

R E S E A R C H   R E P O R T

**Characterisation of surface deposits and corrosion layers of thermal power plant materials by glow discharge optical emission spectroscopy (GD-OES)**

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Rikard Norling*

**KIMAB 2015-539**

**Limited distribution, open after 2019-12-31**

**Project No.: 12073/ÅF 13-317**

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## Summary

The internal surfaces of thermal power plants become covered with deposits from the combusted material (fuel) as well as a gradual build-up of various corrosion products. The formed layers are highly complex in composition and structure, varying depending on the alloy, temperature, type of fuel, etc. The elements present in the deposited layers affect the corrosion processes, and thereby the service lifetime of the boilers. In order to better understand these corrosion processes, compositional depth profiling (CDP) of the layers is very valuable analytical information. A radio frequency (RF) Glow Discharge Optical Emission Spectroscopy (GD-OES) method has been developed for quantitative depth profile analysis of these surface deposits.

Some of the major elements of interest are Cl, S, Ca, Na and K, and there are no commercially available solid reference materials (RM) with mass fractions in the range found in these materials. It was therefore necessary to produce dedicated RM's for calibration. The method devised within the project was to spray salt solutions onto steel substrates and subsequently dry these, producing coatings of well-known composition for calibration. The average thicknesses (or rather coating weight/area) of the coatings were determined by weighing the samples before and after deposition. This method was shown to work satisfactory.

A comparison with SEM cross section images have also shown that the in-depth structure of the depth profiles qualitatively agree well with the observed structure in the images. However, the analytical work has also shown that some of these types of materials are "difficult" to analyse by GD-OES, in the sense that the plasma discharge tends to be unstable. It should therefore be noted that not all materials of this type will be amenable to GD-OES analysis.

Comparing some field exposures of 16Mo3 and 310S it has been shown that differences in corrosion mechanisms can be detected with the GD-OES method. By observing the positions in the depth profile of primarily K and Cl, the ability of a material to withstand corrosion can be deduced.

The GD-OES method developed is a valuable analytical tool in continued research on the corrosion properties of thermal power plants, as well as the chemical processes responsible for this corrosion.



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# 1. Background

The internal surfaces of thermal power plants become covered with deposits from the combusted material (fuel) as well as a gradual build-up of various corrosion products. Affected components are primarily furnace walls and super heater tubes. The formed layers are highly complex in composition and structure, varying depending on the alloy, temperature, type of fuel, etc. The elements present in the deposited layers affect the corrosion processes, and thereby the service lifetime of the boilers. In order to better understand these corrosion processes, compositional depth profiling (CDP) of the layers is very valuable analytical information. Examples of elements of interest present in high concentrations are Cl, K, Na, Ca, S, Pb, Zn etc. Commonly used materials include 15Mo3, 13CrMo44, 347H, 310S, Sanicro 28, Inconel 625 etc. Examples of corrosion mechanisms associated with the layer composition and in-depth distribution are:

- Chlorine induced corrosion; HCl, NaCl and KCl are released from the fuel and can increase the corrosion rate.
- Decomposition of protective oxides; e.g. KCl can react with chromium oxides, form chromates and thereby deplete the Cr content of the oxide, resulting in decreased corrosion protection.
- Corrosion due to molten salt; the protective oxide layer can also be decomposed by molten salts, e.g. ZnCl<sub>2</sub>, PbCl<sub>2</sub> and FeCl<sub>2</sub>.

The in-depth variation of these complex and normally non-conductive layers are difficult to analyse by conventional techniques such as SEM, unless they are exceptionally thick and reliable cross-sections can thereby be obtained. However, recent trials have shown that Radio Frequency (RF) Glow Discharge Optical Emission Spectroscopy (GD-OES) [1, 2] is an analytical technique capable of CDP of this type of layers. In GD-OES, the surface layer is sputtered by argon ion bombardment in a low pressure plasma (the glow discharge). With a high current density in the plasma, the sputtering rate is high compared with all other sputter depth profiling techniques, allowing analysis of layers up to 100 µm in less than an hour. Sputtered atoms from the sample surface are energetically excited in the plasma, and emit element-specific optical emission. The optical emission spectrum is analysed by an optical emission spectrometer (OES), sampled at a frequency from 1 to 200 Hz (depending on the application) and recorded as a function of time. In this way, an elemental depth profile through the surface layers into the steel matrix is obtained. This depth profile can be quantified, provided that suitable calibration samples are available. A major advantage of GD-OES is that the light elements O, N, C, P and S can be analysed with high sensitivity. This is also true for alkali elements, where the sensitivity of GD-OES is very high. For Cl, previous exploratory work performed on different corrosion layers have shown that the analytical sensitivity is good, but the major remaining difficulty is to obtain suitable reference materials for calibration. Even H can be determined, but it is the most “difficult” element in the sense that there exists a substantial spectral background which is not easily separated from the true signal from the sample. Another feature of GD-OES is that there is very limited lateral resolution, the sputtered spot is 4 or 2 mm wide and the elemental composition is obtained as an average over this relatively large area. In this type of application, this feature can actually be an advantage over analytical techniques providing data on a microscale.

The complex layers at internal surfaces of a boiler present several additional challenges requiring further research and development in order to obtain as accurate analytical information as possible. These include preferential sputtering effects, depth calibration of partly porous layers and determination of the degree of non-linearity of highly sensitive spectral lines from key elements, e.g. Ca, S, Na and K. Furthermore, due to the abundance of light elements in these layers, a comprehensive investigation of possible background emission from several molecular species is required. Sample preparation is also an important issue; the uneven and slightly porous deposition layers require mounting smaller samples in either a solder or a special holder in order to obtain a vacuum seal.

KIMAB has a unique competence in the field of quantitative CDP with GD-OES; the method currently used by leading GD-OES instrument manufacturers was originally developed by KIMAB and licensed to these manufacturers. In this project, it is proposed to develop a dedicated GD-OES method for quantitative CDP of deposited layers from boilers. This includes optimization of the glow discharge parameters, obtaining calibration samples, and verification by detailed study of a wide range of deposition layers.

Deposited materials for chemical analysis are typically collected by scraping from boiler surfaces during maintenance periods or by using dedicated sampling probes during operation. Occasionally pieces of boiler or super heater tubes are cut from the plants during maintenance for more detailed microstructural analysis. All these types of samples are suitable for quantitative CDP with GD-OES and they would yield substantially more information regarding the corrosion process, if analysed regarding their in-depth distribution of elements in the deposits.

## 2. Aims

The objectives of the project are:

- To develop a dedicated GD-OES method for quantitative depth profiling through layers of deposits and corrosion products collected from thermal power plants.
- To study correlations between the GD-OES depth profiles and corrosion processes in the boilers.

## 3. Project plan

**WP 1.** Sampling of materials with deposition layers from laboratory and field tests.

**WP2.** Optimisation of GD-OES operating parameters for this application.

**WP3.** Obtaining and analysing calibration samples, calibration of a dedicated GD-OES analytical method.

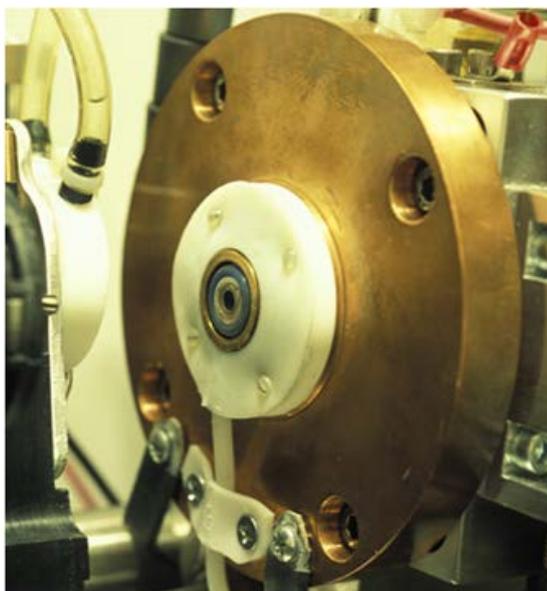
**WP4.** Detailed analysis of a range of deposition layers obtained in WP1.

**WP5.** Study of the correlation between GD-OES depth profiles and corrosion mechanisms, reporting.

## 4. Experimental

### 4.1 Development of an adapted GD-OES method

As was mentioned in the background, surface deposits and corrosion layers in thermal power plants is a very technically challenging application for GD-OES. This can be understood from the picture of the front of the glow discharge source below.



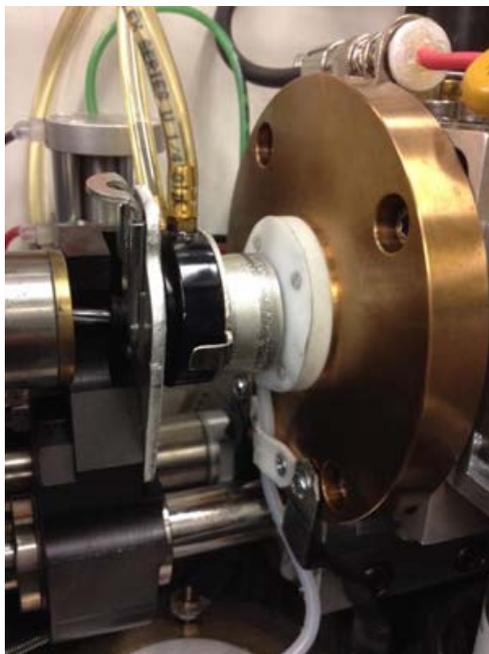
**Figure 1.** The front of the Glow Discharge (GD) lamp, here the Radio Frequency (RF) type capable of sputtering non-conductive layers.

A GD is a small vacuum system, and the sample therefore has to seal against the O-ring seen in Figure 1. This means that the samples of this project cannot be mounted on the GD as they are, since the surface layers are typically both uneven and porous. Therefore, it was necessary to develop a method to mount small samples by casting them in a SnBi alloy with very low melting point (about 140 C), see Figure 2.



**Figure 2.** Mounted sample from an incinerator lab simulation, before (left) and after (right) sputtering in the GD. Note that in this figure the sputter spot is 4 mm, in the major part of the project a 2 mm spot was used.

The function of the cast is twofold; to provide a tight seal against the O-ring and to conduct heat from the sample during sputtering. The GD lamp with the cast sample mounted is shown in Figure 3.



**Figure 3.** The GD lamp with a cast sample mounted. Behind the sample is a cooling puck with flowing water held at 10 C.

## 4.2 Calibration of the GD-OES analytical method

### 4.2.1 Calibration procedure

In order to calibrate the GD-OES a method with salted steel samples were used. Salt of different amounts were solved in ultra-pure water (Milli Q) and the solution was sprayed on heated metal samples. These samples were then run in depth profiling mode until complete removal of the coating, see Figure 4. The average intensities of the analytes in the coating and the sputtering time were calculated from the depth profiles. As is evident from the depth profile, there was some “preferential sputtering” and/or chemical separation in the interface, causing some uncertainty in the sputtering time determination. The discharge also became unstable as the steel starts to sputter; this is probably the result of significant differences in the electrical properties of the salt and the steel but not important for the calibration data.

From the sputtering time and the coating weight of the salt layers, the sputtering rate (SR) in units of  $\mu\text{g/s}$  was calculated. The calibration function is determined by fitting a polynomial to concentration x SR vs. average intensity (see also Figures 5 – 9). From this function, the sputtered mass/element is calculated. In each depth segment, the elemental concentrations (more correctly *mass fractions*) are then determined by a sum normalisation to all measured elements. This requires that nearly 100% of the existing elements are measured, a reasonable assumption in most cases. The total sputtered mass of all elements is converted to depth by division with the sputtered area and the density. In this application, the density has to be estimated from known/estimated physical properties of the deposits, it cannot be correctly calculated by the software.

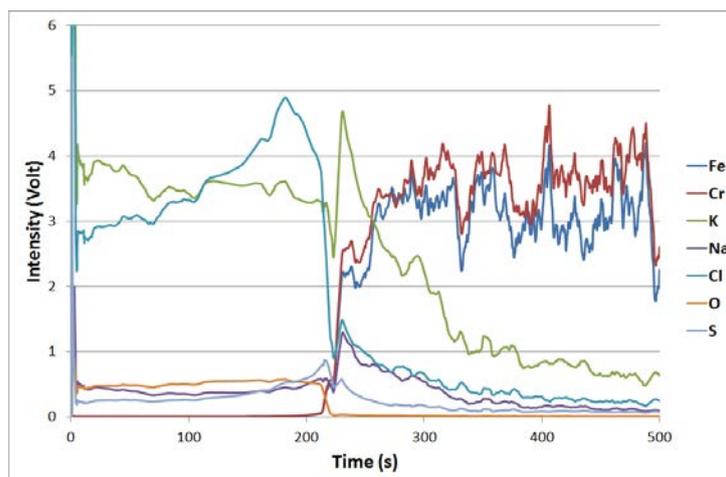


Figure 4. Time-intensity depth profile of a Na 6%/Cl 39%/K 43%/O 8%/S 4% calibration sample.

In order to achieve a range from low to high element concentrations in the calibration curves, amounts from low to high was blended. The elements calibrated with this method were K, Na, Cl, S and Ca. The salts used were KCl, NaCl, Na<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> and the different calibration data is presented in Table 1-Table 3.

Table 1. Calibration samples matrix A (NaCl +KCl)

Concentration [wt%]				Salt deposited [ $\mu\text{g}/\text{cm}^2$ ]
Sample	Na	K	Cl	
1	39.3	-	60.7	1997
2	38.8	0.7	60.5	2238
3	34.5	6.5	59.0	427
4	27.6	15.7	56.8	2550
5	17.3	29.4	53.3	3498
6	8.2	41.6	50.3	2902
7	3.2	48.3	48.6	2126
8	0.3	52.0	47.7	621
9	-	52.5	47.6	1220

Table 2. Calibration samples matrix B (KCl +Na<sub>2</sub>SO<sub>4</sub>)

Concentration [wt%]						Salt deposited [ $\mu\text{g}/\text{cm}^2$ ]
Sample	Na	K	Cl	O	S	
1	32.37	-	-	45.05	22.57	812
2	27.55	7.81	7.08	38.35	19.21	2898
3	12.57	32.08	29.08	17.50	8.77	2711
4	5.66	43.28	39.24	7.87	3.94	2395
5	0.61	51.46	46.65	0.85	0.43	3122

Table 3. Calibration samples matrix C (KCl + CaCl<sub>2</sub>)

Concentration [wt%]				Salt deposited [ $\mu\text{g}/\text{cm}^2$ ]
Sample	K	Ca	Cl	
1	35.05	11.98	52.97	3858
2	21.07	21.60	57.32	1776

## 4.2.2 Intensity drift correction

Signal intensities drift with time to a varying extent in all spectrometer systems. The most common reason is contamination/degradation of optical components (windows, mirrors, lenses), but the detector sensitivity may also change with time. Therefore, a standard procedure in several types of spectrochemical analysis is to perform a drift correction prior to quantitative analysis. Normally, the drift correction is carried out using a small set of solid (bulk) drift samples that were run as part of the basic calibration, providing a “high” point for each element included in the analytical method. In this application, such “high drift” samples are lacking for the major elements Na, K, Cl, S and Ca. Therefore, a limited set of salted samples were prepared some weeks after the initial calibration in order to perform the drift correction.

### 4.2.2.1 Control of salt spray method

The salt spray method was evaluated using wet chemical analysis. Selected salt solution were analysed before salt spraying using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Also some salted samples were leached in ultra-pure water and analysed using ICP-OES. This step was made in order to control the specific salt concentration present at the calibration samples. In this way possible source of error is evaluated.

## 4.3 Study of field and laboratory samples

In work package 1, field samples and laboratory samples were collected and prepared for analysis using the new method. The samples were also evaluated using scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS), X-ray diffraction (XRD) and focused ion beam (FIB) in order to compare the results from these commonly used methods with the results obtained using the GD-OES method.

### 4.3.1 Field samples

Three different steels were sampled from field tests and the test parameters for these are presented in Table 4.

**Table 4. Field samples analysed with developed method.**

Sample	Material	Test environment	
		Fuel	Metal temperature [°C]
W2	16Mo3	Waste wood	350
S2	16Mo3	Waste wood + sewage sludge	350
W3	310S	Waste wood	350
S3	310S	Waste wood + sewage sludge	350
REFa	304	Waste wood	560
ASLa	304	Waste wood + ChlorOut additive	560
REFb	304	Waste wood	600
ASLb	304	Waste wood + ChlorOut additive	600

### 4.3.2 Laboratory samples

In order to also have some samples from a controlled environment, laboratory tests were performed. The parameters for these samples are presented in Table 5. For all samples,

KCl was deposited before exposure. Some of the samples were pre oxidised before the lab test and as reference the only pre oxidised samples were also evaluated using GD-OES. Data for the pre oxidation is shown in Table 6.

**Table 5. Samples exposed with KCl in dry air at 400 °C.**

Sample	Material	Test environment				
		Gas composition	Pre-treatment of sample	Temperature [°C]	Duration [h]	Salt deposited [ $\mu\text{g}/\text{cm}^2$ ]
A	16Mo3	Dry air	-	400 ± 3	12	1600
C	304		-			400
D	304		Pre oxidation 600 °C 72h			500
E	310		-			300
F	310		Pre oxidation 600 °C 72h			400

**Table 6. Reference samples, only pre oxidised.**

Sample	Material	Gas composition	Temperature [°C]	Test duration [h]
G	304	Dry air	600	72
H	310			

## 5. Results

### 5.1 Optimisation of the GD lamp parameters

The glow discharge source can be operated in Direct Current (DC) or Radio Frequency (RF) mode. The DC mode requires electrically conducting samples, but provides the best control of the source parameters. In this application, the surface layers are non-conductive, and therefore requires the RF mode. In this mode, most non-conductive surface oxides and several types of polymer coatings can be sputtered. The main limitation in non-conductive applications is the limited heat conductivity of the layers. The GD is operated at power levels from a few W to several tenths of W; a large fraction of this power is dissipated as heat in the sample surface as a consequence of the sputtering process. With good heat conductivity and back end cooling of the sample, the sample surface does not get very hot, but for layers with poor heat conductivity overheating can result in instability due to excessive outgassing, melting etc. A low power can alleviate such problems, but this has the drawback of weak signals and low sputtering rate. Another parameter that can be varied is the anode tube diameter defining the sputter area, the options 4 mm (standard) and 2 mm are available. The 2 mm anode allows a lower total power with retained power density in the spot, at the expense of somewhat lower signal intensity and depth resolution. However, it increases the possibility to run “difficult” samples with uneven surfaces and poor heat conductivity, and was therefore selected for this application.

In the initial trials, several combinations of power and voltage were tested. There is always a trade-off between sputtering rate, signal levels and plasma stability. In applications with very “thick” layers, as in this case, it is desirable to use conditions with a high sputtering rate, i.e. high power – high voltage. At constant power, high voltage gives high sputtering rate, while a high effective current is better for high signal intensity and thereby high analytical sensitivity. The main objective was to use highest possible power with acceptable plasma stability for these samples. After several trials, it was decided to use 8W at 700V. This is a fairly high power level for the 2 mm lamp, and the voltage is a typical “compromise” for the demands on sputtering rate and sensitivity. At these conditions, steel is sputtered at approximately 4  $\mu\text{m}/\text{min}$  and iron oxide (oxide scale) at 2,5  $\mu\text{m}/\text{min}$ .

It should be mentioned here that in spite of the optimisation, not all samples of the project could be run with stable plasma throughout the analysis. The materials of this project are very “challenging” for GD-OES – as they are for any other analytical technique available.

### 5.2 Calibration

#### 5.2.1 Calibration curves

The calibration measurements showed that all elements were possible to calibrate using this method, Figure 5 - 10. Most of the curves show considerable scattering of the points, due to both salt layer inhomogeneity and the technical difficulties to run these rather porous layers. A few of the curves show substantial non-linearity due to an effect called “self-absorption”; occurring at higher concentrations when a very sensitive emission line is used. However, it must be stressed that this in itself is not a problem for the quantitative analysis, as long as there are sufficient data points to get a good fit to a higher order polynomial. Note that the salt spray samples could not be used for O calibration, so the only “high” point available is from the oxide scale of a hot rolled steel sample. Furthermore, it is likely that the Ca curve is non-linear; but due to the lack of sufficient

“high” points a linear function was fitted. This can only give a substantial error for very low concentrations.

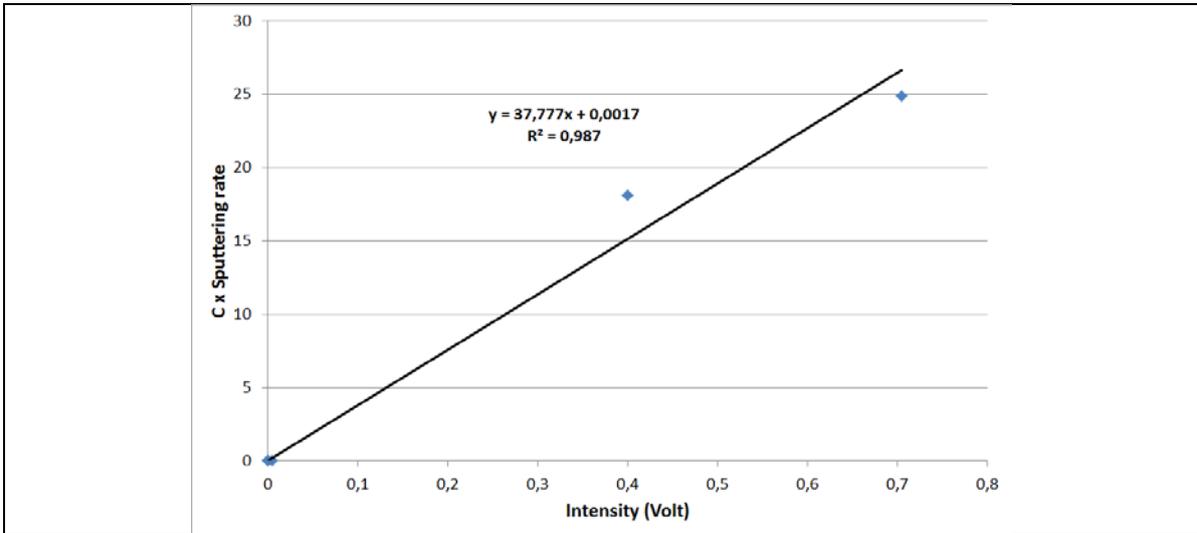


Figure 5. Ca

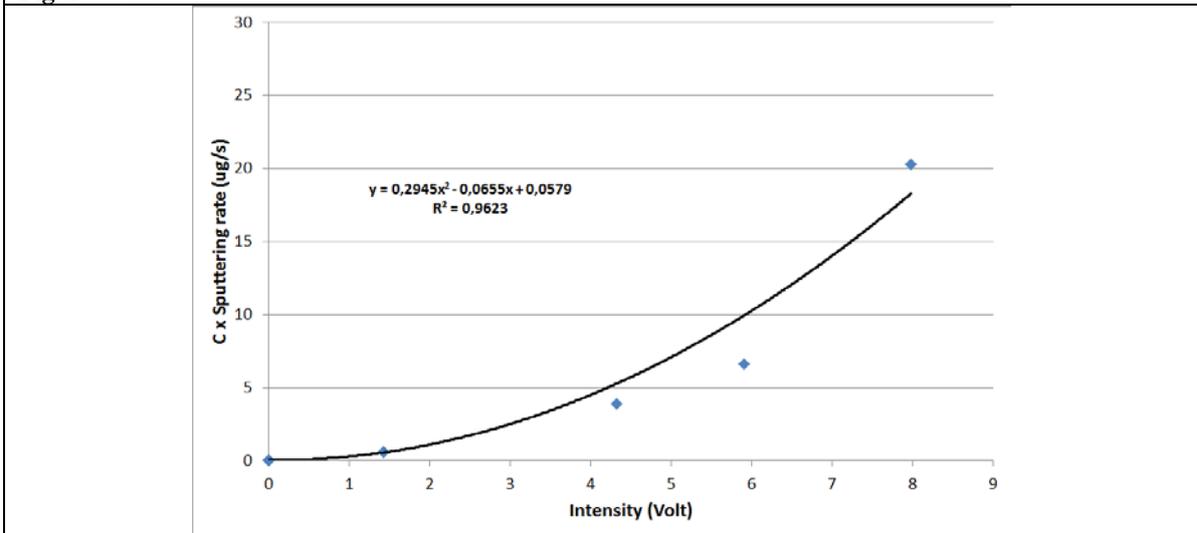


Figure 6. Na

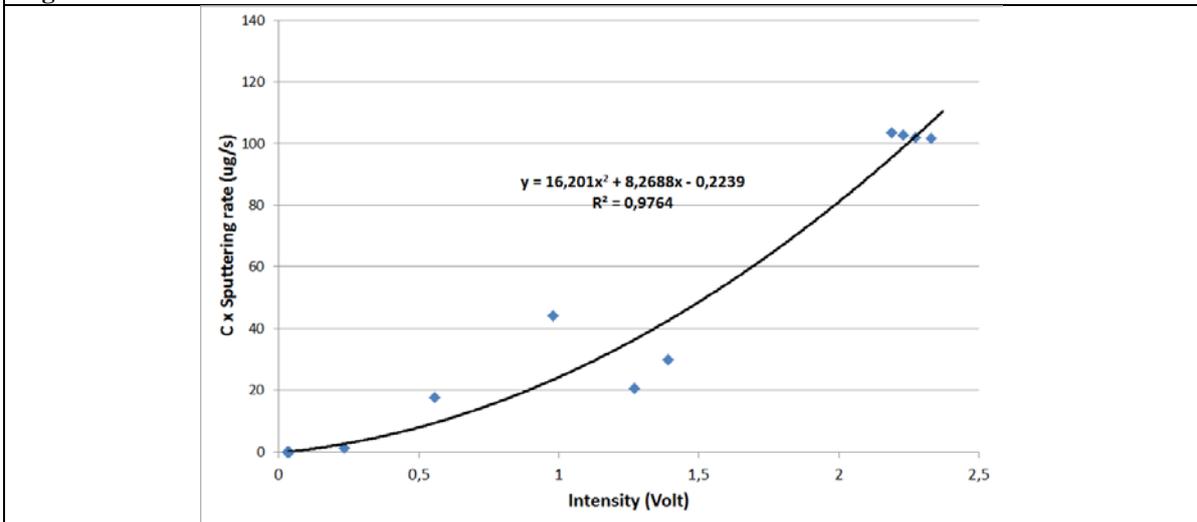


Figure 7. K

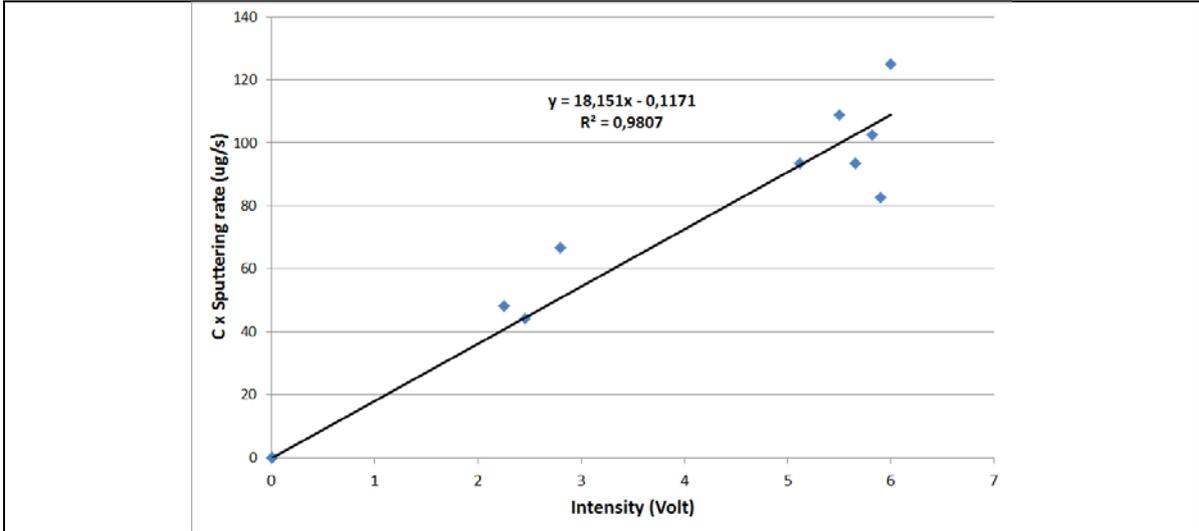


Figure 8. Cl

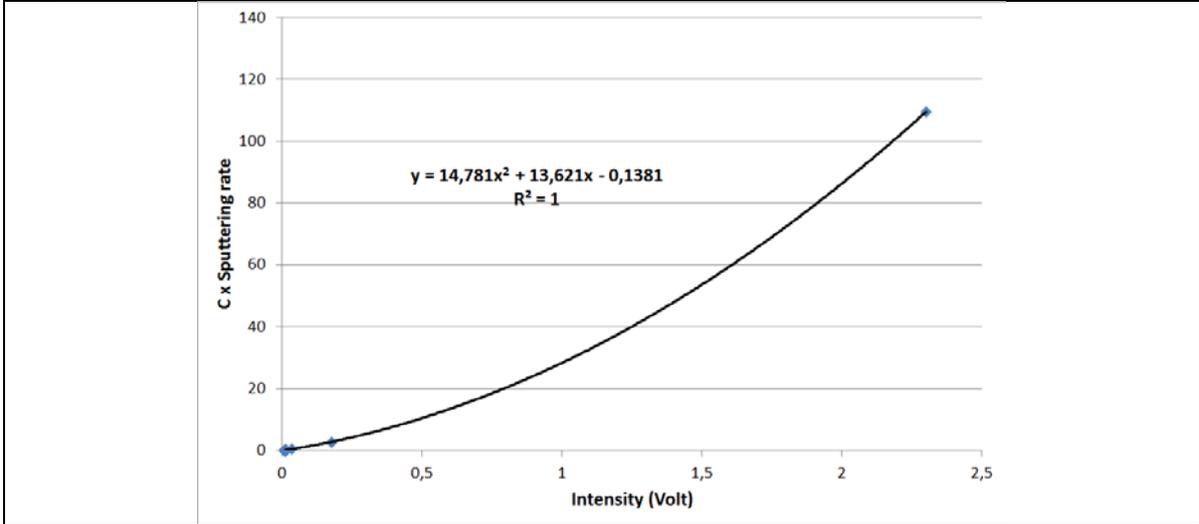


Figure 9. S

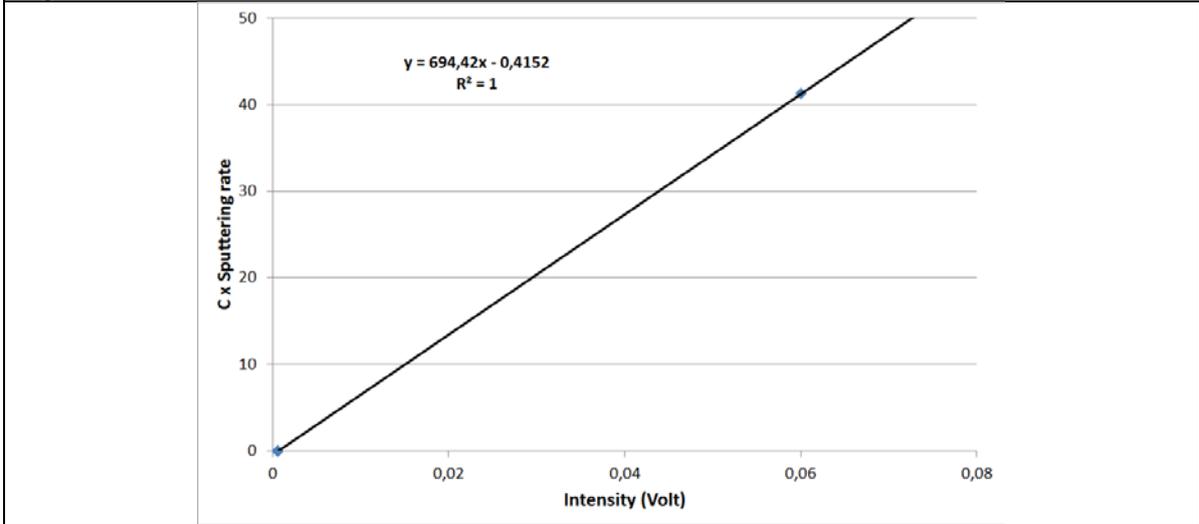


Figure 10. O

### 5.2.2 Control of the salt spray method

The analysis from ICP-OES showed that the salt solution contained the expected concentrations of ions in most cases. However, the measured chloride concentration is higher than expected in all samples. The results are presented in Table 7. For sample C (salt solution 6) where  $\text{CaCl}_2$  was involved the hygroscopic behaviour of the salt have most probably resulted in an underestimation of the weight due to water uptake in the salt during blending, which explains the lower concentration of K and Ca measured in the solution. This, however, does not explain the high Cl-concentration. In general, for samples with a mixture of NaCl and KCl, the determined concentrations of Na and Cl are as expected. Where this is not the case, the K concentration is slightly lower. This could be a result of an underestimation of the weight of the salt, but is more likely due to measurement uncertainty of ion chromatography method used. Therefore, within the statistical uncertainty limits the Cl determinations are in agreement with the expected values from the known stoichiometry of the salts.

**Table 7. Results from analysis of salt solutions.**

Sample	Salt solution	Salt concentration [mg/l]									
		Na (e)	Na (a)	K (e)	K (a)	Cl (e)	Cl (a)	S (e)	S (a)	Ca (e)	Ca (a)
A	2	172	179	49	48	44	54	120	118		
B	4	23	24	176	169	160	176	16	15		
C	6			147	133	222	244			50	43
D	9	86	84	49	45	177	188				
E	12	1.0	0.9	193	182	177	214				
(e) = expected, (a) = analysed											
difference <7 mg/l		difference >7 mg/l									

For the salt sprayed metal samples leached in ultra-pure water the results were mainly as expected, Table 8. However, for sample J, salt solution 6, the lower levels compared to expected is most probably a result of the hygroscopic properties of the salt when  $\text{CaCl}_2$  is involved resulting in an underestimation of the weight of the salt present at the surface before leaching. Sample H is difficult to explain but it seems as if there could be some errors in the salt deposition when blending 75 mole% of NaCl and 25 mole % of KCl. Since the chloride concentration could not be analysed it is not known if the total amount of Cl is as expected. Also S in the samples where KCl and  $\text{Na}_2\text{SO}_4$  is mixed becomes too low but the Na and K levels are as expected. Possibly S is less efficiently atomised in these samples forming e.g. stable  $\text{SO}_4^-$  ions, reducing the fraction of S atoms in the plasma.

**Table 8. Results from leaching of salted metal samples, mg/l.**

Sample	Salt solution	Salt concentration [mg/l]									
		Na (e)	Na (a)	K (e)	K (a)	Cl (e)	Cl (a)	S (e)	S (a)	Ca (e)	Ca (a)
F	2	54	56	15	15	14	n/a	75	36		
G	4	27	28	203	197	184	n/a	37	19		
H	9	47	60	27	18	96	n/a				
I	12	0.8	0.7	132	131	121	n/a				
J	6	0	0.2	195	186	294	n/a			66	56
(e) = expected, (a) = analysed * The sample amount was not enough for Cl analysis.											
difference <7 mg/l		difference >7 mg/l				difference > 50%					

Since the calibration is performed based on weight percent of the salt on the sprayed metal samples, the analysed salt deposition is converted in Table 9. Since no Cl-concentration could be analysed the expected Cl-concentration is included in the total salt amount on the sample. The results show that most of the samples have the wt% of salt as expected but still sample H and J give the biggest deviation from the expected concentration. If also the analysed Cl-concentrations would have followed the concentration in the liquid solutions, the mass fraction needs to be adjusted accordingly. However, this is unlikely given the stoichiometry of the salts. To verify this, new samples were prepared of salt solutions 2 and 9. The chloride was scraped from these samples and analysed by a different method of ion chromatography. In this analysis the Cl mass fractions was shown to agree with expected values.

**Table 9. Results from leaching of salted metal samples, wt%.**

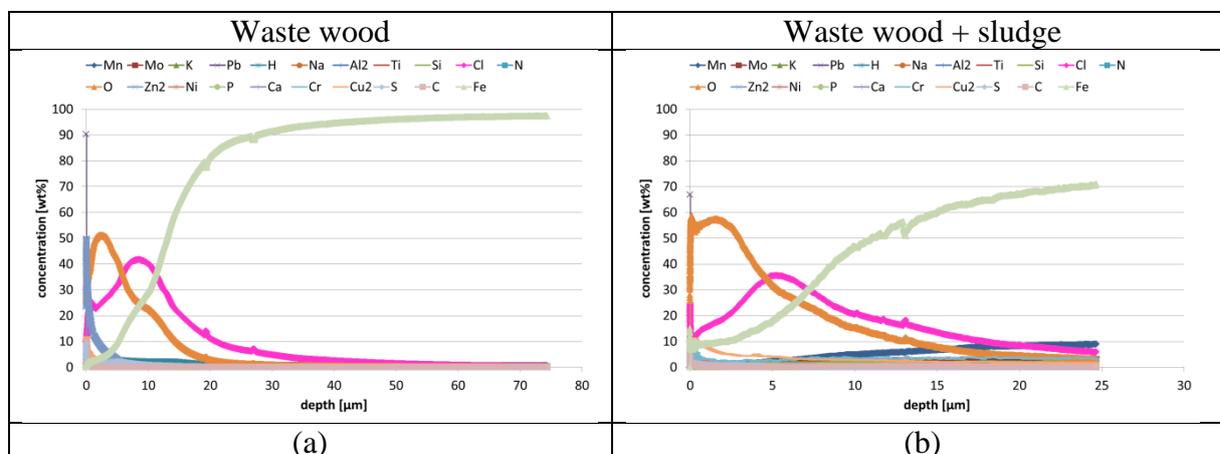
Sample	Salt solution	Salt concentration [wt%]										Salt on sample* [mg]
		Na (e)	Na (a)	K (e)	K (a)	Cl (e)	Cl (a)	S (e)	S (a)	Ca (e)	Ca (a)	
F	2	45	46	13	12	11	n/a	31	30			121
G	4	6	7	47	46	43	n/a	4	4			428
H	9	28	34	16	10	57	n/a					174
I	12	0.3	0.3	52	52	48	n/a					253
J	6			35	35	53	n/a			12	10	536
(e) = expected, (a) = analysed , *Cl from expected data included in the total salt amount												
		difference <2 wt%		difference >2 wt%				no analysed performed				

## 5.3 Study of field and laboratory samples

### 5.3.1 Field samples

#### 5.3.1.1 Samples with and without sludge

The results from analysed field samples of 16Mo3, **Fel! Hittar inte referensskälla.**, show that both samples have high concentration of chlorine at the metal/oxide interface.



**Figure 11. Depth profiles for 16Mo3 exposed to waste wood (a) and waste wood + sludge (b). The graphs are from ref. [3], modified.**

No clear difference is seen regarding the different elements in the deposits. This could be a result of the deposit falling off before (when moulding samples) or during sputtering. In the investigation using focused ion beam (FIB), Figure 12, it can be seen that the deposit for the waste wood sample is thinner compared to the waste wood and sludge sample which should be reflected in the GDOES-spectra. However, the thickness measured by FIB is sensitive to local variation.

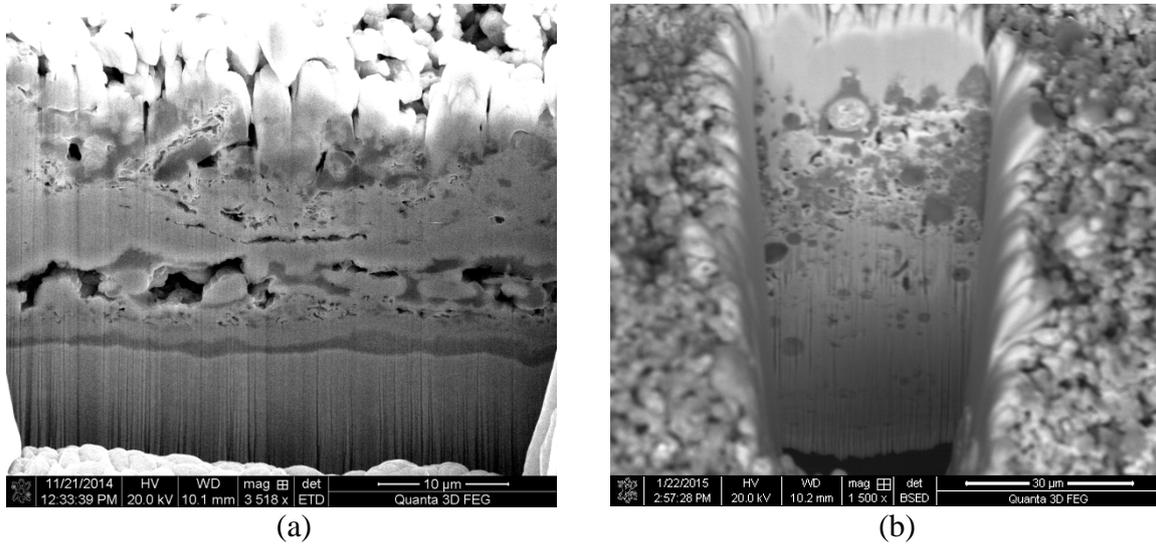


Figure 12. FIB cross section of 16Mo3 exposed (a) to waste wood and (b) waste wood + sludge.

The results from analyses of 310S samples also exposed to waste wood and waste wood + sludge, Figure 13, shows that the deposit for these samples seems to be adherent during the sputtering since elements known to be in the deposit is detected (S, Ca, K and O). Compared to the 16Mo3 samples the chlorine content is not so high at the metal/oxide interface but instead potassium seems to be present in this area. These results corresponds well with results from x-ray diffraction analysis which shows high amounts of  $\text{Ca}(\text{SO}_4)$  and  $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$  in the deposits.

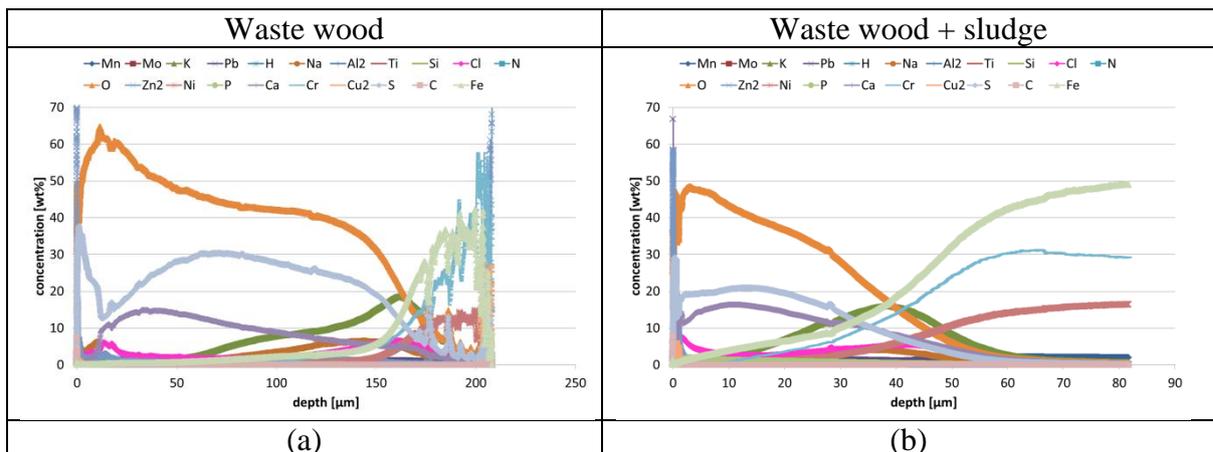


Figure 13. Depth profiles for 310S exposed to waste wood (a) and waste wood + sludge (b). The graphs are from ref. [3], modified.

For these samples the deposit seems to be thicker for the waste wood only sample which corresponds well to what can be seen using FIB, Figure 14. However, for the FIB-cut, the

thinnest area was selected for both samples but in general the deposit is thicker for the waste wood sample so it still reflects a representative area.

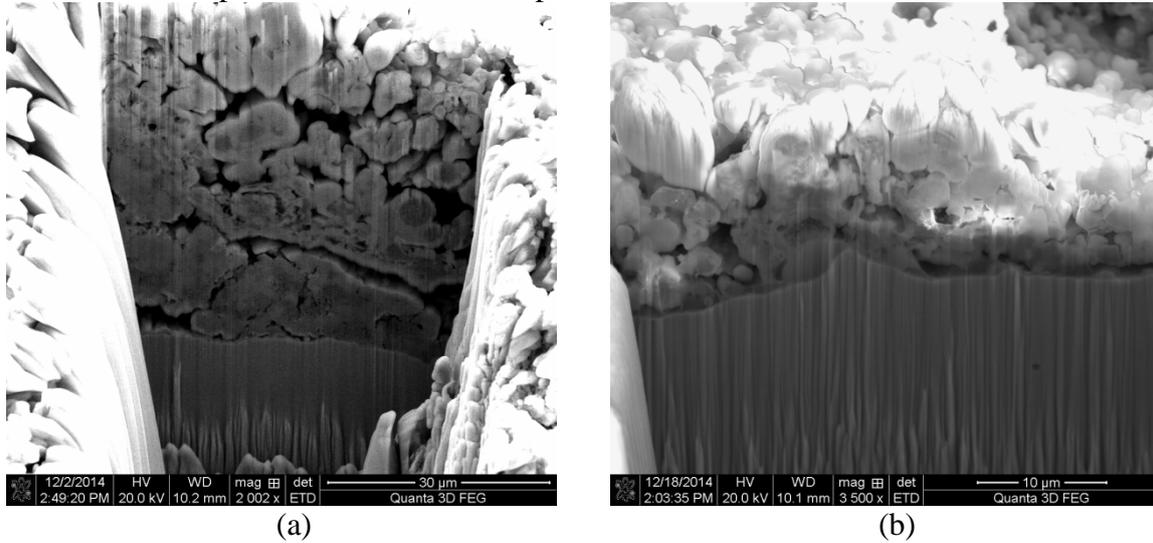


Figure 14. FIB cross section of 310S exposed (a) to waste wood and (b) waste wood + sludge.

### 5.3.1.2 Samples with and without ChlorOut additive

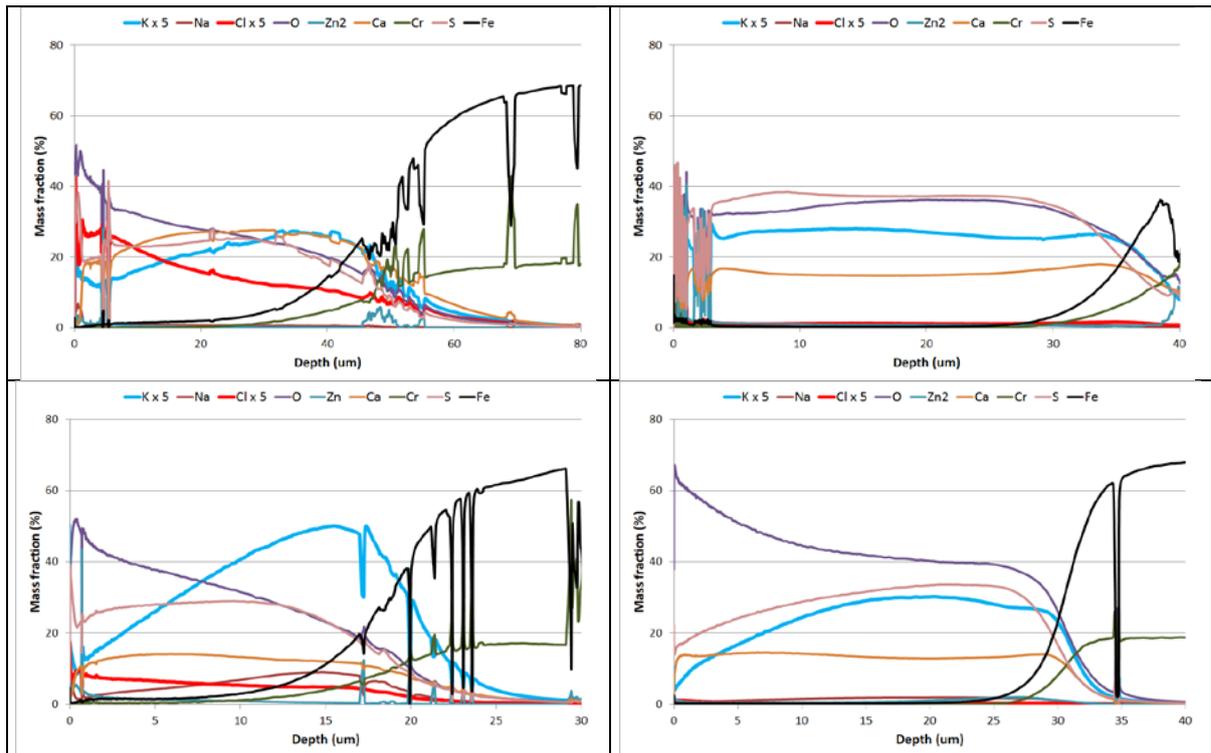


Figure 15. GD-OES Depth profiles of REF and ASL field samples (see table 4). The elements K and Cl are expanded a factor 5 and highlighted for better visibility.

XRD – results from these samples show KCl in the deposit in the reference samples while this compound was not detected in the deposit for the ASL samples. For the REF samples a higher amount of  $Ca_2SO_4$  was detected in the deposit compared to ASL while the concentration of  $K_2Ca_2(SO_4)$  was higher in ASL. As is obvious from the numerous spikes in the GD-OES depth profiles in Figure 15, these samples were difficult to run with a stable discharge, but the main features of the surface deposits’ depth profiles can be seen.

Cl is only detected in the REF samples, in agreement with the XRD results but the Cl/K ratio is considerably lower in REFb compared with REFa. A substantial amount of K is found in all samples. Large contents of Ca, S and O are found in all samples, in agreement with the XRD results, but GD-OES cannot distinguish between the K in different compounds. K may also be present in oxides in addition to sulphates. An additional difference between the REF and ASL samples is a much higher content of Na in the REF samples, probably NaCl.

### 5.3.2 Laboratory samples

The visual appearances of the samples exposed in the laboratory test are presented in Figure 16. It can be seen that 16Mo3 shows a smoother oxide compared to the other materials.

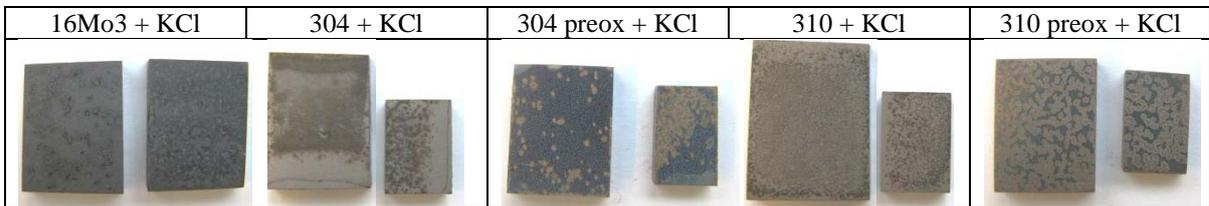


Figure 16. Visual appearance for samples exposed in air with KCl deposition at 400 °C for 24 h.

#### 5.3.2.1. 16Mo3

The corrosion products at 16Mo3 did not show good adherence and had spalled after the GD-OES sputtering. The only oxide seen is iron oxide, Figure 17.

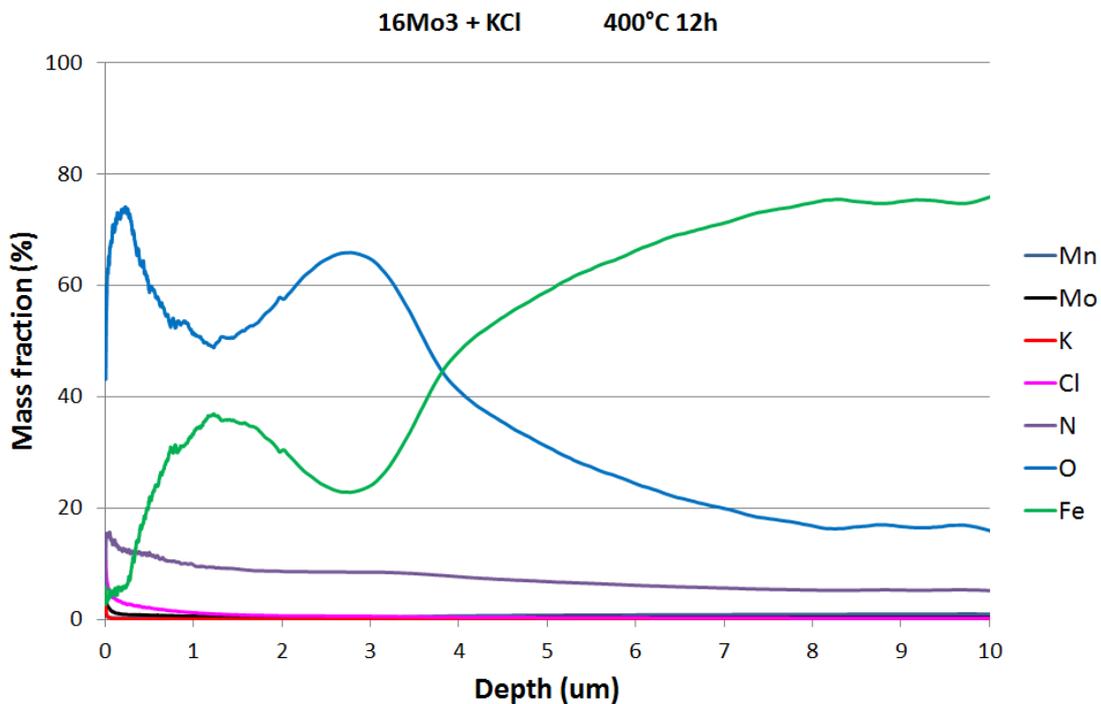


Figure 17. GD-OES depth profile for 16Mo3 exposed in air with KCl deposition at 400 °C for 12 h.

### 5.3.2.2 Stainless steel 304

After pre oxidation an oxide enriched in Cr, Mn and Fe is seen for the 304 material, Figure 18.

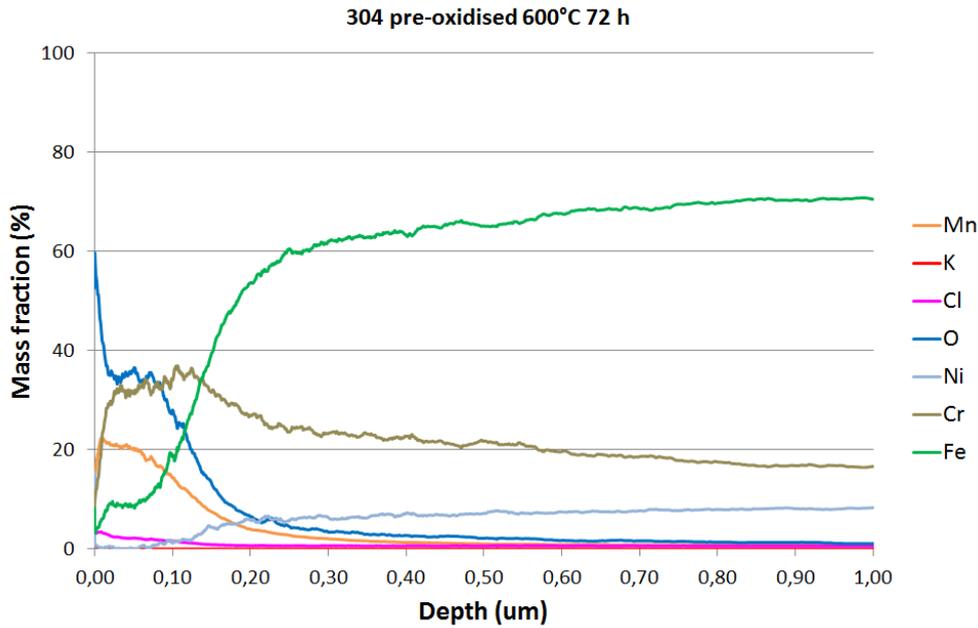


Figure 18. GD-OES depth profile for 304 pre-oxidised in air at 600 °C for 72 h.

When the pre-oxidised 304 is exposed to KCl for 12 h at 400 °C; the result shows that KCl seems to still be present at the sample surface, Figure 119. However, K and Cr seem to follow each other further in close to the metal/oxide interface while chlorine is showing a more flat behaviour. This could possibly be explained by the fact that potassium chromates are present in the corrosion products. The enrichment in Mn shown in the not exposed sample is not as large after KCl exposure but a slight enrichment is still seen close to the metal/oxide interface. A further complication is that the sample surface is not homogeneous, small “dots” are visible within the sputtered spot. These dots are likely to have a composition that differs from the surrounding surface; since the entire area within the sputtered spot is sputtered simultaneously this will “blur” the appearance of the depth profile. No Fe rich oxide is seen for the sample but rather some Cr enriched oxide.

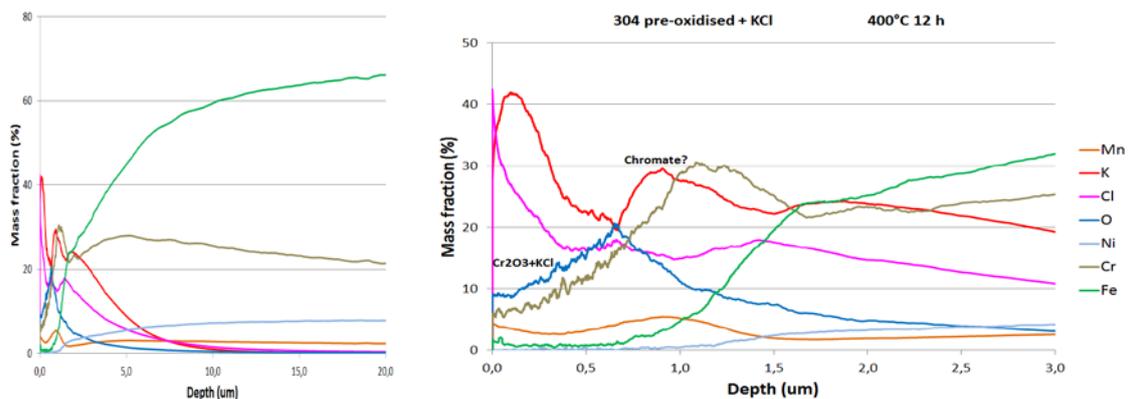


Figure 19. GD-OES depth profile for 304 pre-oxidised and exposed to KCl in air at 400 °C for 12 h.

When 304 is exposed to KCl without any pre oxidation the results show that the oxide formed is most probably less protective since the Cr content in the oxide is much lower compared to the pre-oxidised sample, Figure 20. Mainly KCl is seen together with the oxide.

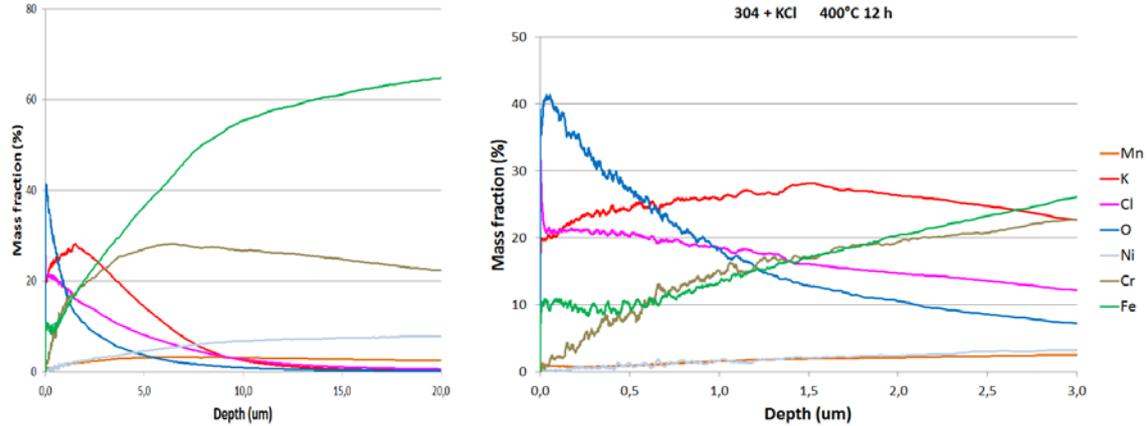


Figure 20. GD-OES depth profile for 304 exposed to KCl in air at 400 °C for 12 h.

A Focused Ion Beam (FIB) image of a cross section of the sample in figure 20 is shown in Figure 21.

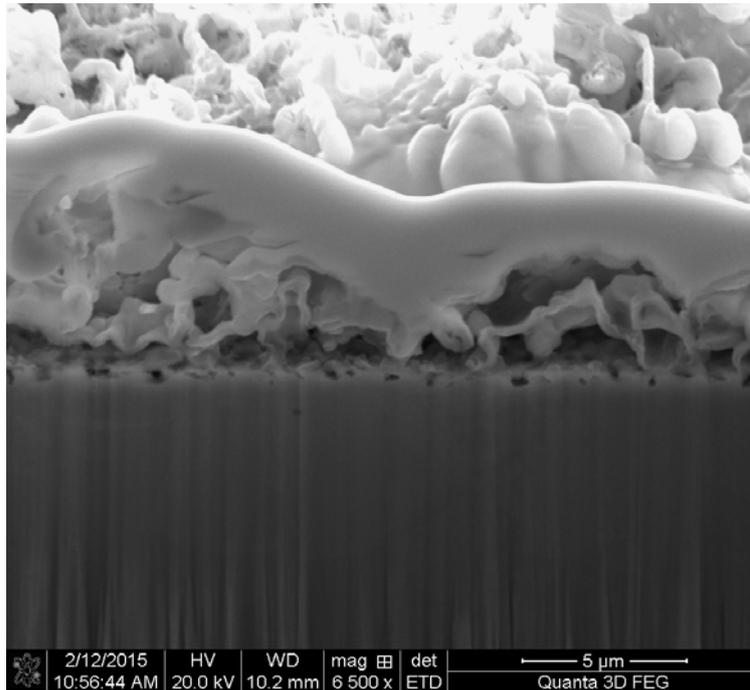


Figure 21. FIB cross section image of 304 exposed to KCl in air at 400 °C for 12 h.

Figure 21 shows that the surface deposit layer is in the order of 5 – 10 µm thick, in good agreement with the GD-OES results. The image also shows that the layer is both porous and uneven, the main reason for the poor depth resolution of the GD-OES profiles.

XRD results of the exposed 304 show mainly iron oxides and potassium chloride at the surface of the samples.

### 5.3.2.2 Stainless steel 310S

After pre oxidation an oxide enriched in Cr, Mn and Fe is seen for the 310S material, Figure 22. Compared to the 304 material, this oxide has higher Cr content and is believed to be more protective.

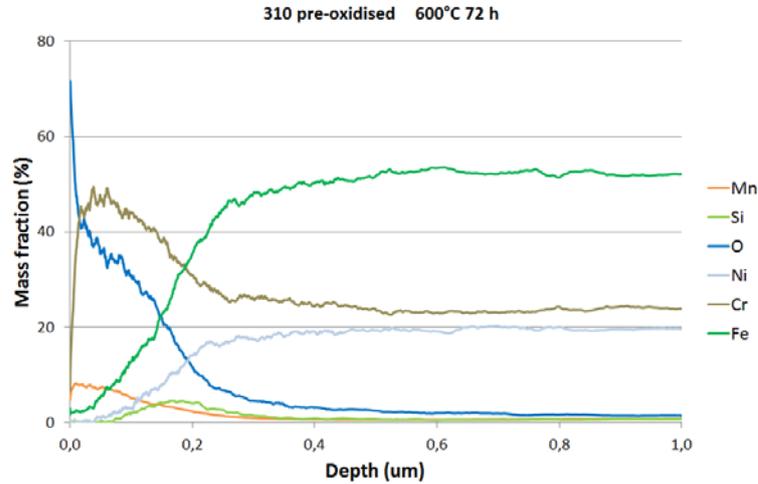


Figure 22. GD-OES depth profile for 310 pre-oxidised in air at 600 °C for 72 h.

When exposing the 310S material to KCl in air at 400 °C for 12 h no clear difference is seen between samples with and without pre-oxidation, in contrast to the results for 304.

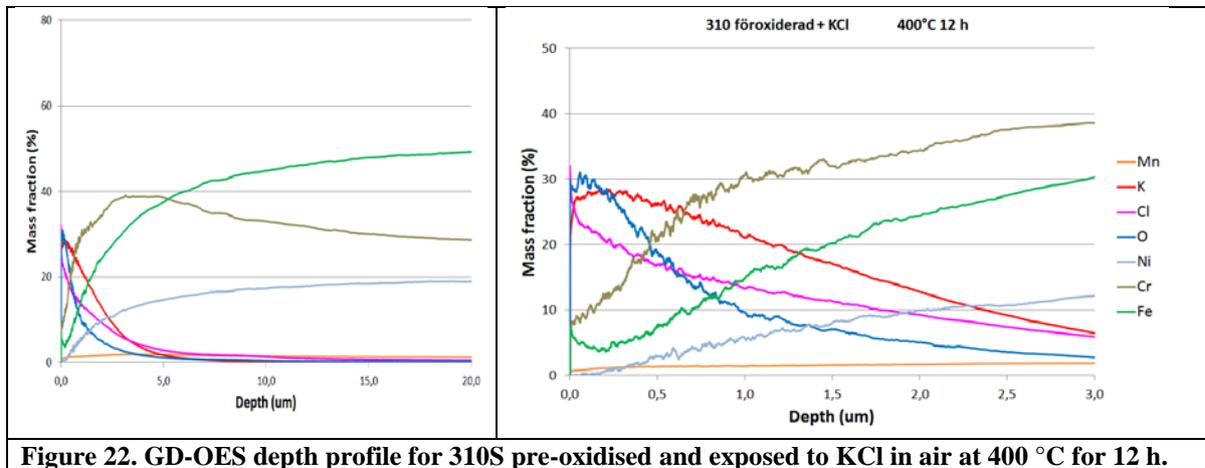


Figure 22. GD-OES depth profile for 310S pre-oxidised and exposed to KCl in air at 400 °C for 12 h.

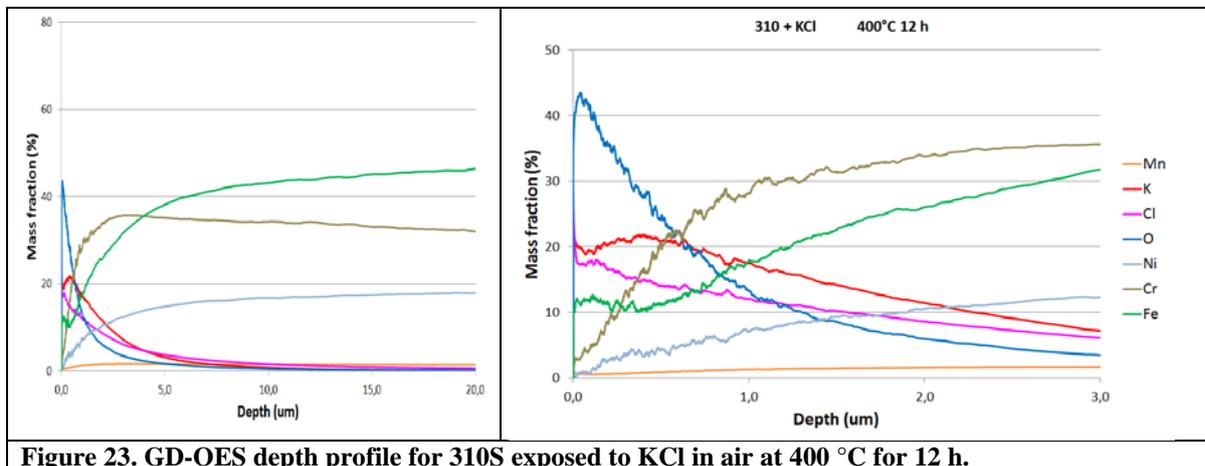


Figure 23. GD-OES depth profile for 310S exposed to KCl in air at 400 °C for 12 h.

### 5.3.3 Correlations between GD-OES depth profile and corrosion mechanisms

Comparing some field exposures of 16Mo3 and 310S it can be seen that differences in corrosion mechanisms can be detected with the GD-OES method.

For 16Mo3, Figure 24, it is seen in SEM/EDS that the main element close to the metal/oxide interface is Cl. The same result is seen also by using GD-OES. KCl is the product which is suspected to cause corrosion problems in this kind of exposures but in this case the corrosion mechanisms seem to be mainly connected to chlorine and potassium is found further out in the deposit.

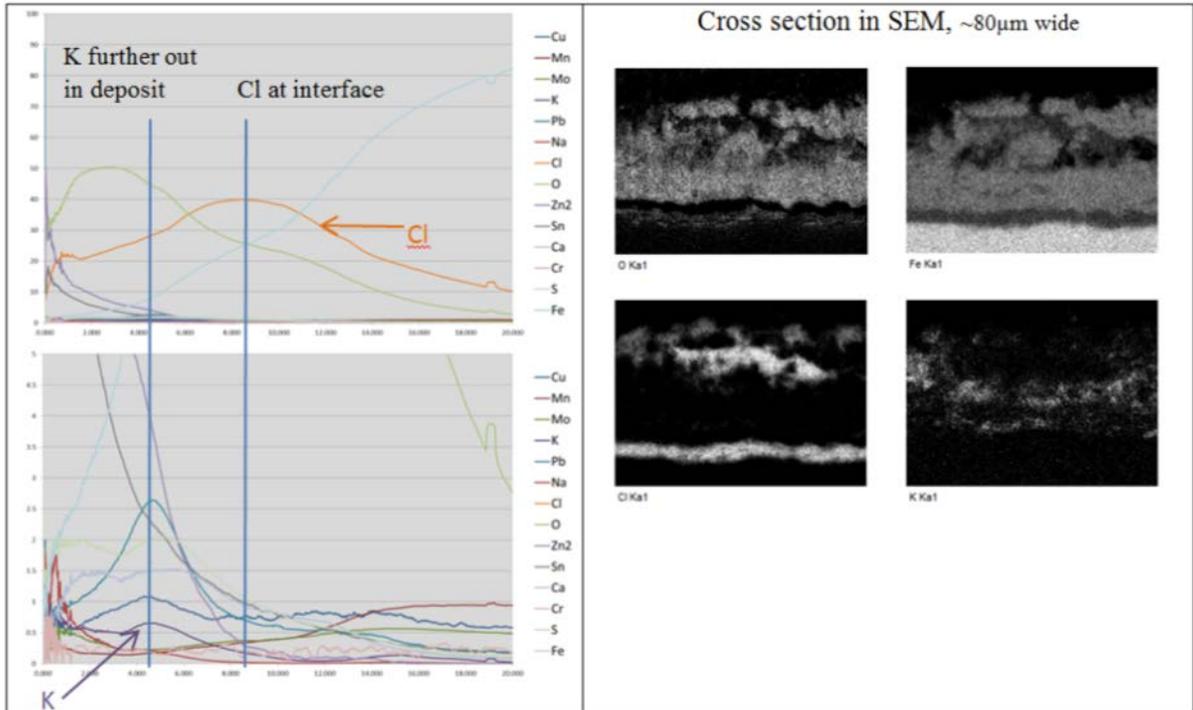


Figure 23. Comparison between depth profile from GD-OES and element analysis using SEM/EDS for 16Mo3 exposed to waste wood. The graphs are from ref. [3], modified.

For 310, the result looks different. For this material, which has better corrosion properties compared to 16Mo3, K and Cl is located at similar positions both when investigating with SEM/EDS and GD-OES. This result strongly indicates that this material withstand corrosion from this compound better than the 16Mo3 steel.

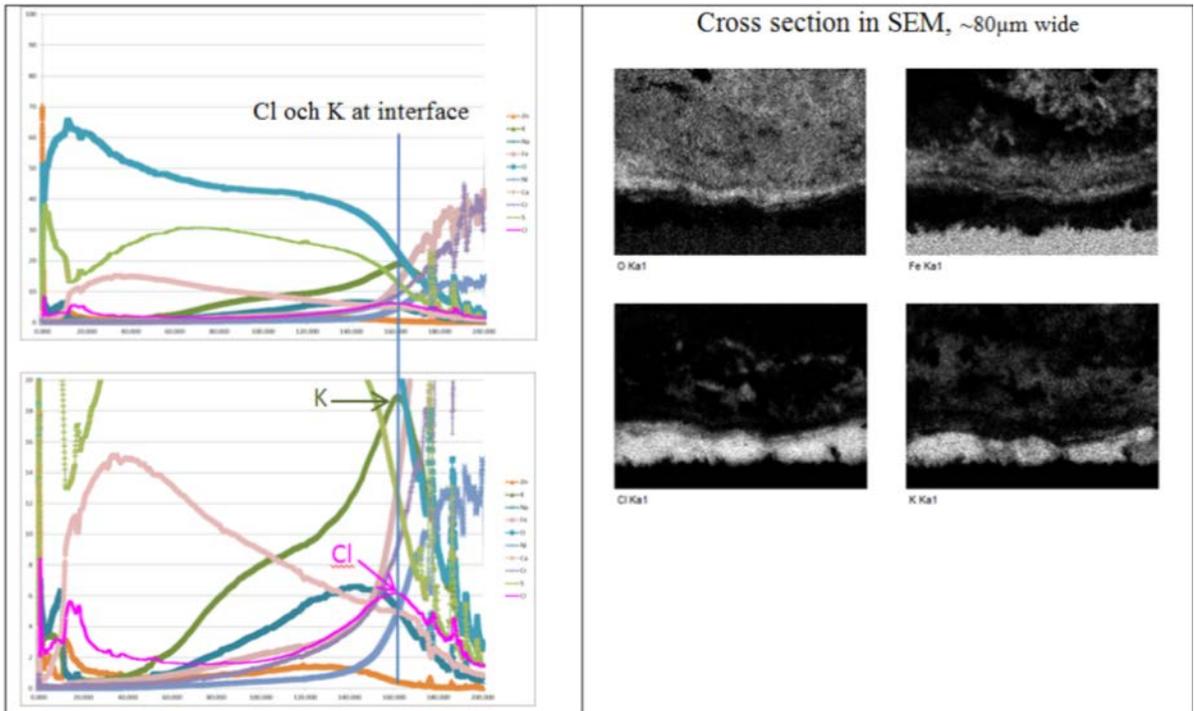


Figure 25. Comparison between depth profile from GD-OES and element analysis using SEM/EDS for 310S exposed to waste wood. The graphs are from ref. [3], modified.

## 6. Discussion

This work has shown that radio frequency (RF) GD-OES can be used for quantitative depth profile analysis of surface deposits and corrosion layers of thermal power plant materials. This is the first objective of the project, which has been achieved as anticipated. A comparison with SEM cross section images have also shown that the in-depth structure of the depth profiles qualitatively agree well with the observed structure in the images. However, the analytical work has also shown that some of these types of materials are “difficult” to analyse by GD-OES, in the sense that the plasma discharge tends to be unstable. It should therefore be noted that not all materials of this type will be amenable to GD-OES analysis.

There are no commercially available solid reference materials (RM) with mass fractions of Cl, S, Ca, Na and K in the range found in these materials; it was therefore necessary to produce dedicated RM's for calibration. The method devised within the project was to spray salt solutions onto steel substrates and subsequently dry these, producing coatings of well-known composition for calibration. The thicknesses (or rather coating weight/area) of the coatings were determined by weighing the samples before and after deposition. This method was shown to work satisfactory, although a relatively large statistical spread in some of the calibration curves was observed.

Comparing some field exposures of 16Mo3 and 310S it has been shown that differences in corrosion mechanisms can be detected with the GD-OES method. This is the second objective of the project, which has also been achieved. By observing the positions in the depth profiles of primarily K and Cl, the ability of a material to withstand corrosion can be deduced.

## 7. Conclusions

The major objectives of the project have been achieved in a satisfactory way. This means that at Swerea KIMAB, we now have an added and unique analytical tool to perform in-depth elemental analysis of the complex surface deposits formed on thermal power plant materials. The GD-OES method provides additional analytical information that cannot be obtained with other methods; in addition it requires relatively little sample preparation and is not very time-consuming. This analytical tool is a valuable asset in continued research on the corrosion properties of thermal power plants, as well as the chemical processes responsible for this corrosion.

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