen content (λ). In the study where three different excess air levels and three different injection rates of AS was tested it was shown that when increasing the oxygen level the effect of AS was enhanced. A better sulphation of the flue gas could consequently be achieved by using both increased sulphate injection rates and increased excess air ratios. The lowered KCl (g) levels in the flue gas were reflected in the deposit composition which changed from KCl rich to K_2SO_4 rich. The best effect for decreasing chlorine in deposits when adding ammonium sulphate was seen when also the excess air was increased.

The deposit chemistry has also seemed to slightly be depending on metal temperature. This is however mainly seen for the addition of AS where the chlorine content in the deposit seem to be reduced with increasing metal temperature. A slight tendency for this is also seen for the reference case from the trials in Jordbro. A decrease in chlorine content is seen when increasing the temperature but it can also be seen that the deposits show a difference in thickness and it is not known how this is influencing the result since the results seen for the reference case in the AS/MAP additive trials in Gothenburg are somewhat contradictable to this with increased chlorine content in the deposit with temperature for the reference case. Due to this no no conclusions can be drawn regarding the temperature dependence for the case without AS addition.

4.2 Initial corrosion and deposit chemistry

The initial corrosion has been studied in several ways. For the first exposure where Sanicro 28 was exposed the corrosion rate was expected to be very low and not measurable in cross section. Instead the initial corrosion was measured as a function of surface roughness and spallation for the different samples. This showed that the initial corrosion seemed to be less connected to the chloride content in the deposit but rather influenced by the KCl content in the flue gas. The cases with higher KCl in the flue gas showed to have the highest degree of initial corrosion. However, an increase in sulphur addition and oxygen level seemed to decrease the risk of corrosion where the oxygen level showed to have an important role.

The pronounced corrosion attack that was observed, despite no or little chlorine being observed in the deposit, when ammonium sulphate was

injected at low air excess, can be explained by an initial deposition of KCl(s) on the tube surface and a subsequent sulphation by a heterogeneous reaction. During the initial residence time of KCl(s) it may react with the alloy forming poorly protective corrosion products.

These findings however show that it may not always be enough to only measure the chlorine content in the deposits in order to predict an accelerated chloride-induced initial corrosion attack. In this investigation the cases where KCl (g) in the flue gas was highest also the fastest initial corrosion attack was seen.

In the case where ammonium sulphate (AS) and mono ammonium phosphate (MAP) was used as additive the study of the initial corrosion was performed in cross sections of the low alloyed steel 2218. This investigation showed that the additives seemed to have a slight effect of the initial corrosion although it was not very pronounced. It was shown that the local corrosion attacks occurring for all samples played an important role in the evaluation. Since these occurred also for the cases where the highest levels of additives were used it is believed that the high temperatures for this steel is the most considerable reason for corrosion and no clear conclusions can be drawn regarding the effect of the additives. It was however seen in the cross section that the additive decreased the chloride content at the metal/oxide interface giving even more reason to believe that the corrosion is connected to the temperature and not the deposited KCl (s) at the surface.

When investigating the stainless steel 2352 and the effect of ammonium sulphate addition at increased metal temperatures (up to 640°C) internal corrosion was seen for the reference case at the highest temperature. This internal corrosion was not seen when adding ammonium sulphate showing that the corrosion mechanism partly has been changed. Two different injection rates were tested and it was shown that already the lowest injection rate seemed to be sufficient in order to avoid internal corrosion. Together with the results achieved in the test with injection of AS and MAP it can be concluded that ammonium sulphide has a clear effect of the initial corrosion even at low injection rates. Depending on temperature the deposit composition and structure seems to give different results in initial corrosion behaviour for the reference case indicating that different mechanisms is occurring at the two temperatures.

4.3 Use of analysis methods

The deposit composition has been evaluated with several methods in this project and all these methods have shown to give similar conclusions. However, the different techniques differ from each other regarding analysed area, sample size needed and achieved information.

4.3.1 Element analysis

Three methods that are giving similar information are SEM/EDS, IC/ICP-OES and XRF. These methods are all giving quantitative data of the elemental composition of the deposit. Even though the methods give similar results they are different when comparing analysed area. In IC/ICP-OES the whole sample is dissolved in water and acids in order to analyse the elements. This is useful when comparing for instance several samples within a test series. It is however more difficult to say anything about the local variations at the sample surface. Due to this the method can mostly be recommended when the mean value is wanted and when homogenous deposits are assumed. By using the XRF-analysis method a more local area can be analysed. In the utilized equipment, a sample size of 10*23 mm^2 has been used. In order to analyse the exposed ring specimen with this technique the samples needed to be cut before analysis. Then both windward and leeward sides can be chosen for analysis. When the technique is evaluated regarding usefulness the cutting is however needed to be taken into account since some time is needed for the cutting. This is less time consuming than the dissolving process though. It is preferable to cut the samples dry since water soluble elements are wanted to stay in the deposit which makes it slightly more time consuming. Another disadvantage of cutting is that it may result in flaking of the deposits from the surface. This is also the case for analysis performed with SEM/EDS where some cutting also is needed. In the SEM however, larger samples can be fitted and it is not a big problem with somewhat curved samples. By using SEM/EDS an even more local area of the samples can be analysed, in this project the largest area has been 2*2.5mm^2. This is giving good opportunities in order to study variations at the windward and leeward sides comparing with the IC/ICP-OES technique. Slightly more caution is needed though when comparing different samples since it is difficult to pinpoint the same analysis positions. It is also important to use several areas in order to get good statistics.

The methods are also different regarding analysed elements. By using SEM/EDS more or less all important elements can be analysed. For some sample it is however needed to complement the analysis also with WDS (wave-length dispersed spectrometry) in order to separate some elements that have an overlap in energies. Molybdenum and sulphur is one important example of typically problematic elements for this research area. Therefore, rings of Mo-free alloys are a preferred choice when performing deposit studies when SEM/EDS is considered as analysis method. Also for the XRF analysis some elements are problematic to analyse for instance B, C, N, O and F. In IC/ICP-OES all elements between Li and U in the periodic system, including P and S, can be analysed quantitatively even at low levels with the exception of oxygen and nitrogen due to that air is present in the analysis. In SEM the analysis is performed in vacuum and the problem with oxygen is eliminated. Still, nitrogen is difficult to quantify with SEM/EDS.

It can though be concluded that all these techniques are suitable for these kinds of investigations. What needs to be taken in account is if local differences are to be studied or if mean values are sufficient for evaluation. It has been shown in this investigation that local differences between the windward and leeward positions at the samples show different results for some cases.

4.3.2 Compound analysis

By using XRD and TOF-SIMS it is possible to study in what form different elements are present at the samples. In XRD results of crystalline products like KCl and K_2SO_4 is given. A drawback with this technique is however that no non-crystalline products can be analysed. In the investigation where mono ammonium phosphate was added to the flue gas it was expected to find phosphorus containing compounds at the samples. No such compounds were found with the XRD probably due to the fact that these were poorly crystalline. By using TOF-SIMS as additional analysis method also phosphorous containing compound was found since this technique can detect both crystalline and non-crystalline compounds. The TOF-SIMS are giving information about what ions that can be found at the surface and are thereby not dependent on if the compound is crystalline or not.

Both of the techniques are useful in this kind of investigation but they are different when comparing analysed area. In XRD a relatively large area can be analysed and by moving the sample, different positions like windward and leeward side of a sample can be analysed. This is also the case for TOF-SIMS but a much smaller area are analysed ($500*500\mu m^2$). Due to this also cutting of the samples are needed for the TOF-SIMS analysis. Since this method is a very surface sensitive technique it is very important not to contaminate the surface during preparation. This means that this technique is relatively demanding compared to the XRD.

Even though a very small area is analysed with TOF-SIMS one additional feature that is possible to use with this technique is to illustrate the distribution of different compounds at the surface. This cannot be achieved by using the XRD and has been a positive feature within this project.

Also for the compound analysis methods it can be concluded that both methods are suitable for these kinds of investigations. What needs to be taken in account is mainly the preparation of the samples and what size of the samples that is desired to study. If the compounds are non-crystalline or imaging of the distribution is important, TOF-SIMS is required. It is worth noting that TOF-SIMS is considered a very exclusive analysis technique and is usually more costly than the other techniques.

4.4 Guideline for deposit and corrosion analysis

Already at the planning stage of a project intending to investigate deposits and/or corrosion in boilers it is important to take into account what analysis methods are of interest. Below is listed a number of points that are of importance to consider in that work. The list is aimed to serve as a guideline. The contents reflect the findings from this work and it cannot be excluded that other factors of importance exist. Based on the limitations of this project the guideline considers only deposit collection and initial corrosion exposure made by cooled probes. Other analysis methods than the ones listed are available, but are not frequently used for this types of studies.

The exposure rings must be suitable for the intended study

- For precise studies of the behaviour of a *particular* alloy regarding deposit build-up on it or its corrosion behaviour that particular alloy must be used.
  - The surface condition of such a sample shall be in as-delivery condition.
- For more general studies it is often advantages to use materials having as less complex composition as possible, but a distinction between low alloyed and stainless steels, as well as Ni-based materials is required.
- If SEM/EDS are considered for the analysis, the alloying element Mo is preferably avoided to allow easy detection of S.
- Machined and even ground surfaces facilitates analysis of the samples when it comes to studies of initial corrosion, as original surface defects are removed.
  - The behaviour of modified surfaces may differ somewhat from the as-delivered condition and it must be considered if this can be accepted.

Choice of analysis method for deposits depends on the purpose of the study

- If analysis costs are of importance, they need to be evaluated for specific cases.
  - The cost depends on who performs the analysis and their agreements with the client, what specific information is expected from the analysis and the number of samples.
- For elemental analysis SEM/EDS, IC/ICP, and XRF are suitable and give comparable information.

- SEM/EDS allows small analysis points and detection of element distribution.
  - Cutting of the samples must be made without lubricants (dry) to avoid dissolution of some elements.
- IC/ICP allows quantitative determination of the total mass of specific elements deposited on the samples.
  - Complex sample preparation through leaching and dissolving in acid.
  - Distribution of elements can only be determined by (dry) cutting of the samples into sections which are separately leached and dissolved in acid.
- XRF is comparable to SEM/EDS in many aspects but have several drawbacks.
  - Fewer elements are detected and element distribution is not given.
  - Large samples are required.
  - The technique is not widely spread and the results appear to be highly dependent on the evaluation algorithm.
- For compound analysis XRD and TOF-SIMS are suitable.
- XRD has an advantage in giving the crystallographic structure of the compounds.
  - It is widely available, but usually requires separate input from another analysis method regarding the elements being present in the deposits.
- TOF-SIMS gives the distribution of elements that are combined to each other
  - Highly specialised and exclusive analysis method only available at few places.

The choice of analysis method for initial corrosion depends on the amount of corrosion attack

- It is recommended to first section the sample in halves by (dry) cutting to allow several analysis techniques to be used.
- Normally, it is most useful to analyse cross-sections.
  - By SEM/EDS it is possible to study the chemical composition of the oxide and the zones next to it.

- By SEM/EDS it is possible to observe onset of internal corrosion along for example grain boundaries.
- The thickness of oxides can be determined as an indication of the corrosion rate.
- If the original sample thickness is known and the corrosion attack is extensive, the metal loss rate can be determined.

- For small corrosion attacks, it is often only possible to evaluate these from observing the surface in top-view.

  - The deposits and oxides must be removed by mechanical or chemical descaling.
  - The descaling may have an impact on the appearance of the corroded surface, but does not prevent comparison of sample being treated by the same method.
  - The analysis technique allows only ranking of the amount of corrosion attack from the observed roughness of the surfaces and the presence of other defects such as pits.
  - The use of ground samples facilitates the evaluation substantially.

5 Conclusions

From the project the following conclusions can be drawn:

Deposit chemistry

- A better sulphation of the flue gas is achieved with both increased sulphate injection rates and increased excess air ratios. The lowered KCl(g) levels in the flue gas is reflected in the deposit composition which changes from KCl rich to K_2SO_4 rich.
- Both ammonium sulphate and mono ammonium phosphate can be used as additives to decrease the KCl(g) content in the flue gas.
- When injecting mono ammonium phosphate the deposit composition correlates well to the flue gas analyses, with lowered KCl(s) content when lowering the KCl(g) content in the flue gas.
- Injection of mono ammonium phosphate results in conversion of alkali chloride only in the gas phase (homogenous reactions).
- When injecting ammonium sulphate the deposit composition does not reflect the flue gas analyses and the chlorine concentration in the deposit becomes very low irrespective of injection rate within the investigated interval.
- Injection of ammonium sulphate results in conversion of alkali chloride both in the gas phase (homogenous reactions) and in the solid state (heterogeneous reactions).
- For ammonium sulphate slight temperature dependence is seen regarding chloride content in the deposit with decreased chlorine content with increased metal temperature.
- The chloride content in the deposit is not affected much depending on injection rate which indicates that even a relatively low injection rate is sufficient to avoid chlorine content in the deposit.

Initial corrosion

- A more pronounced corrosion attack could be observed without sulphate injection and at low excess air ratio.
- The pronounced corrosion attack that was observed, despite no or little chlorine being observed in the deposit, when ammonium sulphate was injected at low excess air, can be explained by an initial deposition of KCl(s) on the tube surface and a subsequent sulphation by a heterogeneous reaction. During the initial residence time of KCl(s) it may react with the alloy forming poorly protective corrosion products.
- At high metal temperatures (640°C) internal corrosion can be avoided by the use of ammonium sulphate injection.

- Additives seemed to have reduced the initial corrosion of material 2218 although the effect was not very pronounced at the high temperatures investigated.

Analysis methods

- Most importantly all analyse methods individually give similar conclusions. However, it is not recommended to only use one method since the use of several methods gives better conditions in order to draw the right conclusion.
- IC/ICP is advantages over SEM by being more quantitative and capable of analysing low concentrations, while SEM allows small analysis areas.
- XRF is a versatile tool but no particular advantage over the other techniques has been identified.
- XRD is advantages over TOF-SIMS for compound analysis by its ease of use and by allowing better statistics from large analysis areas, while TOF-SIMS allows analysis of non-crystalline compounds and imaging with high spatial resolution.

6 Goal fulfilment

Most project goals have been fulfilled and increased knowledge and understanding regarding the effect of steam temperatures and use of additives upon deposit formation and initial corrosion of superheater tubes has been achieved in following ways:

- Exposures in a pilot plant boiler have been performed and showed that the composition of the deposit and the flue gas is different depending on used additive. It has also been given results showing the importance of excess air ratio in the boiler. Information about how metal temperature affects the effect of additive and initial corrosion has also been achieved.
- Exposures in a full scale boiler have been performed and showed that additives are useful also at higher metal temperatures. Also in this exposure results which indicated a metal temperature dependence upon deposit chemistry and initial corrosion was achieved.

The secondary objective, to establish a guideline for deposit and corrosion analysis has also been fulfilled by comparing and evaluating five different analysis techniques. All techniques have shown to be useful and knowledge about time and cost for the different techniques have been achieved.

A goal that has not fully been fulfilled includes studying which particular types of chlorides are the first/last to be sulphated. The project plan within the pilot plant focused primarily on KCl. Other chlorides may have been present in the full scale trial. The elements Pb and Zn were indeed found in the deposits, but it was not possible to verify if they had been present as chlorides and if they have been sulphated. Although scientifically interesting, this question may not necessarily be of industrial relevance, since the study showed that the amounts Pb and Zn were not affected by ammonium sulphate injection and yet the chlorine content became negligible.

To establish schemes for controlled dosage of additives proved to be difficult in particular for ammonium sulphate. In fact, during injection the exact dosage was shown to be of lesser importance than the excess air ratio for the studied conditions. This information is highly valuable though, since the excess air ratio is typically decided from other criteria than corrosion, such as economic.

The overall goals of KME have been fulfilled by in cooperation between industry, institute and university building scientific knowledge of industrial interest on the effects of different additives on corrosion abatement. This will allow safer plant operation at higher steam temperatures and/or the use of wider fuel ranges. This will result in higher energy or cost efficiency promoting increased use of renewable or recycled energy sources, which in a global perspective counteracts global warming.

7 Suggestions for future research work

The positive effect of ammonium sulphate injection on combating corrosion on superheater tubes has been demonstrated for a low alloyed steel and an ordinary stainless steel by the use of corrosion probes. For safe life assessment it would be valuable to perform long-term field testing by incorporating pieces of various new and typical superheater alloys into a real superheater tube in operation and test these under actual operational conditions.

The positive effect of mono ammonium phosphate is clear, but an injection rate dependence have been identified. Injection of mono ammonium phosphate is probably not of industrial interest, but recently the interest of sludge as an additive to combat furnace wall corrosion has increased. The phosphor content of the sludge may have a positive influence on the superheater corrosion. When field tests are made regarding the use of sludge against furnace wall corrosion it is definitely worthwhile to investigate its influence on superheater corrosion as well. Showing a positive effect also on the superheater corrosion would strengthen the arguments for the use of this additive.

8 Literature references

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

[2] N. Folkeson, L.-G. Johansson, J.-E. Svensson, Initial Stages of the HCl-induced High Temperature Corrosion of Alloy 310, Journal of The Electrochemical Society, 154 (9), C515-521, 2007.

[3] C. Pettersson, J. Pettersson, H. Asteman, J.-E. Svensson, L.-G. Johansson, KCl-induced high temperature corrosion of the austenitic Fe–Cr–Ni alloys 304L and Sanicro 28 at 600°C, Corrosion Science 48 (2006) 1368–1378.

[4] J. Pettersson, N. Folkeson, L.-G. Johansson, J.-E. Svensson, The Effects of KCl, K_2SO_4 and K_2CO_3 on the High Temperature Corrosion of a 304-Type Austenitic Stainless Steel, Oxidation of metals vol.76, pp. 93-109, 2013

[5] T. Ishitsuka, K. Nose, Stability of protective oxide films in waste incineration environment-solubility measurements of oxides in molten chlorides, Corrosion Science 44, 2002, p.247-263

[6] M. Spiegel, Salt melt induced corrosion of metallic materials in waste incineration plants, Materials and Corrosion 50, 373-393, 1999

[7] D. Bankiewicz, S. Enestam, P. Yrjasa, M. Hupa, *Lab-scale Investigations of Zn and Pb Induced High Temperature Corrosion of Two Commercially Used Superheater Materials*, Proceeding of Impacts of Fuel Quality on Power Production and the Environment, Finland 2010

[8] P. Henderson, "Utvärdering av MELTGUARD" Värmeforsk report 751, October 2001.

[9] K. Iisa, Y. Lu, and K. Salmenoja, Sulphatation of potassium chloride at combustion conditions. *Energy & Fuels*, 13, pp. 1184-1190, (1999).

[10] P. Henderson, H. Kassman, C. Andersson and J. Högberg, "The use of fuel additives in biomass boilers to reduce corrosion problems" Presented at 12th European Conf. on Biomass for Energy , Amsterdam June 2002

[11] P. Henderson, C. Andersson and H Kassman,"The use of fuel additives in wood-fired boilers to reduce corrosion and fouling problems". Presented at Finnish- Swedish flame Days. Sept 2002.

[12] K. Salmenoja, Field and laboratory studies on chlorine–induced superheater corrosion in boilers fired with biofuels, Thesis, Report 00-1, Åbo Akademi, Åbo, Finland, 2000.

[13] J. Grabke, E. Reese and M. Spiegel, The effects of chlorides, HCl and sulphur dioxide in the oxidation of steels below deposits, *Corrosion Science*, 37, pp. 1023-1043, (1995).

[14] H. Krause, D. A. Vaughan, P. W. Cover, W. K. Boyd and R. A. Olexsey, Corrosion and deposits from combustion of solid waste. Part VI: *Trans. ASME, Journal of Engineering for Power*, 101, pp. 592-597, (1979).

[15] K. Salmenoja, K. Mäkelä, Prevention of superheater corrosion in the combustion of biofuels, Corrosion 2000, Paper No. 238, 2000.

[16] P. Szakalos, P. Henderson, R. Petterssson, KME-135 "Role of chlorine in superheater corrosion in waste and biomass fired boilers, 2004

[17] P. Viklund, P. Henderson, A. Stålenheim, A. Hjörnhede, P. Sjövall, R. Pettersson, KME-408 " Mitigation of chloride-induced corrosion in waste and biomass fired boilers. Phase II."

[18] K. Iisa, , Y. Lu, and K. Salmenoja, Sulphation of potassium chloride at combustion conditions. *Energy & Fuels*, 13, pp. 1184-1190, (1999).

[19] E. Skog et al. KME-411 "Evaluation of different fuel additives' ability to master corrosion and deposition on steam superheaters in a waste fired CFB-boiler."

[20] M. Almark, E. Edvardsson, M. Berg, Reduction of alkali chlorides in flue gas and chlorine in deposits by phosphate addition, Proceeding of Impacts of Fuel Quality on Power Production and the Environment, Finland 2010

[21] P.Viklund, "Superheater corrosion in biomass and waste fired boilers", Doctoral Thesis in Corrosion Science, Stockholm, 2013

9 Publications

1. Deposit chemistry and initial corrosion during biomass combustion – The influence of excess O_2 and sulphate injection. P. Viklund, H.Kassman, L-E. Åmand, Materials and corrosion, 2011

2. "Effects of sulphate and phosphate additives on mitigation superheater corrosion". P.Viklund, R.Norling, M.Berg, Published as paper V in Doctoral Thesis in Corrosion Science by Peter Viklund, Stockholm, 2013

3. Influence of ammonium sulphate additive on superheater corrosion at increased steam temperature during combustion of recycled wood. A.Talus, R.Norling, P.Henderson, Abstract accepted for a poster presentation at the 10th "Conference on Materials for Advanced Power Engineering" in Liege 2014.

10 Appendices

Appendix I

SP report”XRF analysis of combustion deposits in KME-504” by Bertil Magnusson and Peter Sjövall

Appendix II

SP report “TOF-SIMS analysis of combustion deposits in KME-504” by Peter Sjövall

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XRF analysis of combustion deposits in KME-504

Objective

Quantitative element analysis of combustion deposit film samples using XRF (X-ray fluorescence).

Samples

The samples analysed by XRF are specified in Table 1 below.

Sample	Additive	KCl level, ppm	Temperature °C
A1	MAP	20	600
A3	MAP	20	550
A6	MAP	20	500
N1	AS	20	600
N3	AS	20	550
N6	AS	20	500
D3	None	20	550
D6	None	20	500
E1	None	40	600
E6	None	40	500

Table 1 Specification of deposit samples analysed by XRF. MAP: mono ammonium phosphate, AS: ammonium sulphate.

Analysis method

Survey analysis was carried out according to method SP 4343, using a Thermo Advant-X XRF instrument and UniQuant® software. The method comprises semiquantitative analysis of the surface layer and is applicable to ca 70 of the 80 most common elements in the periodic system and provides approximate estimates of the concentrations. The probed surface layer is thinner for lighter elements. Important elements that are not measured are boron, carbon, nitrogen, oxygen and fluor.

Evaluation: The metal on the back side of one of the samples was analysed and used as background (substrate) for the evaluation. The concentrations in the deposit on top of the metal substrate were evaluated as oxides and are reported as elements. The concentrations are normally reported with

one significant digit. For comparison between samples, concentrations above 1% are reported with two significant digits.

Results

Grundämne	A1	A3	A6	N1	N3	N6
Natrium, Na, vikt-%	ca 0,5	ca 0,7	ca 0,6	ca 1,4	ca 1,0	ca 0,9
Magnesium, Mg, vikt-%	ca 1,2	ca 1,6	ca 1,3	ca 1,5	ca 1,3	ca 1,3
Aluminium, Al, vikt-%	ca 3,1	ca 4,6	ca 3,2	ca 4,7	ca 4,3	ca 4,2
Kisel, Si, vikt-%	ca 3,6	ca 5,4	ca 3,7	ca 5,0	ca 4,7	ca 4,7
Fosfor, P, vikt-%	ca 3,6	ca 4,7	ca 3,6	ca 0,7	ca 0,7	ca 0,7
Svavel, S, vikt-%	ca 2,8	ca 1,6	ca 2,5	ca 7,0	ca 5,5	ca 5,7
Klor, Cl, vikt-%	ca 13	ca 11	ca 13	ca 0,5	ca 4,9	ca 3,8
Kalium, K, vikt-%	ca 33	ca 25	ca 32	ca 31	ca 31	ca 31
Kalcium, Ca, vikt-%	ca 10	ca 13	ca 10	ca 12	ca 12	ca 13

Grundämne	D3	D6	E1	E6
Natrium, Na, vikt-%	ca 0,4	ca 0,4	ca 0,5	ca 0,6
Magnesium, Mg, vikt-%	ca 2,3	ca 2,3	ca 1,6	ca 1,9
Aluminium, Al, vikt-%	ca 5,8	ca 6,2	ca 5,2	ca 6,3
Kisel, Si, vikt-%	ca 6,5	ca 6,9	ca 5,6	ca 6,8
Fosfor, P, vikt-%	ca 1,4	ca 1,4	ca 1,0	ca 1,1
Svavel, S, vikt-%	ca 2,2	ca 2,2	ca 1,5	ca 1,7
Klor, Cl, vikt-%	ca 10	ca 10	ca 17	ca 14
Kalium, K, vikt-%	ca 22	ca 23	ca 27	ca 23
Kalcium, Ca, vikt-%	ca 16	ca 15	ca 12	ca 14

Table 2 Results from XRF analysis of combustion deposit samples.

The diagrams below show bar graphs of the concentrations determined by XRF, for some of the analysed elements. These results are consistent with the TOF-SIMS results (Appendix 2) showing qualitatively similar trends between the samples. In analogy with the corresponding diagrams for TOF-SIMS, the results from sample A3 has been removed due to deviating results suggesting possible problems with this sample.

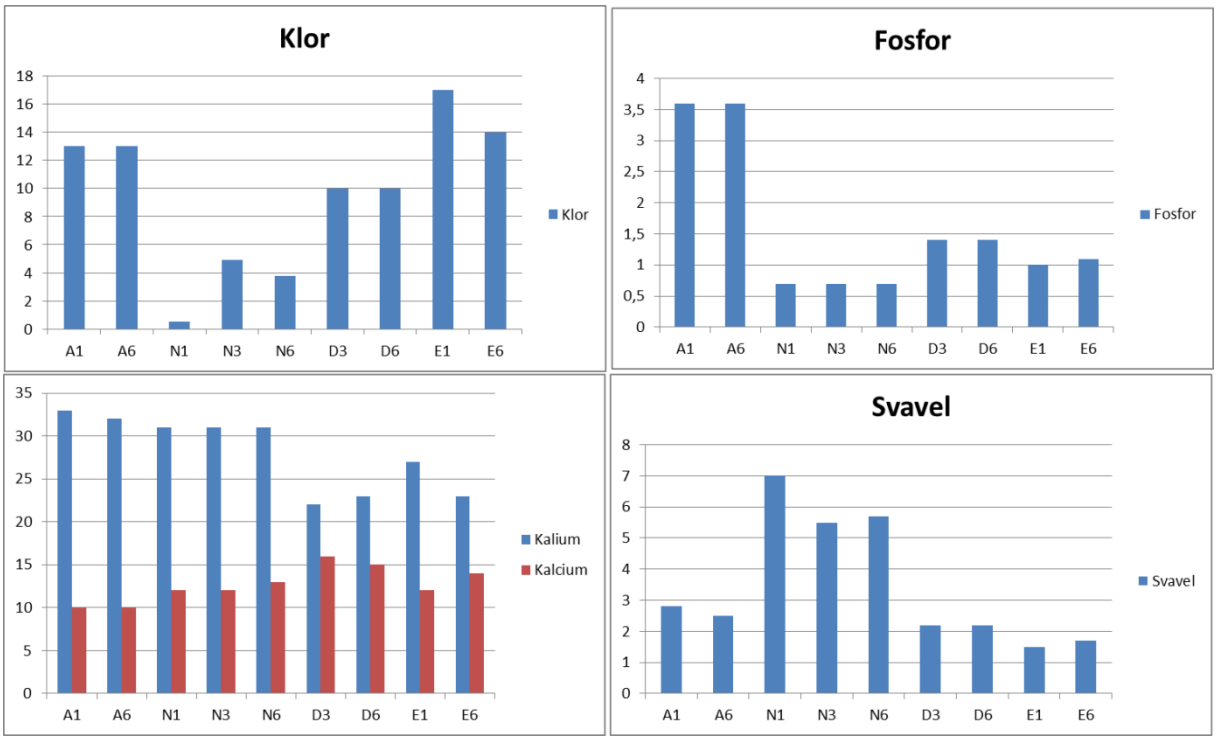

Figure 1 Diagrams comparing the concentrations (%) of selected elements, determined by XRF, between the different samples.

TOF-SIMS analysis of combustion deposits in KME-504

Objective

The objective with this study was to characterize the chemical composition of 10 deposit film samples obtained during different combustion conditions within the KME-504 project using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). ToF-SIMS is capable of spatially resolved detection of specific compounds on solid sample surfaces and the purpose of this study was to compare the different samples with respect to the abundance of the main chemical compounds and to provide information about the spatial distribution of the different compounds on the deposit surfaces.

Samples

The samples analysed by ToF-SIMS in this study are specified in Table 1 below.

Sample	Additive	KCl level, ppm	Temperature °C
A1	MAP	20	600
A3	MAP	20	550
A6	MAP	20	500
N1	AS	20	600
N3	AS	20	550
N6	AS	20	500
D3	None	20	550
D6	None	20	500
E1	None	40	600
E6	None	40	500

Table 1 Specification of deposit samples analysed by ToF-SIMS. MAP: mono ammonium phosphate, AS: ammonium sulphate.

The samples, which consisted of ca 15x20 mm^2 metal segments with combusion deposits on the outer surface, were cut out from the sample rings at Swerea KIMAB and sent to SP for analysis. The samples were loosely wrapped in Al foil, without the foil touching the sample surface, and placed in a plastic box for shipping. Upon analysis, the samples were mounted on the instrument sample holder and immediately inserted into the vacuum chamber of the ToF-SIMS instrument, with close attention not to touch or otherwise add contamination to the sample surface.

Analysis method

In TOF-SIMS, chemical information about the sample surface is obtained by bombarding the surface with high energy (primary) ions and analyzing the (secondary) ions emitted from the sample surface during the collision process. The secondary ions produce a mass spectrum where the peaks contain chemical information about the emitted secondary ions and thereby detailed chemical information about the sample surface. During analysis, the primary ion beam is scanned over a selected area on the sample surface and data is recorded separately from a selected number of raster points within the analysis area (typically 128x128 or 256x256 pixels). The recorded data can then be used to produce (i) ion images showing the signal intensity of a selected ion within the analysis area, (ii) total area mass spectra and (iii) mass spectra from selected regions of interest (ROI's) within the analysis area. Separate measurements are made to record data for positively and negatively charged secondary ions, respectively. Furthermore, the instrument can be optimized for maximum mass resolution (bunched mode: mass resolution $m/\Delta m$ ~7,000) or for maximum image resolution (burst alignment, spatial resolution 300-500 nm), since both the mass and lateral resolution cannot be maximized at the same time.

Quantitative information from ToF-SIMS is mainly limited to relative quantification between different samples for each compound separately (absolute quantification is possible only after determination of sensitivity factors using standard samples with similar but known compositions, and even then the uncertainties are relatively high). The numbers provided in the present report are the recorded signal intensities normalized to the total ion signal intensity, which means that comparisons of the signal intensity for a certain ion species between different samples reflect differences in the abundance of the corresponding compound between the samples. However, the differences in signal intensity from different compounds in the same sample do not reflect the relative abundances of the different compounds in this sample.

The TOF-SIMS data was acquired using a TOF-SIMS IV instrument (IONTOF GmbH) with a 25 keV Bi_3^+ primary ion beam and a low energy electron beam for charge neutralization of the sample surface. The pulsed primary ion current was 0.10 pA in the bunched mode and 0.05 pA in the burst alignment mode.

For each sample, positive and negative ion data were recorded in three different positions in the bunched mode (high mass resolution) at 500 x 500 μm^2 analysis area, and in one position in the burst alignment mode (high image resolution) at 200 x 200 μm^2.

Results and discussion

Characteristic peaks of various compounds were recorded in order to (i) compare the abundance of these compounds between the different samples and (ii) determine the spatial distributions of these compounds on the sample surface. Examples of secondary ions recorded and the compounds they represent are given in Table 2.

Table 2 Examples of recorded secondary ion peaks used to represent chemical compounds

Positive ions

Peak Label	Mass	Compound
$CaCl^+$	74,94	$CaCl_2$
Na_2Cl^+	80,95	NaCl
$CaPO_2^+$	102,93	Ca_xPO_y
$CaSO_2^+$	103,93	Ca_xSO_y
$Na_2PO_2^+$	108,95	Na_xPO_y
K_2Cl^+	112,90	KCl
$^{41}KKCl^+$	114,89	KCl
$K_2PO_2^+$	140,90	K_xPO_y
$K_2PO_3^+$	156,89	K_xPO_y
$Na_3SO_4^+$	164,92	Na_2SO_4
$K_3Cl_2^+$	186,82	KCl
$K_3SO_3^+$	196,86	K_2SO_4
$K_3SO_4^+$	212,85	K_2SO_4

Negative ions

Peak Label	Mass	Compound
PO_2^-	62,97	Phosphates
SO_2^-	63,97	Sulphates
PO_3^-	78,97	Phosphates
SO_3^-	79,96	Sulphates
$NaCl_2^-$	92,94	NaCl
KCl_2^-	108,91	KCl
$CaCl_3^-$	144,90	$CaCl_2$

Comparisons between the different samples of characteristic signals from a variety of compounds are shown in figures 1-6. One of the samples (A3) showed markedly deviating results, both in ToF-SIMS and XRF. Although the reason for this deviation is not known, it was concluded that sample A3 most likely has been compromised in some way and the results from this sample has therefore been removed from the diagrams in figs. 1-6. The results from sample A3 are instead provided separately in Table 3.

Figure 1 compares how the signal intensities of potassium chloride and potassium sulphate vary between the samples. The high signal from potassium chloride in the samples obtained without additives (D3-E6) is strongly reduced in the samples obtained with additives, with AS (N1-N6) resulting in a significantly lower potassium chloride signal than MAP (A1, A6). As expected, the signal from potassium sulphate is considerably increased in the AS samples as compared to the samples without additives. The observed increase in the potassium sulphate signal in the MAP samples compared to the non-additive samples is most likely caused by a contribution to the potassium sulphate signal (K3SO3+) from potassium phosphate (K3PO3H+) and should therefore be considered as highly uncertain.

Figure 2 shows that the sodium chloride content in the deposits is only marginally reduced by the additives, while the sodium sulphate signal is significantly higher in the AS samples as compared to the MAP and non-additive samples.

The comparison between calcium compounds in Fig. 3 shows that the calcium phosphate signal is higher in the MAP samples as compared to the AS and non-additive samples, while neither calcium chloride nor calcium sulphate show significant differences between the samples.

Figure 4 shows that, similarly to calcium phosphate, also the potassium phosphate signal is increased in the MAP samples as compared to the AS and non-additive samples. However, the very small increase observed for sodium phosphate in the MAP samples cannot be considered significant.

Figures 5 and 6 show results from negative ion data, which qualitatively agree with the positive ion data shown in the previous figures.

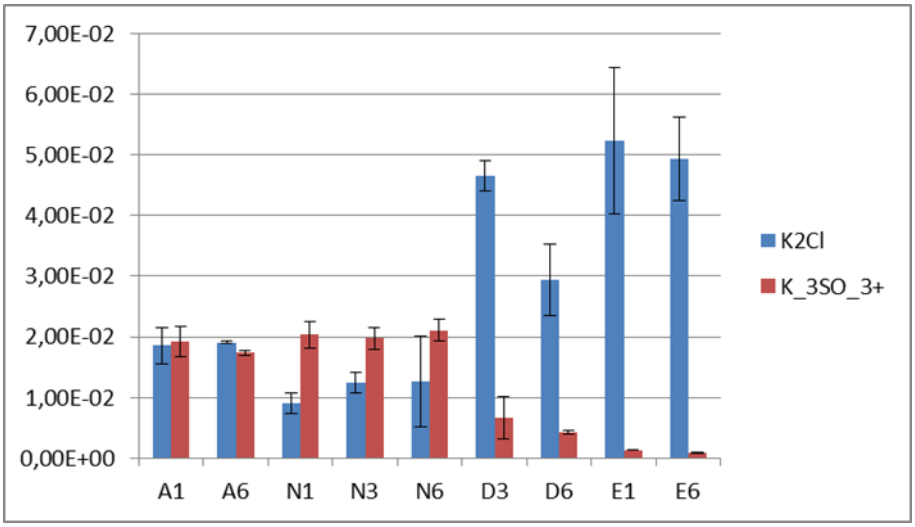

Figure 1 Normalised signal intensities from positive secondary ions representing potassium chloride (K2Cl) and potassium sulphate (K_3SO_3+). Each bar shows the average value from three measurements and the error bars show the standard deviations.

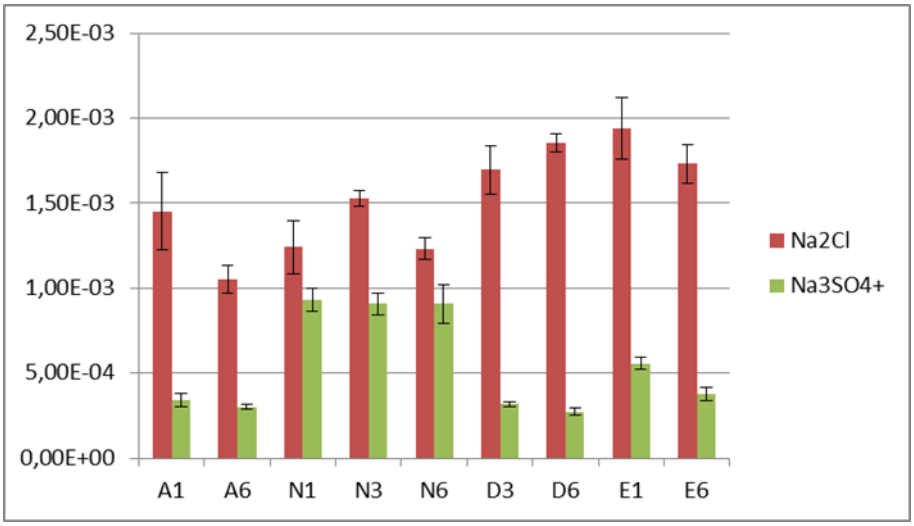

Figure 2 Normalised signal intensities from positive secondary ions representing sodium chloride (Na2Cl) and sodium sulphate (Na3SO4+). Each bar shows the average value from three measurements and the error bars show the standard deviations.

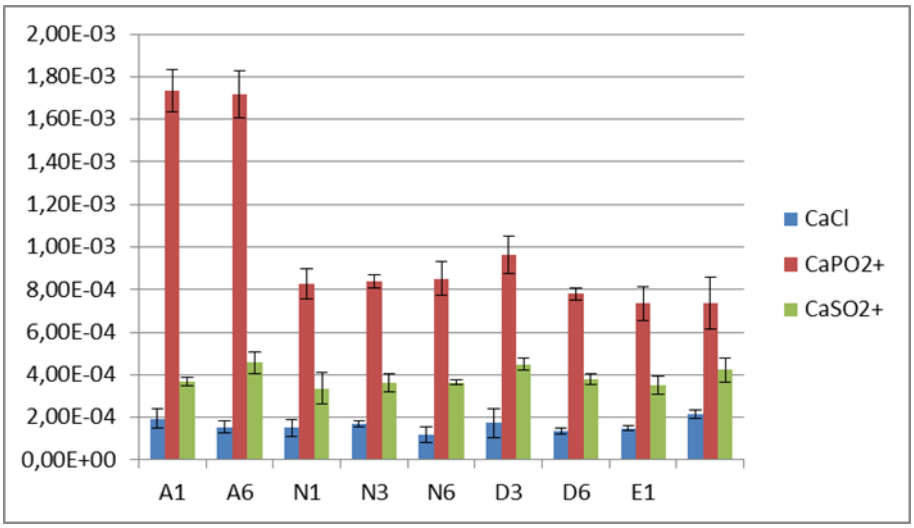

Figure 3 Normalised signal intensities from positive secondary ions representing calcium chloride (CaCl), calcium phosphate (CaPO2+) and calcium sulphate (CaSO2+). Each bar shows the average value from three measurements and the error bars show the standard deviations.

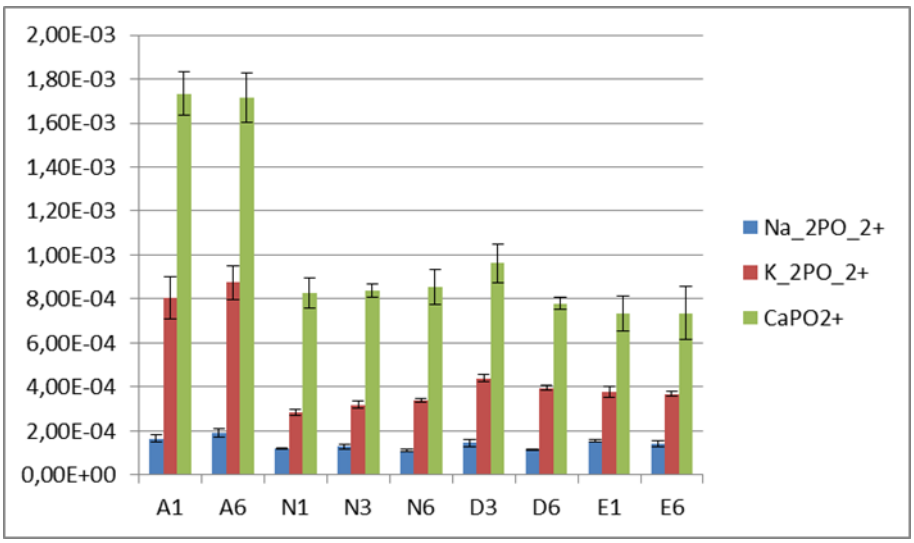

Figure 4 Normalised signal intensities from positive secondary ions representing sodium phosphate (Na_2PO_2+), potassium phosphate (K_2PO_2+) and calcium phosphate (CaPO2+). Each bar shows the average value from three measurements and the error bars show the standard deviations.

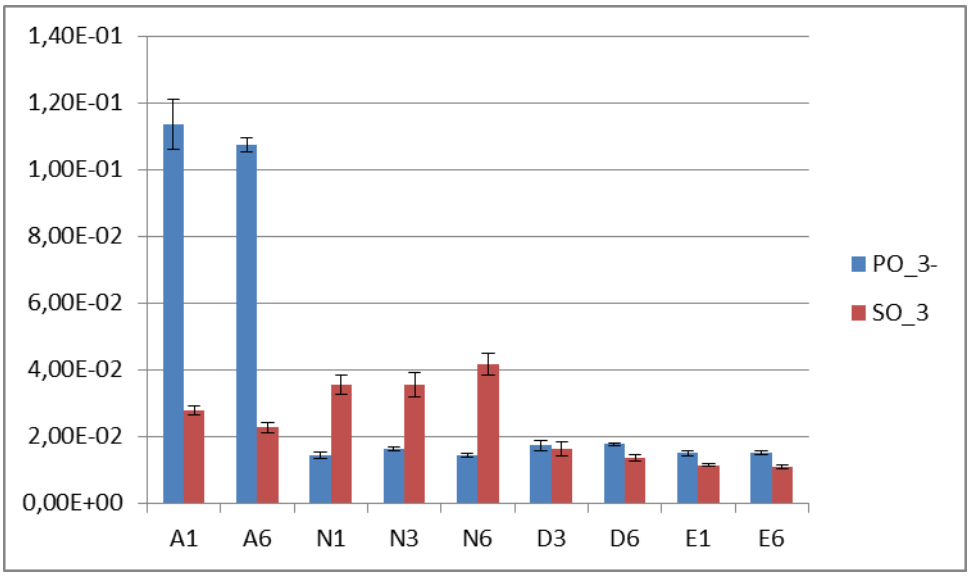

Figure 5 Normalised signal intensities from negative secondary ions representing phosphates (PO_3-) and sulphates (SO_3-). Each bar shows the average value from three measurements and the error bars show the standard deviations.

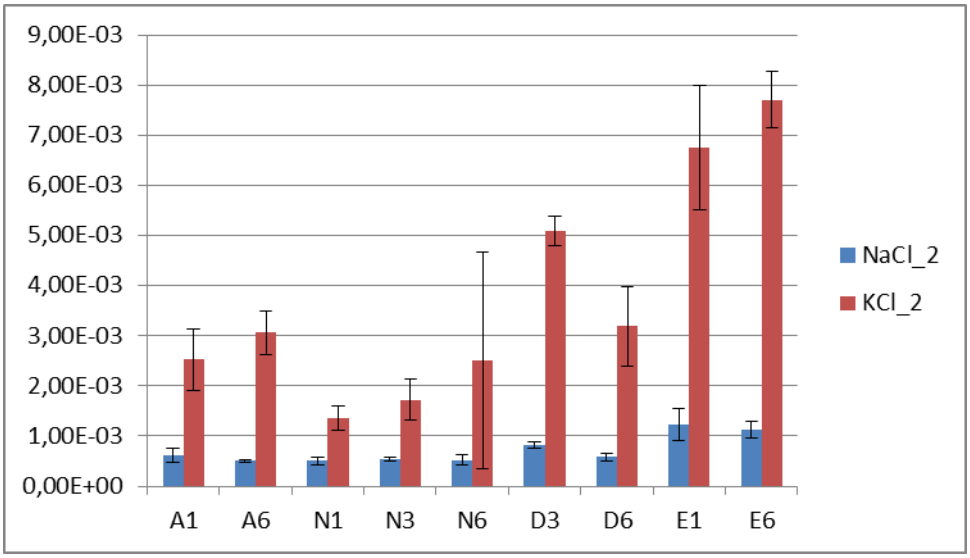

Figure 6 Normalised signal intensities from negative secondary ions representing sodium chloride (NaCl_2-) and potassium chloride (KCl_2-). Each bar shows the average value from three measurements and the error bars show the standard deviations.

Table 3 Recorded signal intensities for sample A3.

Positive

Mass	Peak Label	Av Signal	St Dev
74,94	CaCl+	1,31E-04	±7,11E-05
80,95	Na2Cl+	8,98E-04	±2,35E-05
102,93	CaPO2+	1,21E-03	±1,96E-04
103,93	CaSO2+	5,26E-04	±9,59E-05
108,95	Na2PO2+	1,97E-04	±3,80E-05
112,90	K2Cl+	4,76E-02	±1,39E-03
140,90	K2PO2+	1,88E-03	±3,22E-04
164,92	Na3SO4+	2,24E-04	±2,77E-05
196,86	K3SO3+	9,08E-03	±6,82E-04

Negative

Mass	Peak Label	Av Signal	St Dev
78,97	PO_3-	1,51E-01	±2,05E-02
79,96	SO_3	1,42E-02	±1,66E-03
92,94	NaCl_2	1,09E-03	±7,77E-05
108,91	KCl_2	1,24E-02	±1,65E-03

Figure 7-12 show TOF-SIMS images of selected compounds in three of the analysed samples: A1 (MAP, 600 °C, 20 ppm KCl), N1 (AS, 600 °C, 20 ppm KCl) and E1 (no additive, 600 °C, 40 ppm KCl). For each sample, TOF-SIMS images obtained in the bunched mode (high mass resolution) at an analysis area of a 500 x 500 μm^2 as well as high resolution images obtained in the burst alignment mode at an analysis area of 200 x 200 μm^2 are displayed.

Potassium chloride and potassium sulphate both display pronounced particle-like distributions on the deposit surfaces, with the potassium chloride particles being generally slightly larger and less dense than those of potassium sulphate. The relative distribution of potassium chloride and potassium sulphate is particularly highlighted in the high-resolution red-green overlay images. These images show that the majority of the particles on the deposit surface are either potassium chloride (red) or potassium sulphate (green), and not mixed particles containing both compounds. If the latter would be the case, the color of the particles would be a mix of red and green, i.e. yellow. The fact that most particles are either red or green, and not yellow, therefore indicates that separate potassium chloride and potassium sulphate particles dominate on the deposit surface. This observation seems to be valid independently on the type of the samples, i.e. for both types of additives and without additive.

Sodium chloride and sodium sulphate show occasional particle structure, which also may coincide, indicating mixed sodium chloride and sodium sulphate particles. However, these particles are not sufficiently abundant to allow for general conclusions. Calcium sulphate and calcium phosphate both provide signal to the Ca2O+ ion that is mapped in the bunched images. These images show mainly a homogeneous distribution on the surface.

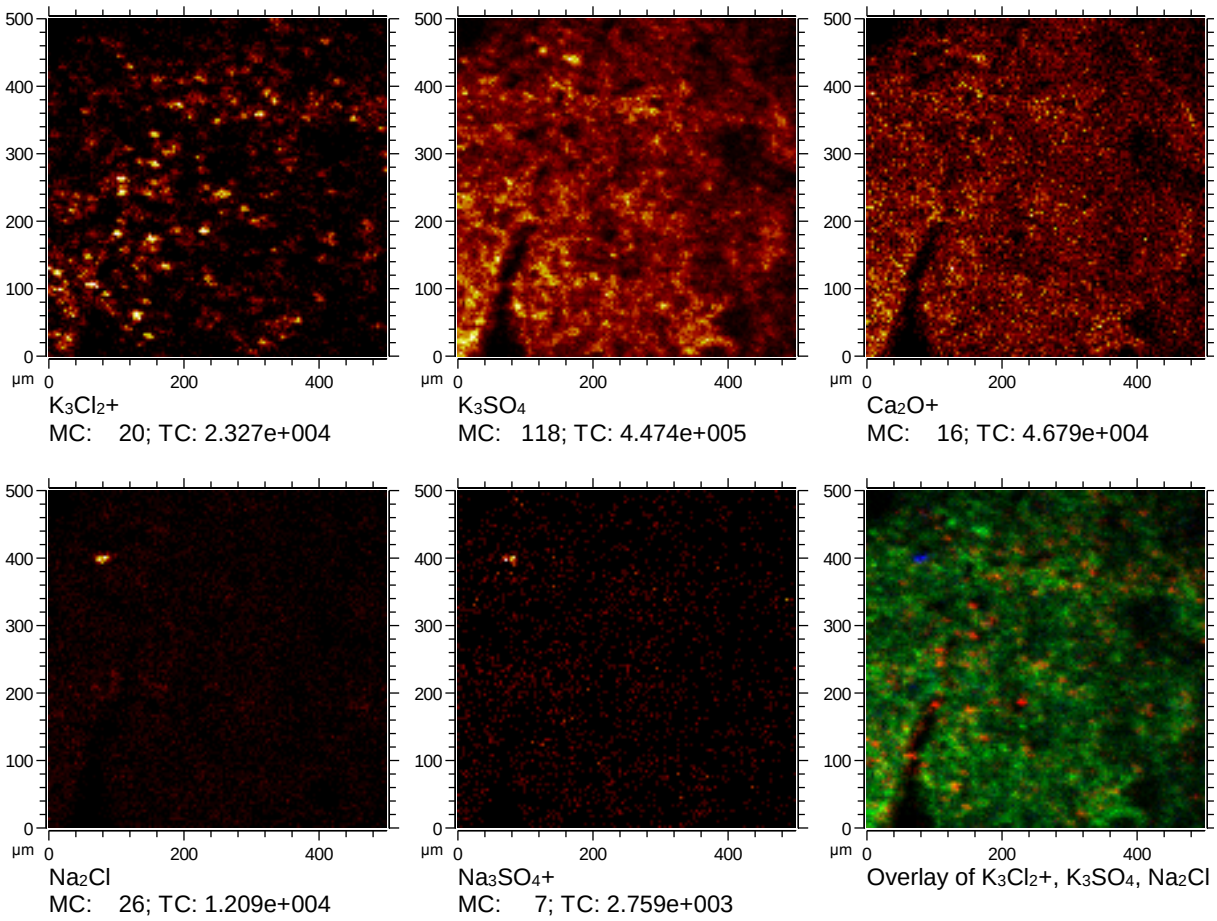

Figure 7 TOF-SIMS images obtained in the bunched mode from sample A1 (MAP, 600 °C) showing the spatial distributions of potassium chloride (K3Cl2+), potassium sulphate (K3SO4+), calcium phosphate/sulphate (Ca2O+), sodium chloride (Na2Cl+) and sodium sulphate (Na3SO4+). The three-color overlay shows potassium sulphate in red, potassium chloride in green and sodium chloride in blue.

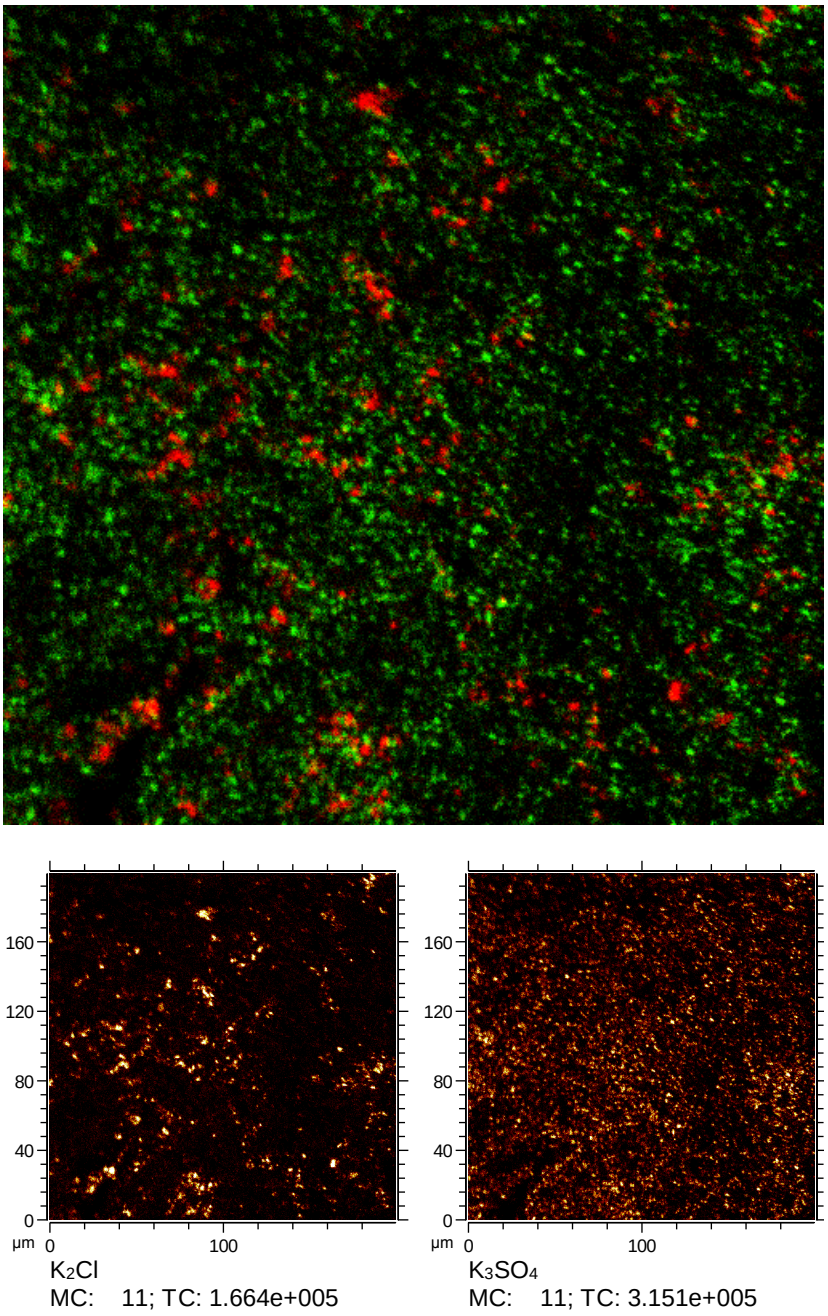

Figure 8 TOF-SIMS images of potassium chloride (K2Cl) and potassium sulphate (K3SO4) on sample A1 (MAP, 600 °C) obtained in the burst alignment mode (high image resolution). The overlay image shows the potassium chloride distribution in red and potassium sulphate in green.

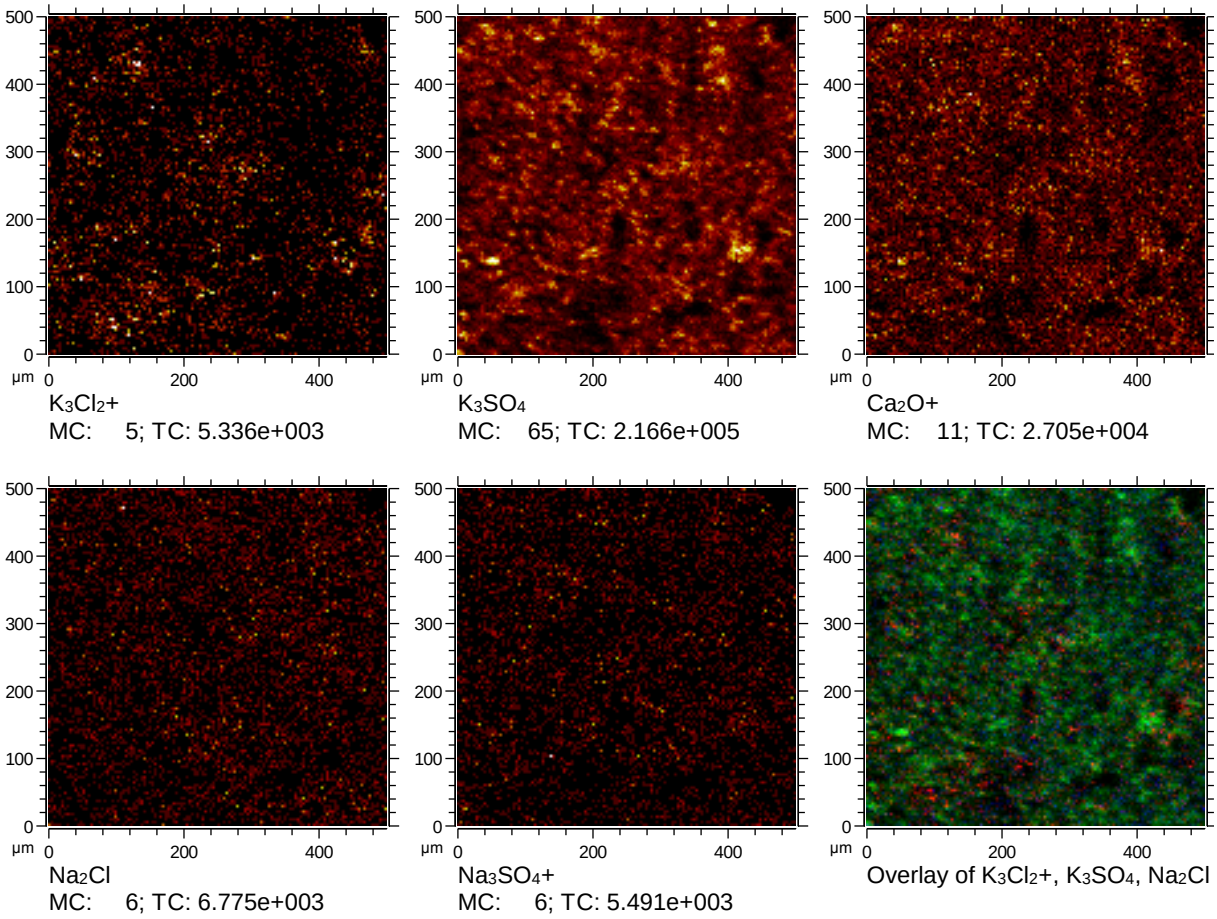

Figure 9 TOF-SIMS images obtained in the bunched mode from sample N1 (AS, 600 °C) showing the spatial distributions of potassium chloride (K3Cl2+), potassium sulphate (K3SO4+), calcium phosphate/sulphate (Ca2O+), sodium chloride (Na2Cl+) and sodium sulphate (Na3SO4+). The three-color overlay shows potassium sulphate in red, potassium chloride in green and sodium chloride in blue.

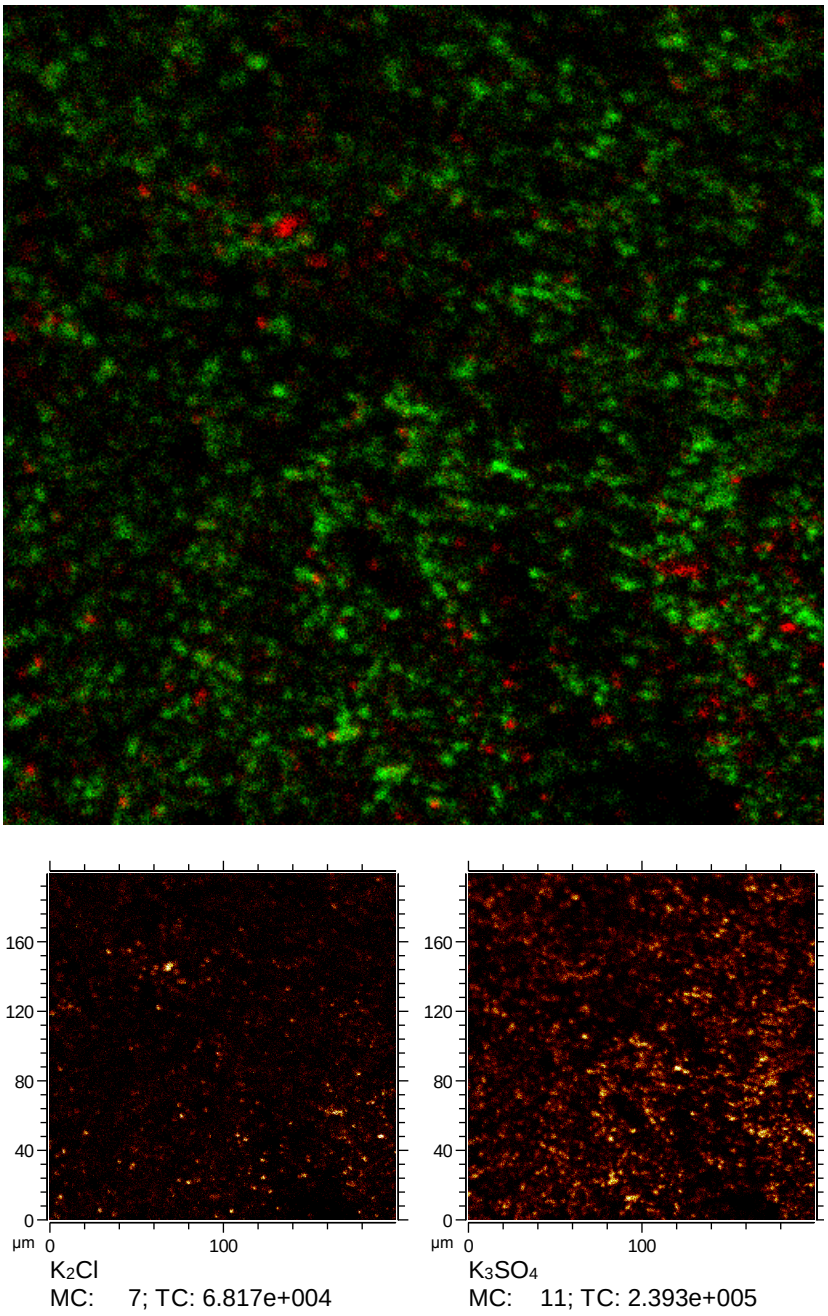

Figure 10 TOF-SIMS images of potassium chloride (K2Cl) and potassium sulphate (K3SO4) on sample N1 (AS, 600 °C) obtained in the burst alignment mode (high image resolution). The overlay image shows the potassium chloride distribution in red and potassium sulphate in green.

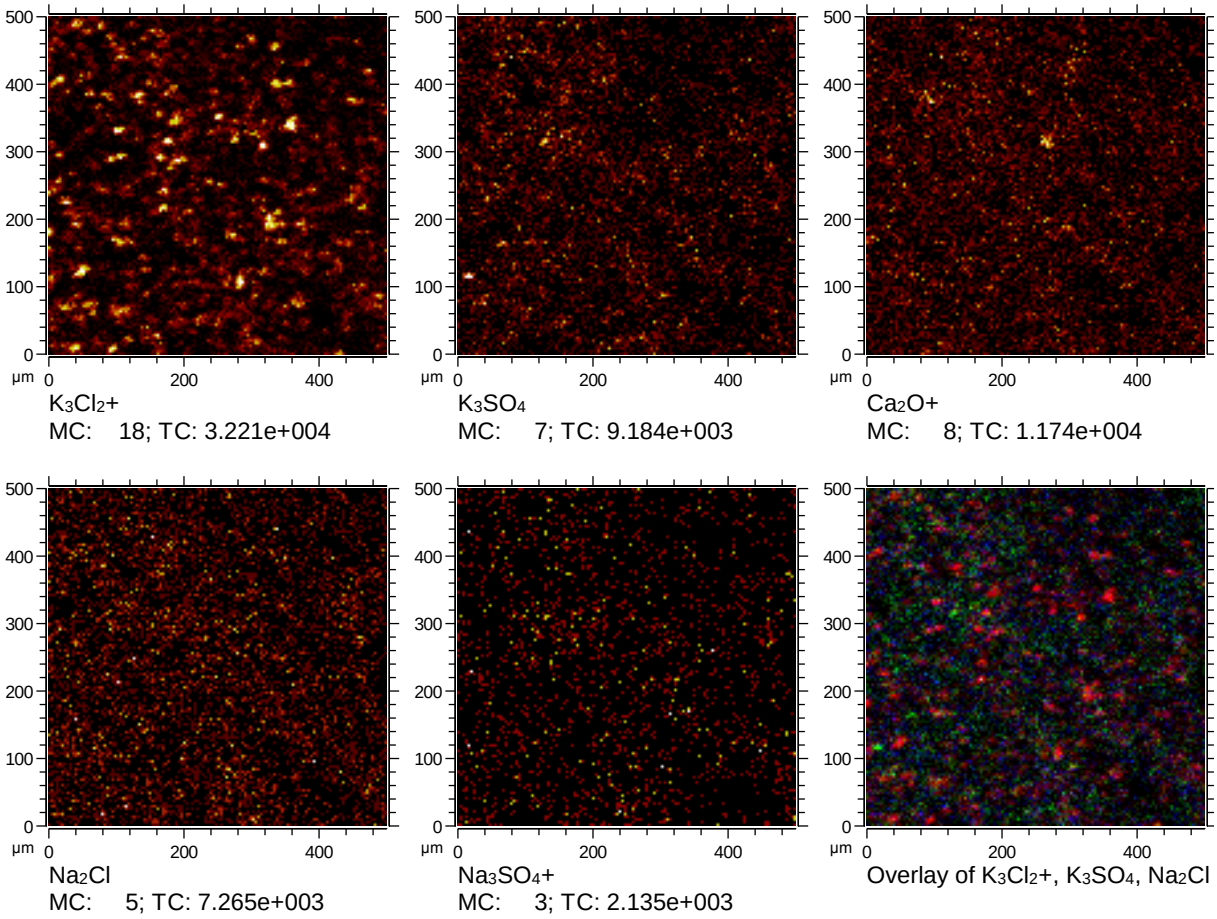

Figure 11 TOF-SIMS images obtained in the bunched mode from sample E1 (no additive, 600 °C, 40 ppm KCl) showing the spatial distributions of potassium chloride (K3Cl2+), potassium sulphate (K3SO4+), calcium phosphate/sulphate (Ca2O+), sodium chloride (Na2Cl+) and sodium sulphate (Na3SO4+). The three-color overlay shows potassium sulphate in red, potassium chloride in green and sodium chloride in blue.

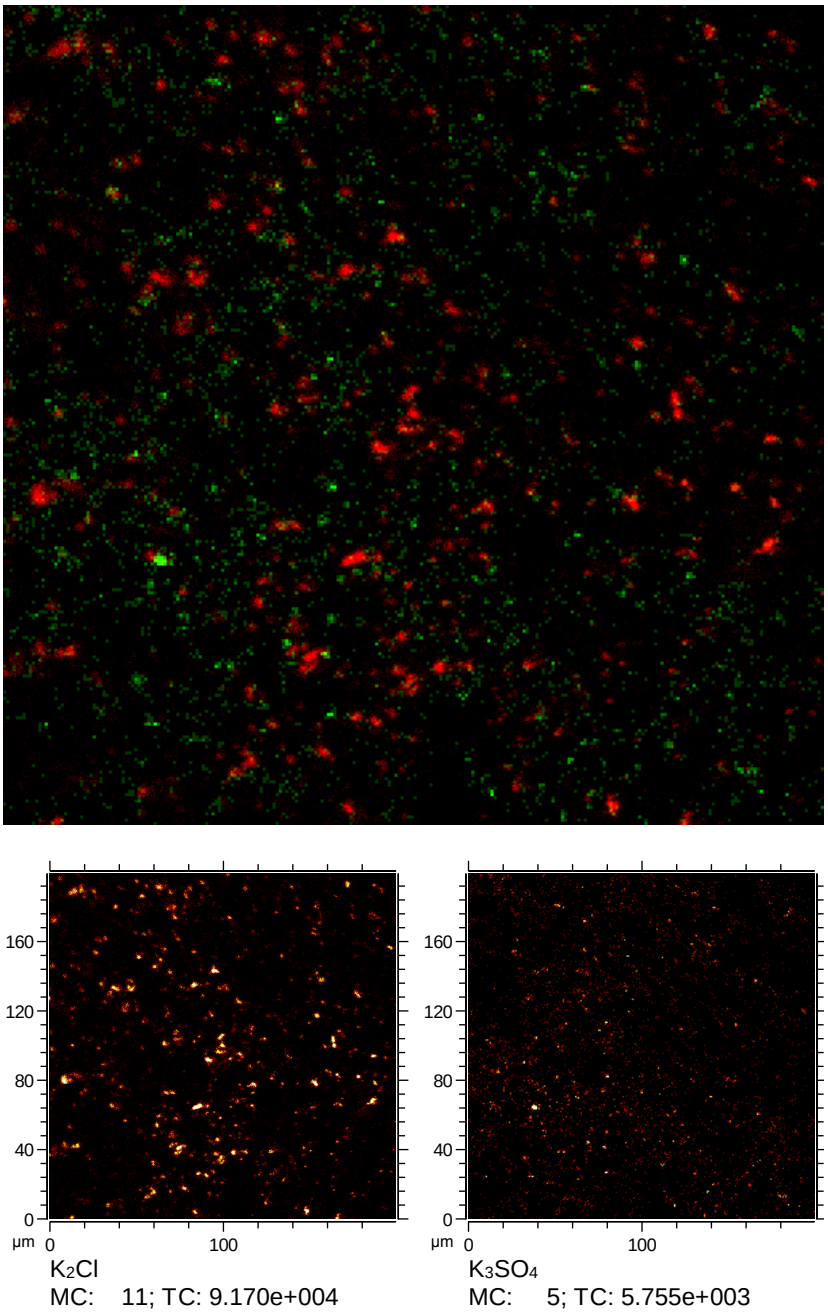

Figure 12 TOF-SIMS images of potassium chloride (K2Cl) and potassium sulphate (K3SO4) on sample E1 (no additive, 600 °C, 40 ppm KCl) obtained in the burst alignment mode (high image resolution). The overlay image shows the potassium chloride distribution in red and potassium sulphate in green.

Conclusions

Detection of specific compounds with TOF-SIMS was used to compare the abundance of various compounds, including alkali chlorides and sulphates, between the different samples and to determine the spatial distributions of these compounds on the deposit surfaces.

It was found that ammonium sulphate strongly reduce the abundance of potassium chloride on the deposit surface and increases the concentration of potassium and sodium sulphate. Sodium chloride

was only marginally reduced and no significant effect was observed for calcium chloride, calcium sulphate or calcium phosphate. Mono ammonium phosphate was found to reduce the abundance of potassium chloride, although not as much as ammonium sulphate did, and increase the abundance of calcium phosphate and potassium phosphate. No significant effect of mono ammonium phosphate was observed for sodium chloride, calcium chloride, calcium or sodium sulphate or sodium phosphate.

Potassium chloride and potassium sulphate are mainly present on the deposit surface as separate particles, without any significant mixing. The size of the particles are in the range 1-2 µm or below for the majority of the particles, but can occasionally be up to 5-6 µm for potassium chloride.