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# Corrosion Caused by Dew Point and Deliquescent Salts in the Boiler and Flue Gas Cleaning

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1	Introduction.....	2
2	Fundamentals.....	3
2.1	Dew Point Corrosion.....	4
2.2	Corrosion through Hygroscopic and Deliquescent Salts.....	6
2.3	Sampling of Hygroscopic/ Deliquescent Salts in the Boiler and Laboratory Tests.....	9
2.3.1	Diagnosis in Operation.....	9
2.3.2	Corrosion Tests in the Laboratory.....	12
2.4	Deliquescent Ammonium Chloride and Bromide.....	12
2.4.1	Formation of Ammonium Chloride in the Boiler.....	13
2.4.2	Formation of HCl (HBr) through Fuel and Firing.....	15
2.4.3	Formation of NH <sub>3</sub> through Fuel and Firing.....	15
3	Case Studies regarding Renewable Fuels.....	18
4	Case Studies on Waste Fuels.....	21
4.1	Case Study: Power Plant with NCR and with Ammonia Slip.....	22
4.2	Case Study: Waste-to-Energy Plant with SCR, NH <sub>3</sub> Formation in Firing System.....	26
5	Summary.....	29
6	Literature.....	30

## 1 Introduction

Boilers with difficult fuels such as waste, refuse derived fuels and biomass, may not only be hit by corrosion on the heat transfer surfaces of evaporators or superheaters, but also at the 'cold end', i.e. on ECO and heat transfer surfaces in the preheater area as well as on the evaporator tubes and uncooled steel sheets located there. Corrosion may also occur during subsequent flue gas cleaning, on the raw gas and clean gas sides.

It is known from the combustion of fossil solid fuels that, in most cases, the problems of corrosion at the cold end are to be traced back to sulphuric acid, i.e., the dew point temperature of sulphuric acid constitutes a conditioning factor for operation processes. This dew point temperature is a function of the concentration of gaseous SO<sub>3</sub> and the content of water vapour in the flue gas. In common terminology in the field of coal combustion, the term "dew point corrosion" is synonymously used with sulphuric acid dew point corrosion. This clear correlation has to do with the chemistry of coal as a fuel. If reference is made to the dew point of water, the "water dew point" is expressly referred to.

These common references to dew points and to sulphuric acid as the cause of any corrosion at the cold end (insofar as the water dew point is not even reached) are not to be directly transferred to boilers with difficult fuels. Current findings suggest this. One of the causes here – compared to coal – lies in the significantly changed chemistry of these fuels. But also process-related aspects can play a role, particularly DENO<sub>x</sub> (SNCR, selective non-catalytic reduction).

This article demonstrates that, in the case of difficult fuels, not only sulphuric acid is to be considered as the cause of cold end corrosion, but also salts with hygroscopic and deliquescent properties. Deliquescent salts are hygroscopic to such extent that they deliquesce and form an electrolyte, thus causing corrosion through an aqueous electrolyte. This "deliquescence corrosion" can be distinguished from the dew point corrosion of sulphuric acid and water by the fact that the triggering process, the formation of halogen salts, does not constitute a dew point but, initially, the deposition of a salt resulting from the phase transition from a gaseous to a solid state; it is only afterwards that – with sufficient humidity of the flue gas - the deposited salts deliquesce and form a saturated salt solution, the corrosive electrolyte.

These salts are mainly halogen salts, with chlorides prevailing over bromides. Based on the hygroscopic or deliquescent properties of halogen salts, relevant bonding partners for chlorine or for bromine are less sodium and potassium, but elements such as calcium, magnesium, zinc etc. as well as ammonium. As to ammonium chloride (NH<sub>4</sub>Cl), the focus is shifted to ammonia (NH<sub>3</sub>). Ammonia is the reaction partner to reduce nitrogen oxides in the flue gas and is, for the process of the selective non-catalytic reduction (SNCR), added in the hot part of the boiler. To the extent that parts of the added ammonia do neither react with the nitrogen oxides nor are oxidized ("burn off"), this load reaches the cold end of the boiler (so-called "slip").

Referring to case studies (Chapter 3 and 4), the requirements for the design and operating mode of boilers which are to be derived from deliquescent corrosion, are addressed and sensory methods presented – the so-called "deposit monitors". These help to determine the individually critical temperature thresholds for corrosion as well as the causes of corrosion. The deposit monitors are also fit for use during operation to detect any changes for the temperature thresholds of corrosion which may, for example, be caused by a change of fuels or operating modes, and to take counter-measures at an early stage.

Particular importance is attached to the topic of cold end corrosion by the fact that, in the future, measures will be taken to increase energy efficiency at many WTE and RDF plants/biomass plants. This aspect is foreseeable in terms of "boiler efficiency". One contributing factor of such optimization is to reduce temperatures at the boiler

end. An exacerbating effect with regard to deliquescence corrosion might have the planned further decreased value according to the statutory limit for nitrogen oxides in the clean gas and/ or the planned increase in NOx precipitation efficiency. A first operational adjustment could be the application of ammonia in SNCR processes, rather “highly” dosed (possible increase in the “slip”). The investment costs of other DENOx methods have a similar effect, as well as ever larger boilers, with their limiting impact on an even flow and environment of the flue gas (streaks, imbalances).

From the view of available literature, the problems relating to an ammonia slip, for example as a consequence of non-thorough mixing, control faults/errors in the settings etc., are known as well as its corrosive potential [1] [2] [3] [4]. Current research focuses on impeding the formation of ammonia salts or removing them with regard to SNCR, whose tiny aerosols can even pass fabric filters (baghouses) and dye the flag on the chimney white [5]. It is also described that cold end corrosion occurs unexpectedly from time to time [6]. Other authors report that the formation of salt coatings and subsequent corrosion are promoted “with open eyes” in the course of current efforts for lower ECO temperatures to increase boiler efficiency [7]. In contrast to this, other operators deliberately raise ECO temperatures to avoid massive fouling by ammonium chloride on the ECO tubes which reduces availability [8].

From a practical point of view for both, the unexpected occurrence of cold end corrosion as well as for research projects carried out to examine the lowest possible ECO temperature, cases of corrosion are observed in temperature ranges which occur under clearly higher temperatures than can be explained by the “common” dew points and which are also not accompanied by the commensurate SO<sub>3</sub> concentrations of mostly << 1 mg/Nm<sup>3</sup>, i.e. close to the detection threshold of relevant analytical methods. The prevailing trough-shaped morphology of such pitting degradation corresponds, despite temperatures of >100°C, to the typical structural features of an aqueous, i.e. electrolytically caused corrosion. Microanalysis on the corrosion products of such electrolytically caused corrosion (iron oxides and iron hydroxides) provides - mostly locally enriched - evidence of an excess of chlorine which lacks proportional amounts of cations (e.g. Na, K, Ca etc.). Such findings initially present an analytic conundrum [9]. However, after adjusting analytical methods, e.g. ammonium chloride can be proven.

This article starts with the fundamentals of possible corrosion mechanisms and corrosive agents at the cold end of the boiler, and the corresponding, relevant correlations of fuels and combustions. To this purpose, literature data regarding grate-firing and fluidized bed incineration (circulating and stationary) were analysed. Subsequently, case studies from waste-to-energy plants regarding the combustion of biomass and waste are presented. These examples include the current range of findings, i.e. indifferent findings on the causes of corrosion on the one hand and, on the other hand, findings that are to be attributed to deliquescence corrosion caused by ammonium chloride.

## 2 Fundamentals

The subsequent order and depth of information runs like a common thread leading to deliquescence corrosion through ammonium chloride; further deliquescent salts are treated marginally. As mentioned above, it is difficult to detect nitrogen by means of analysis which, according to the authors, is the main reason for frequently not having identified this cause of corrosion so far or for attributing it to sulphuric acid erroneously. In the following, the focus of examination lies on corrosive phenomena, with their often also relevant share of erosion being dealt with in an example case.

## 2.1 Dew Point Corrosion

If gas temperature falls, the solubility of the gaseous matter dissolved therein decreases; the dissolved matter becomes saturated; Figure 1 illustrates this through the saturation curves in the “hot part” of the boilers. Using the example of water this means that relative humidity (rH<sub>i</sub>) increases. Liquid drops condense at the dew point or condense even earlier on relatively colder surfaces, when the gas is hitting these surfaces.

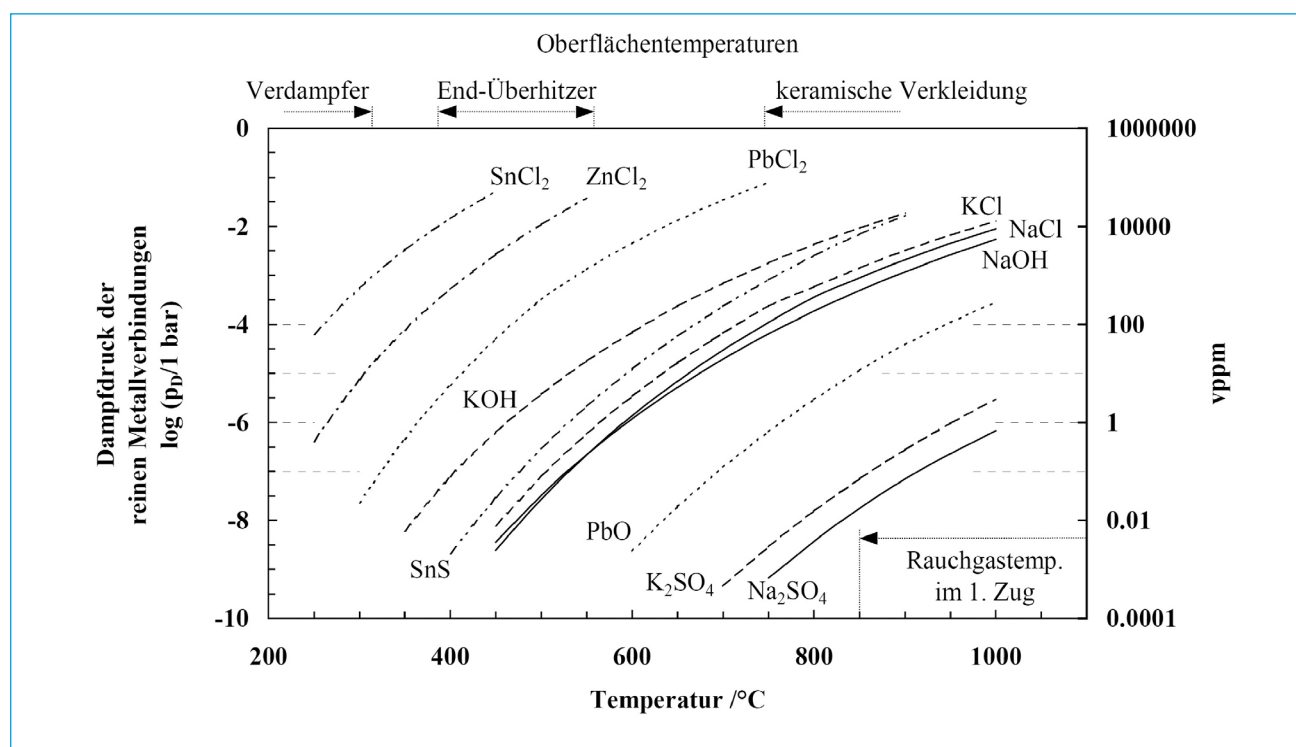


Figure 1: Saturation curves of different species in relation to the surface temperatures of the components in a boiler, with waste and biomass as fuels. Source: [10]

The term “acid dew point” hints at the corrosive medium which is commonly associated with sulphuric acid in power plant technology. Sulphuric acid reaches dew points which lie above those of other acids (sulphurous acid, hydrochloric acid, hydrofluoric acid etc.). In the course of cooling the dew points of the sulphuric acid are therefore reached first.

Figure 2 illustrates the sulphuric acid dew points in the temperature range of <250°C as a function of sulphuric acid concentration and flue gas humidity.

The corrosion mechanism with sulphuric acid causes rather extensively degraded structures which means that it can be visually distinguished from the pitting corrosion caused by other electrolytes; Figure 3. Condensed sulphuric acid forms, with the steel, compounds of iron and sulphur, e.g. iron sulphate. If free water humidifies the corrosion products, iron sulphate will again dissolve in the water, with corrosive sulphuric acid being released anew.

If the fouling (depositions from the flue gas, i.e. salts, oxides, silicates etc.) is or becomes thicker, then the corrosive condensate will primarily humidify the particle surfaces of such deposits instead of component surfaces. This is how fouling reduces corrosion; the thicker the fouling, the stronger its corrosion-reducing effect.

However, heat transfer surfaces always act as a relative cold trap, because the fouling thereon is hotter.

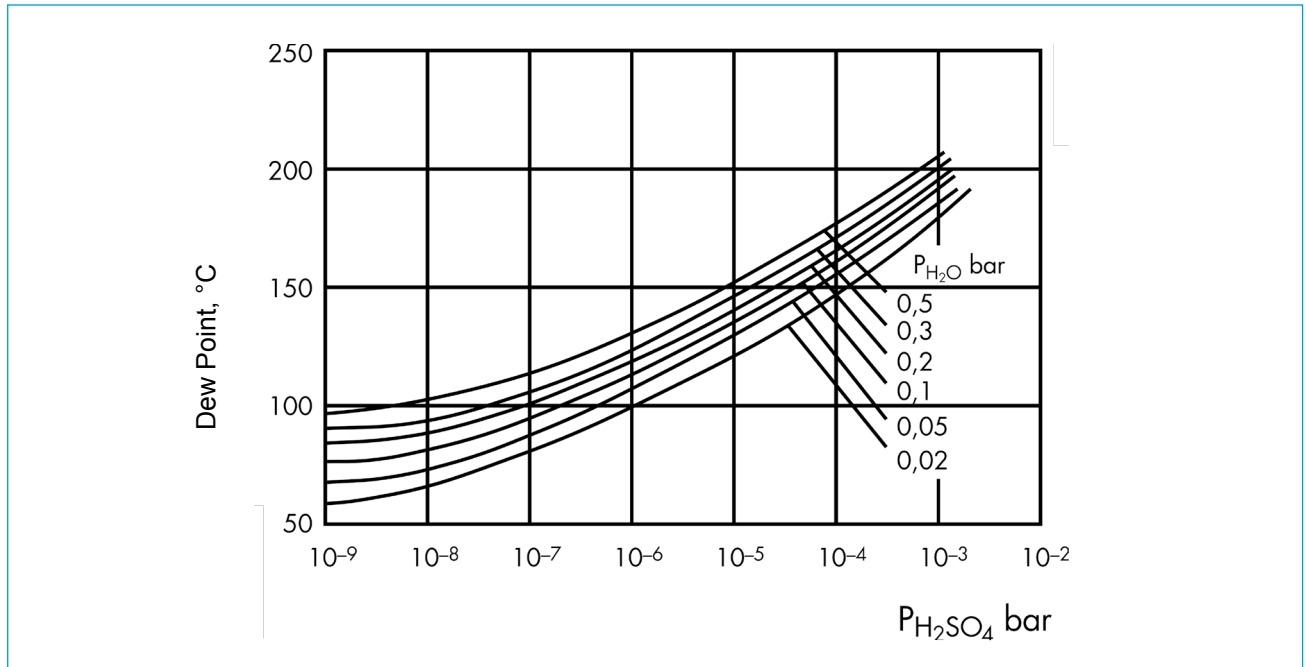


Figure 2: The dew point curves of sulphuric acid as a function of H<sub>2</sub>SO<sub>4</sub> concentration and flue gas humidity. Source: [11]

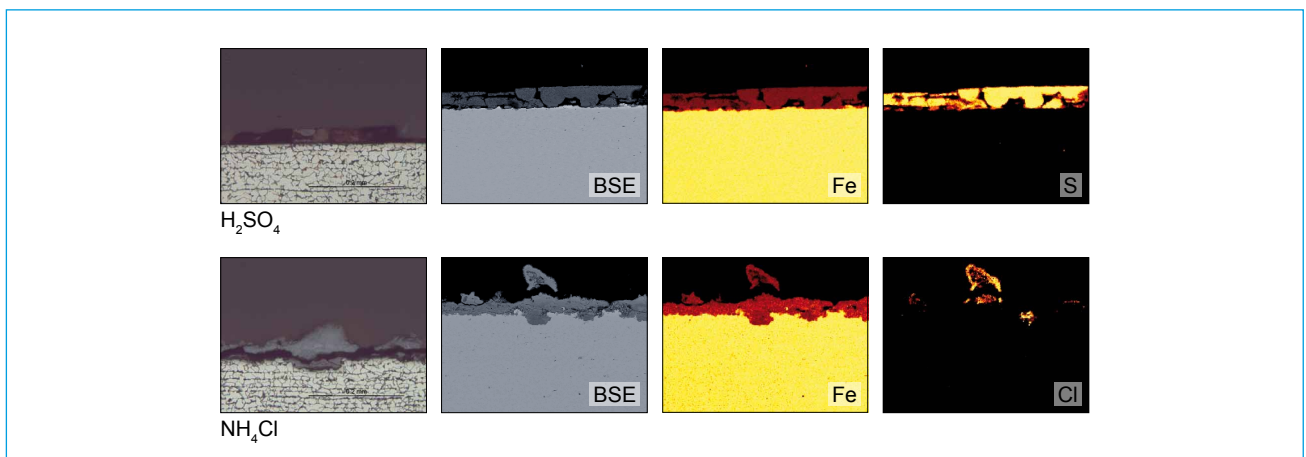


Figure 3: Microscopic features (metallography, nital etching) and microanalytical examination (SEM-EDX) of dew point corrosion through sulphuric acid (upper row) and deliquescent corrosion through NH<sub>4</sub>Cl salt (bottom row). The attacks by sulphuric acid are extensive, the electrolyte of ammonium chloride forms shallow pittings. The result of a serial examination regarding the corrosive features and relative corrosiveness of various agents in the laboratory with the equipment described in Chapter 2.3.2.

## 2.2 Corrosion through Hygroscopic and Deliquescent Salts

Many salts, mostly chlorine salts (chlorides), have the property of absorbing moisture from the surrounding atmosphere: their reaction is hygroscopic. If these salts occur in solid form, e.g. as particles on the tubes of an ECO or on the steel sheets during flue gas cleaning, and if flue gas humidity (related to the respective temperatures) is low, then the particles remain dry and thus solid (dust-like). If, however, relative humidity (rH) increases as a result of falling flue gas temperatures, certain salts cannot only humidify themselves with the available moisture, but also deliquesce in the absorbed water; Figure 4.

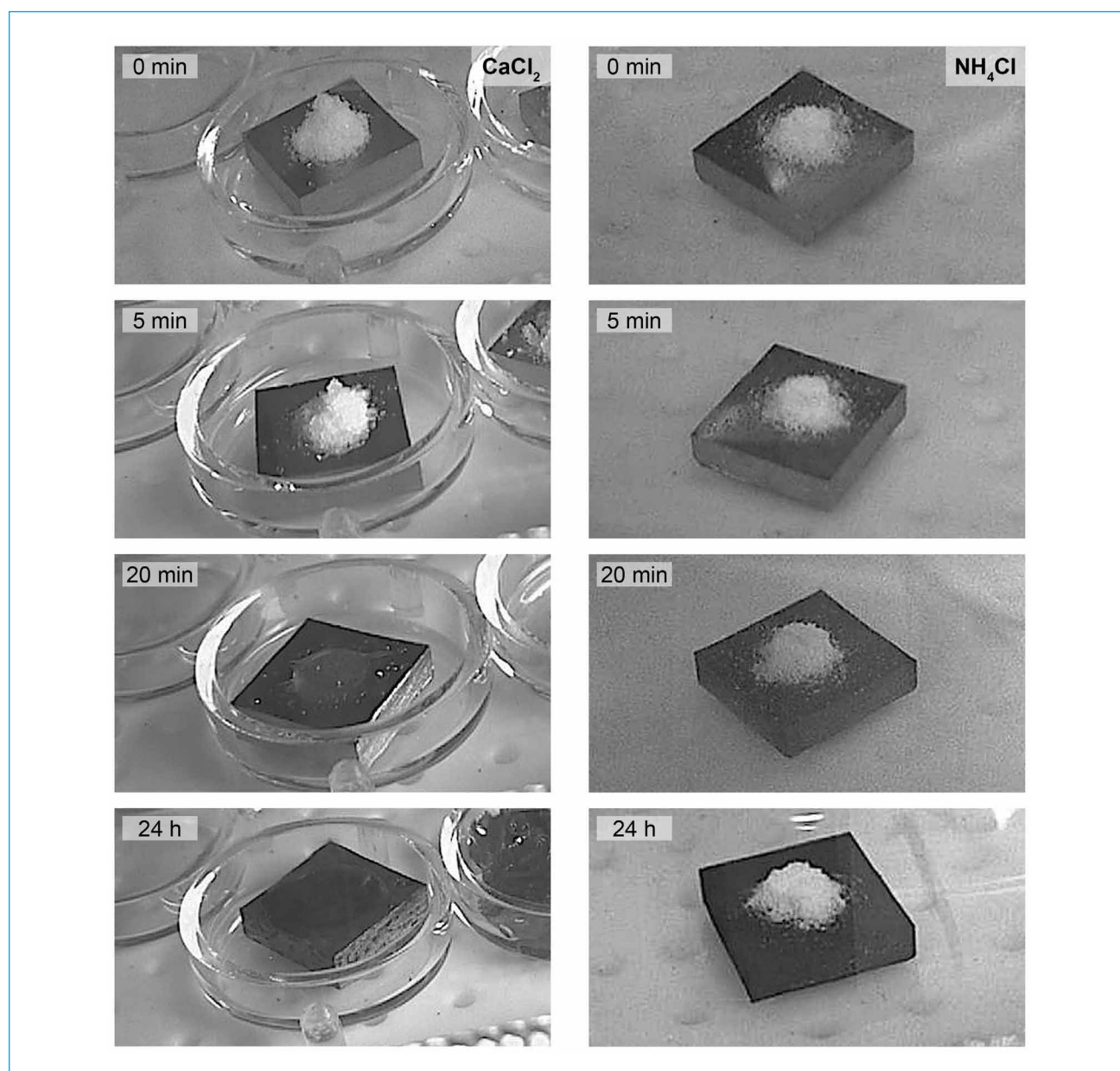


Figure 4: Deliquescent calcium chloride and ammonium chloride deliquesce. Laboratory test with preset material temperature and moisture, over a time span of 24 h. The equipment is explained in Chapter 2.3.2.



In chemistry and atmospheric research, the term Deliquescence Relative Humidity, DRH, is used to designate this point, up to which salts humidify themselves due to their hygroscopic properties and then deliquesce. A detailed description is given by Lindau & Goldschmidt in [12]; originally, this report was written in 2002 in Swedish and in 2008 translated into English [13].

Phenomena of self-humidification are, for example, technically relevant for calcium chloride because this behaviour can reduce the flowability of the residual matter in the case of fabric filters (baghouses). The deliquescence following self-humidification is mitigated by the content of inert ashes and other salts.

Figure 5 shows the DRH curves of calcium and zinc chloride ( $\text{CaCl}_2$ ,  $\text{ZnCl}_2$ ) as well as the saturation curves (relative humidity, rH) for a flue gas humidity of 15 and 25 vol%. Calcium chloride can, with an absolute flue gas humidity of around 25 vol%, form a saturated salt solution below approximately  $110^\circ\text{C}$ ; with approx. 15 vol% of flue gas humidity, a salt solution is formed below approx.  $95^\circ\text{C}$ . With sinking temperatures, the salt solution is more and more diluted.

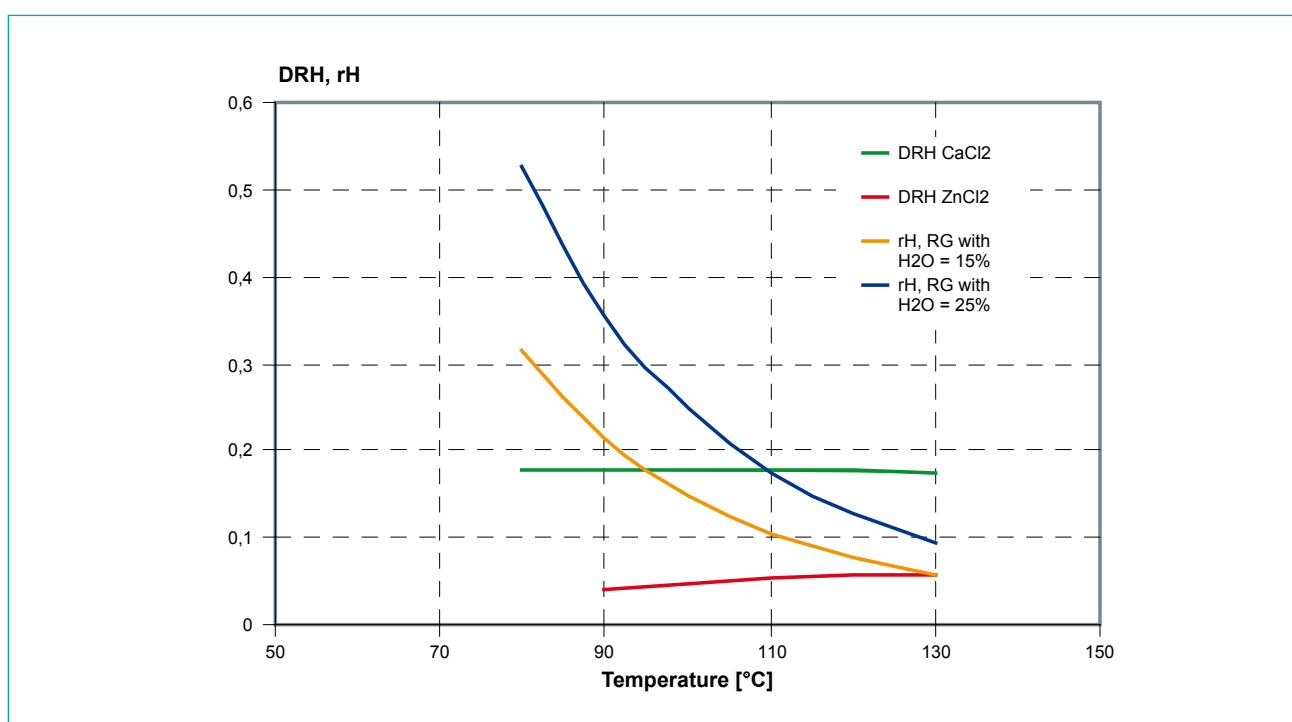


Figure 5: The DRH curves of calcium and zinc chloride ( $\text{CaCl}_2$ ,  $\text{ZnCl}_2$ ) as well as the saturation curves, (relative humidity, rH) for an absolute flue gas humidity of 15 and 25 vol%. Source: [13]

Apart from the already mentioned zinc, calcium and ammonium chlorides, other deliquescent salts are e.g. ammonium nitrate or ammonium sulphate.

In contrast to an extensive two-dimensional corrosion, the saturated solution formed by deliquescent salts attacks, as an electrolyte, in points or on a small area, leaving pits and troughs in the structure of the steel texture; Figure 3 and 15 through to 23. Depending on the attacking salt or salt mixture, the corresponding iron-sulphate and/or iron-chloride compounds are formed, in addition to iron oxides and hydroxides.

Here, the same applies as for dew point corrosion (see above), “rather clean” surfaces, which are covered by a thin layer of deliquescent salts, can most efficiently react with flue gas humidity. Increasingly thick layers of



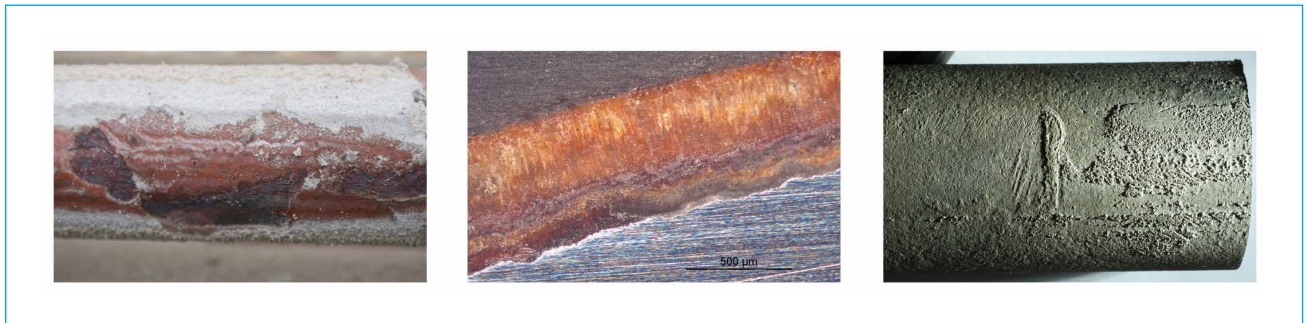


Figure 6: Deposit layer after a provocation test at a WTE plant at a medium temperature of 90°C, flue gas temperature of about 145°, after around 4.000 operating hours, including the products of flue gas cleaning. Colloidal corrosion products, bearing the mark of deliquescent calcium chloride. In a glancing light from the side, the protruding degraded morphology of the cleaned tube can be seen.



Figure 7: Provocation test at a WTE plant at a medium temperature of 90°C, flue gas temperature of about 235°, after around 4,000 operating hours, under the influence of SNCR.

deposit impede, among others, flue gas humidity from entering. And an increasingly thick layer raises the surface temperatures of the fouling, i.e. the absorption of flue gas humidity by the deliquescent salts is increasingly reduced, as illustrated by the diagram in Figure 5.

Another correlation is given by that fact that the size of salt particles has an effect on the deliquescence behaviour of the salts. Minute particles/ aerosols of deliquescent salts have a high specific surface and thus can react very efficiently with flue gas humidity.

Analytical proof of whether any ammonium salts are involved in aqueous corrosive processes cannot be provided by means of the most common analytical method, X-Ray Fluorescence Analysis, applied to ground samples of solid matter (from corrosion products and/ or deposits). Other methods are necessary, see the following examples. In the case of macroscopically visible, mono-mineral layers of e.g. ammonium chloride, a specific, preparative and analytical approach is required to prove this species [9].

By means of provocation tests at a WTE plant (SNCR), a test run with modular installed equipment at a medium temperature of 90°C and flue gas temperatures of 145 °C or 235°C, was evaluated after approx. 4,000 operating hours. The analytical test indicates a more severe corrosive attack caused by calcium chloride (originating from flue gas cleaning) and a weaker corrosive attack caused by ammonium chloride (originating from SNCR). The features of both attacks are very similar but different as to their dynamics under given conditions (material, flue gas temperature and humidity); Figures 6 and 7.

Uncleaned and cleaned piece of tube (corrosion morphology in a glancing light from the side), deposit structure and metallographic section (bottom) and microscopic image of the zone close to the tube (top right). The analytical test of the columnar deposit layer and of the zone close to the tube reveals ammonium chloride above chlorine corrosion products from the tube material.

## 2.3 Sampling of Hygroscopic/ Deliquescent Salts in the Boiler and Laboratory Test

Hygroscopic and deliquescent salts are “sensitive” species as far as their stability and reactivity are concerned. Deposit monitors are used, to record them during operation and for later analysis in the laboratory. Additional laboratory-scale tests are necessary, under conditions to be determined in order to quantify the reactivity and corrosiveness of the substances identified by the deposit monitors and to record their corrosive effect under specifically changed conditions such as moisture, temperature, material. Both possibilities – onsite by means of deposit monitors and in the laboratory by means of a corrosion test rig – are presented hereafter.

### 2.3.1 Diagnosis in Operation

The above mentioned deposit monitors are suitable means to evaluate operating changes or fuel variants (e.g. air ducts, humidity, composition of the fuel), material variations, the effects of online cleaning, decreased feed water temperatures and other effects in relation to their corrosive effects at the cold end of boilers. They can be installed and removed during operation, offering a number of advantages over the option of sampling only during boiler outages. These include, among others:

- The diagnosis of the particles and the deposit, formed through condensation and desublimation, is not interrupted by short-term processes of boiler shutdown.
- The point in time of installing and removing the deposit monitor can be freely chosen and thus be limited exactly to the point in time and duration of relevant (favoured) operating conditions.
- The periodic use of the monitor (e.g. monthly) allows to split rather long operating periods into shorter intervals, and for each interval specific information on the corrosive behaviour at the cold end is provided.

- Foreseeable changes regarding operating mode or fuel can be specifically recorded by placing the monitors in staggered order.

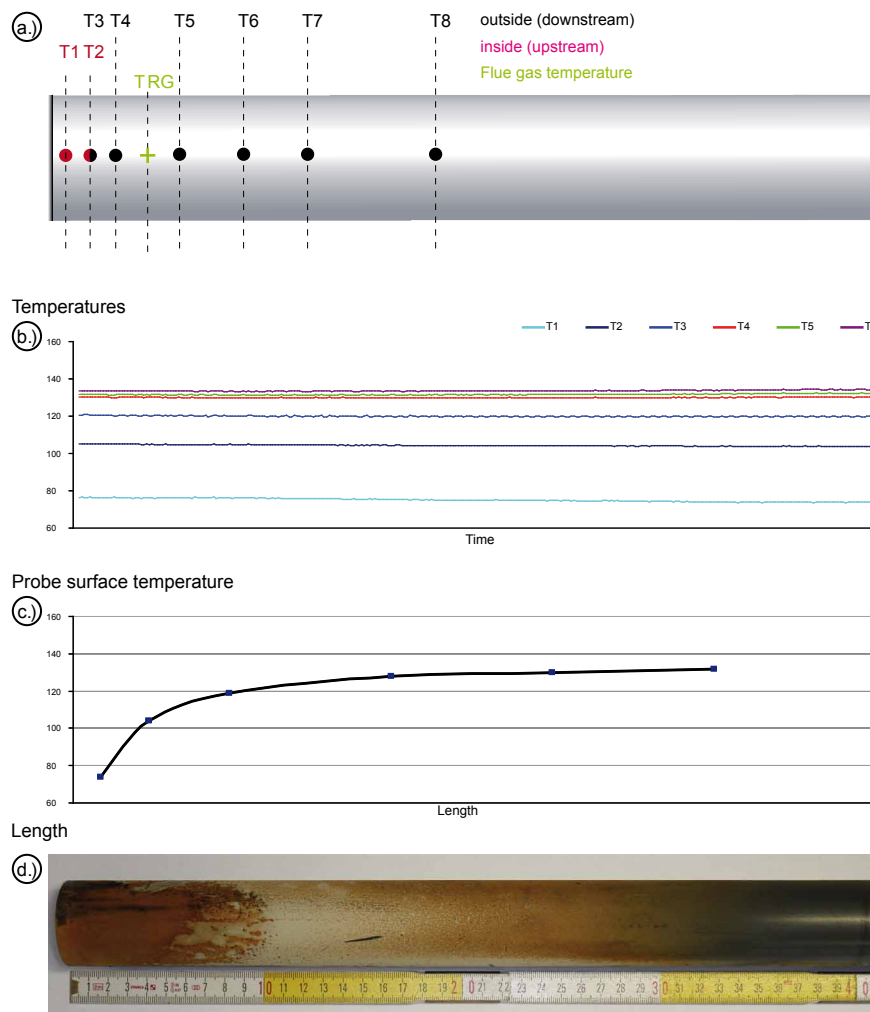


Figure 8: Deposit monitor. a) Drafted setup of temperature measurements in and on the monitor. b) Example for temperature measurement and regulation in the course of time. c) Temperature gradient over the length of a monitor. d) Deposit monitor after its removal from the boiler. This photo shows the formation of deposit and corrosion in relation to the temperature.

The deposit monitor consists of a tube which is cooled from the inside, starting at the tip. Surface temperature is measured with thermocouples inside and outside, over the length of the monitor, Figure 8. Continuous cooling

is regulated by the measuring signals. Over the length of the deposit monitor a temperature gradient develops which is a function of the selected set-point temperature and the temperature of the flue gas. The length of the deposit monitors can be varied, depending on given local conditions. This means that material temperatures can specifically be set on a monitor and dew points - e.g. starting from that of water - be provoked.

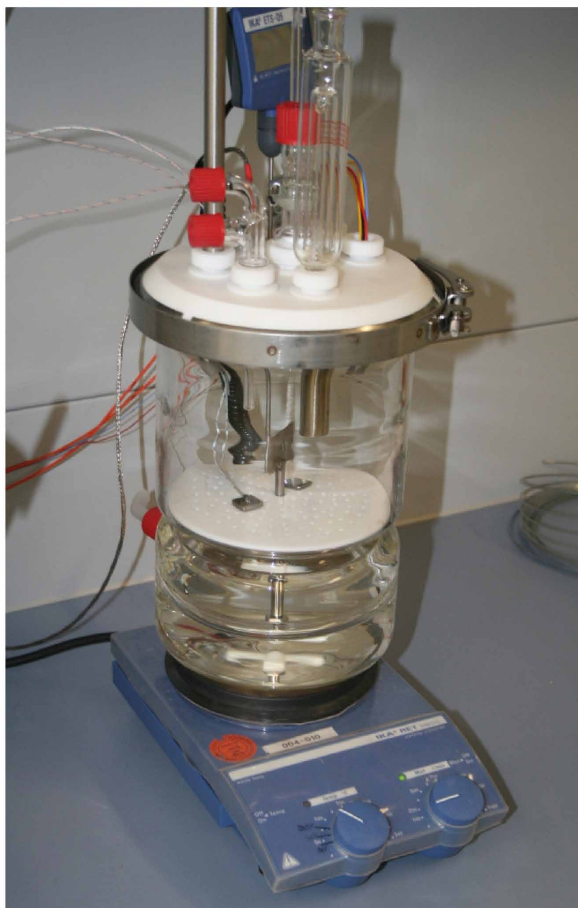
After removing the deposit monitor, the tube segments from the relevant / favoured temperature positions and /or the corroded areas, are cut out in the laboratory and the entire installation consisting of the tube, corrosion products and fouling is prepared to metallographic sections, without disturbance of the original textures. The metallographic sections must be prepared in an absolutely dry environment in order to preserve the water-soluble salts (e.g. calcium chloride, ammonium chloride etc.). The metallographic sections are analyzed spatially-resolved, by means of light microscopy, scanning electronic microscope and other methods.

Moreover, the tube segments can be analyzed with respect to their degradation rate (mm/ 1.000 h) according to the temperature.

These steps of (A), the collection of operating influences (deposit monitor in the boiler) and (B) the preparatory steps in the laboratory (cleaning, etching, preparing of metallographic sections etc.) and (C), analytical methods to be specifically adjusted to the found phenomena, provide a highly conclusive sensory system. The deposit monitors thus provide sensors for electrolyte corrosion at the cold end, reaching far beyond the information obtained from a dew point sensor, as the following information is produced by a deposit monitor:

- 1) Diagnosis as to whether, under freely selected temperatures (e.g. from 80°C to 150°C), a corrosive attack occurs.
- 2) In the event that 1) is true: Diagnosis, from which temperature and, if needed, up to which temperature a corrosive attack occurs – thus determining the temperature window for corrosion.
- 3) Per temperature window: Determination of the corrosion dynamics under changing temperatures. If necessary, the determination of various zones of corrosion phenomena, depending on the temperature within the temperature window.
- 4) Per zone: Determination of the cause(s) of corrosion (salts, acids, water etc.).
- 5) Per zone: Determination of the degradation rates (at least some weeks of retention time for the deposit monitor in the boiler are required by this step).

### 2.3.2 Corrosion Tests in the Laboratory



In the laboratory, diverse corrosive agents and substances can be examined in serial tests, Figure 9. Assessments regarding the relative corrosivity of diverse substances and substance concentrations (in the electrolyte) are possible. The conditions of the corrosion tests can be kept constant regarding humidity, oxygen content and material temperatures. Figure 3 and Figure 4 give examples from the tests.

Figure 9: Test rig for corrosion tests regarding diverse materials and corrosive agents under given material temperatures, percentages of oxygen and humidities.

## 2.4 Deliquescent Ammonium Chloride and Bromide

Ammonium chloride ( $\text{NH}_4\text{Cl}$ ; sublimation point at approx.  $340^\circ\text{C}$ ) is a naturally occurring mineral and, as a white and mostly granular salt, also known under the name of sal ammoniac. In power plant technology, the problems caused by the sometimes massive fouling or build-up of ammonium chloride are familiar. In [8] Hediger gives a comprehensive and practice-related description on the various operating problems as a result of centimetres of thick fouling and their avoidance, e.g. by raising ECO temperatures to  $145^\circ\text{C}$ , as well as carrying out a slip measurement to optimize SNCR injection. But even minute depositions of aerosols can cause difficulties as they occupy the pores of fabric filters [9] [14]. In this context it is discussed that  $\text{NH}_4\text{Cl}$  is formed in the fabric filter or that the particles are so minute that the fabric filter is no barrier to the salt [5] [9]; deliquescent corrosion behind the fabric filter is displayed in Figure 12.

Ammonium bromide ( $\text{NH}_4\text{Br}$ ; sublimation point at approx.  $450^\circ\text{C}$ ) does – in contrast to ammonium chloride - not form any naturally occurring minerals. In cases with sufficient bromine in the fuel, it can be found combined with ammonium chloride in boilers, i.e. as a  $\text{NH}_4\text{Br-NH}_4\text{Cl}$  mixed crystal.



### 2.4.1 Formation of Ammonium Chloride in the Boiler

On the one hand, ammonium chloride grows on ECO tubes mostly in the form of fine needles, all close to each other; Figure 10. This growth form proves that ammonium chloride is not transported as a particle by the flue gas stream in the boiler, but crystallizes from a  $\text{NH}_4\text{Cl}$  gaseous phase through desublimation:

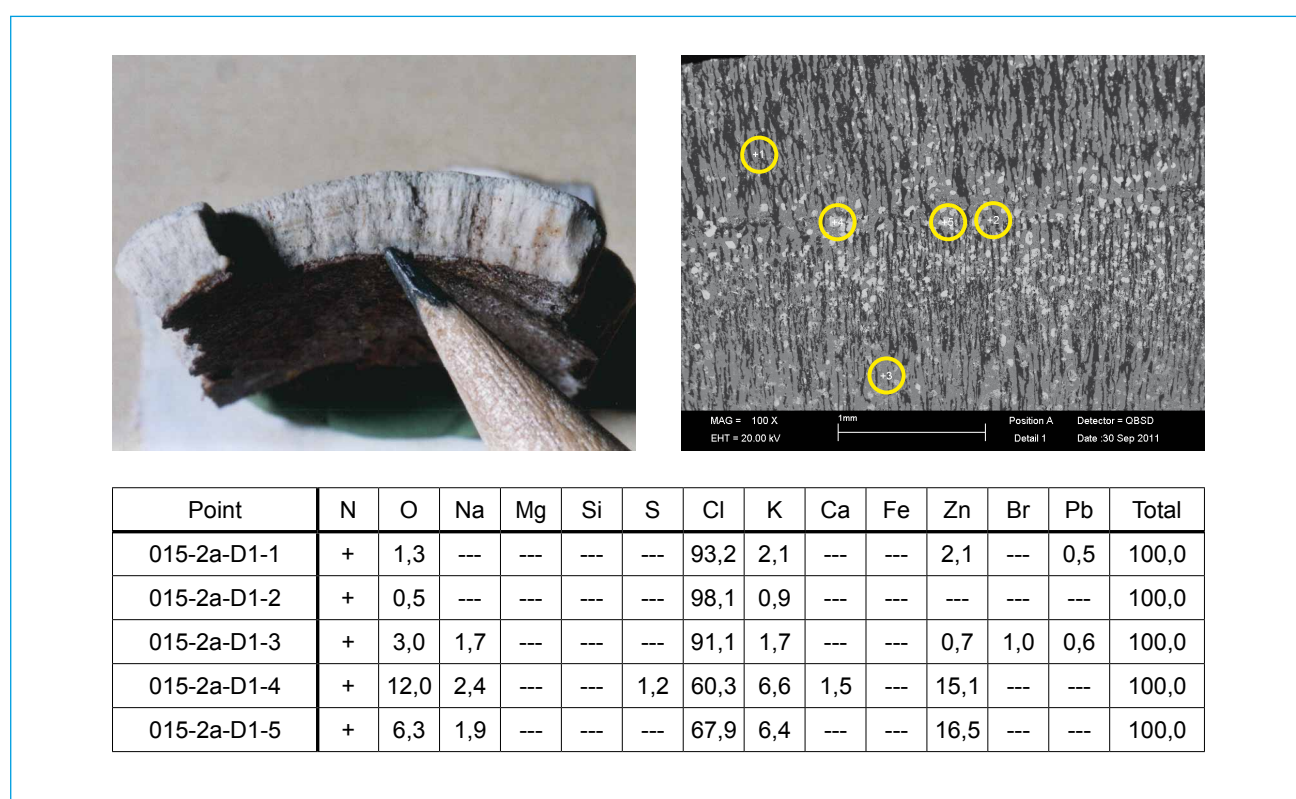
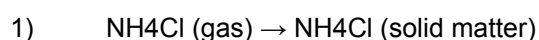


Figure 10: Massive ammonium chloride layer. Its needle-like growth gives evidence of the crystallization of solid  $\text{NH}_4\text{Cl}$ , from a  $\text{NH}_4\text{Cl}$  gaseous phase. Sample from an ECO tube, biomass power station with SNCR  $\text{DENOX}$ , waste wood classes A1 to AIV. To the table: as nitrogen can only be detected qualitatively by the casual available analytical methods, this is indicated by a "+" in the column for N. As the content of nitrogen is not included in the calculation of the sum (100%), the chlorine percentage (Cl) – and proportionately all other percentages – are too high in relative terms.

On the other hand, the test whose result is displayed in Figure 11, is well-known from chemistry lessons. Above a beaker with hydrochloric acid the air becomes saturated with  $\text{HCl}$ . The test tube contains liquid  $\text{NH}_3$ , and the air becomes saturated by ammonia. Combined, both gases form white crystals of ammonium chloride, thus skipping the liquid state:



In chemical terms, equation 2 does not describe the desublimation of a gaseous phase but the formation of a complex by two gases. This behaviour could also occur in the flue gas of the boiler, implying that, possibly, a gaseous  $\text{NH}_4\text{Cl}$  phase does not occur there.



Figure 11: Gaseous  $\text{NH}_3$  forms, together with gaseous  $\text{HCl}$ , solid white crystals. Source: Wikipedia, keyword "ammonium chloride"

Therefore equations 1 and 2 describe different reaction processes. As this article deals with actually occurred cases of damage, this consideration will not be discussed in more detail hereinafter.

The  $\text{NH}_3$  and  $\text{HCl}$  concentrations dissolved in the flue gas determine, from which temperature level the gaseous ammonium chloride is formed in the boiler. Literature provides clues that the salt occurs at temperatures of  $<180^\circ\text{C}$  [15] or at temperatures of  $<140^\circ\text{C}$  in connection with significant  $\text{HCl}$ -concentrations and an ammonia slip [16] [17].

It is likely that flue gas humidity also plays a role during and after the formation of the ammonium chloride aerosols. Subsequently, with increasing relative humidity, the formed  $\text{NH}_4\text{Cl}$  nuclei can again dissolve as  $\text{NH}_3$  and  $\text{HCl}$  [18]. Therefore, the size of the nucleus and the current relative humidity decide about its "survival". This means for analytical tests that small amounts of ammonium chloride, as in Figure 17, are easily and quickly lost, unless the desublimates are stable and well-crystallized as displayed in Figures 7 and 10.

A favourable effect can also be produced by the environmental conditions of the respective location where the nuclei are deposited, or their growth through desublimation. Ammonium chloride, for example, is frequently found on the lee side of ECO tubes. Turbulences favour the mixing of the gas, increasing the probability of reactions among the gas species amongst themselves. Another favourable effect can be produced by the filter cake and filter fabric on the reaction kinetics, by a prolonged retention time of the gases in the pore space.

In parallel to observing the formation of  $\text{NH}_4\text{Cl}$ , whether by the desublimation of a  $\text{NH}_4\text{Cl}$ -gaseous phase (equation 1), or by the reaction of two gaseous phases (equation 2), the formation and the avoidance of  $\text{NH}_3$  and  $\text{HCl}$  are equally interesting. Hereinafter, the  $\text{HCl}$ - ( $\text{HBr}$ ) formation in the firing and the boiler are addressed only shortly, because the fundamentals thereto were and are considered in detail in generally accessible literature. Apart from this, the avoidance of  $\text{HCl}$  is - for almost all difficult fuels - not a promising approach. The conditions for the formation of  $\text{NH}_3$  or their avoidance in the firing system are described in more detail.



### 2.4.2 Formation of HCl (HBr) through Fuel and Firing

Online measurements of gaseous HCl in the flue gas are part of the standard procedure of many power plants with difficult fuels.

#### Waste as a fuel:

In waste-to-energy plants the conversion of chlorine from the fuel and the formation of HCl in the firing system are facts according to online measurements.

The release of chlorine and bromine were intensively researched by Vehlow [19] as well as by Tohka & Zevenhoven [20] in the wake of increasing volumes of electronic waste. Fundamental considerations on thermodynamic behaviour in the flue gas and on corrosion caused by hydrogen chlorine and hydrogen bromine are made by Rademakers et al. [21]. Anthropogenic bromine sources are extensively described in [37].

#### Biomass as a fuel:

In biomass-fired power plants, (high temperature) chlorine corrosion often occurs to the same extent as in waste-fired power plants. Typical chlorine proportions in biomass are:

- Up to 0.02 weight % in wood
- Up to approx. 0.3 weight % in corn (wheat, rye, sunflower, rapeseed etc.)
- Up to approx 0.8 weight % in straw types
- Up to approx 1.4 weight % in grass types/ blade-shaped biomass (lop, miscanthus etc.)

In Scandinavian literature, (high temperature) chlorine corrosion has been focused on since 1989, when the first industrial straw-firing (20 MW thermal) was commissioned in Haslev and, in 2011 a survey of such firing was prepared by Montgomery et al. [22]. Current research on the fuel and firing is mainly targeted towards potassium chloride (KCl), which is often identified as a corrosive agent, and to a lesser extent on the formation of HCl, which was thoroughly contemplated in the Scandinavian market in connection with the co-firing of biomass [23].

The thermodynamic mechanisms are the same as for the combustion of waste (e.g. Deacon Equation:  $\text{HCl} + \text{O}_2 \leftrightarrow \text{H}_2\text{O} + \text{Cl}_2$ ). However, specific temperatures, piece sizes, fuel properties (particularly plant structure) and water content play a major role here. These parameters will be examined more closely in the following with respect to their impact on the formation of  $\text{NH}_3$ .

However, bromine is, in addition to C, O, H, N, S, Cl and F, part of the “ultimate analysis” [24], i.e. it should be given equal weight as chlorine.

Natural bromine sources, such as biomass or peat and coal, and HBr-formation are extensively described in [38].

### 2.4.3 Formation of $\text{NH}_3$ through Fuel and Firing

Ammonium chloride can also be found in boilers without SNCR injection. Thus other  $\text{NH}_3$  sources exist apart from the ammonia slip through SNCR.

Figure 12 illustrates deliquescence corrosion in the ducts of recirculated gas of a biomass power plant (waste wood classes AI and AII), i.e. at a power plant without SNCR. All ducts behind the fabric filter are affected. The

first damage cases were observed at the coldest spots, below 140°C to approx. 120°C. NH<sub>4</sub>Cl or the corrosion product zinc-ammonium-chloride were identified as the corrosive agents by way of diffractometry (the zinc stems from the zinc-coated steel sheet from which NH<sub>4</sub>Cl precipitated). Ammonia and hydrochloric acid are formed from the fuel in the firing and then bond as ammonium chloride, causing corrosion in areas downstream the fabric filter.

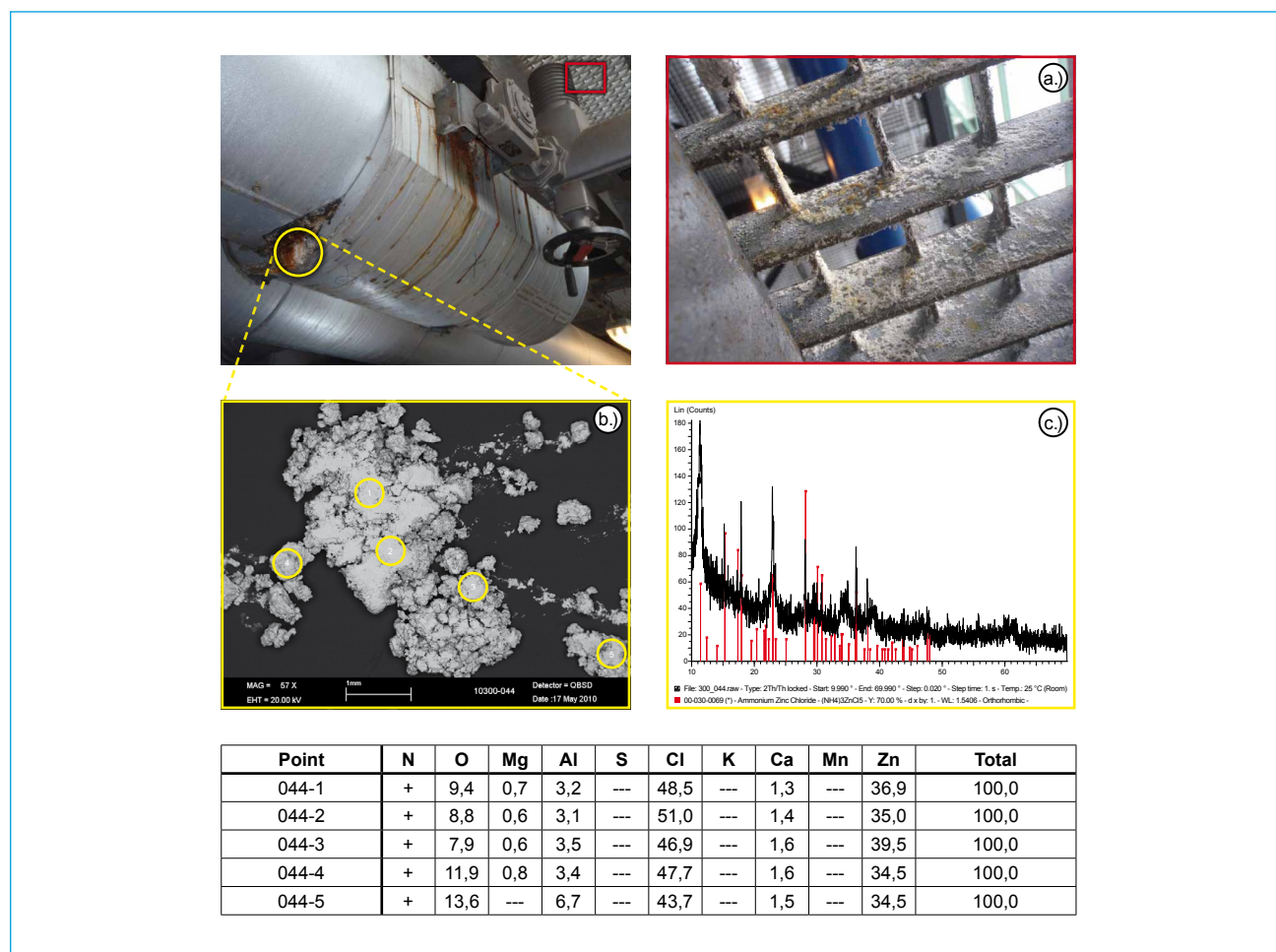


Figure 12: Deliquescence corrosion through ammonium chloride downstream of the fabric filter in the duct for recirculated gas of a waste-wood combustion system (Al-All). Ammonium chloride is released through leaks and not only attacks the ducts from the inside, but all surrounding components (a: e.g. the grates). b: The sample of white salts consists of zinc-ammonium chloride, according to the X-ray diffraction diagram in (c) and chemical analysis (table).

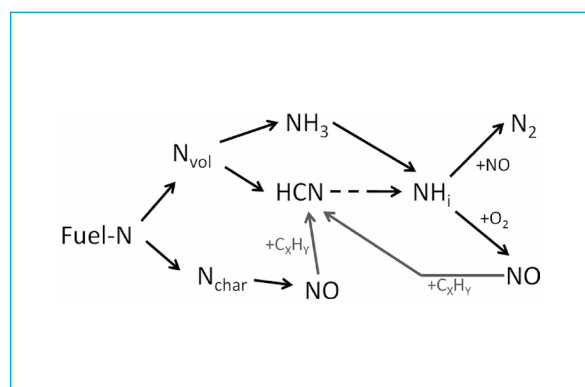


Figure 13: Schematic representation of possible reaction pathways of nitrogen in fluidized bed combustion. Source: [25]

Literature provides further references, particularly in articles on the formation of NO<sub>x</sub>, where NO<sub>x</sub>-precursors such as NH<sub>3</sub> are considered, for grate firing as well as for fluidized bed combustion. Examples are:

- Regarding formation paths: The most current publication on this topic gives a detailed presentation of the reaction pathways of nitrogen during biomass combustion, Figure 13. Other literature states that NH<sub>3</sub> is directly formed, without intermediate steps, during the pyrolysis of waste [38], coal [39] and biomass [40].
- Figure 13: Schematic representation of possible reaction pathways of nitrogen in fluidized bed combustion. Source: [25]
- In terms of temperature: at 800°C a maximum release of NH<sub>3</sub> from brown coal is observed [26] [27]. Fuel tests are frequently carried out at 850°C [28]. During pyrolysis tests it was found that nitrogen, bound by biomass, becomes gaseous at temperatures of >1.000°C (i.e. is burned) and thus reduces the formation of NH<sub>3</sub> [29].
- In terms of heating rate: fuel tests at 400-900°C demonstrate that high heating rates favour the formation of NH<sub>3</sub> [30].
- In terms of piece size: in the course of pyrolysis or incomplete burning, NH<sub>3</sub> formation is increased when the outer, charred shell of the fuel pieces bursts [31]. In general, piece size has an effect on NH<sub>3</sub> formation [30].
- In terms of structural fuel properties: the maximum volume of NH<sub>3</sub> that can be released very much depends on the presence and type of amino acids (e.g. sewage sludge) or on plant structure [28] [32] [33] [34]. Particularly the phenolic macromolecule lignin, with which plant substance lignifies (lignification), favours the formation of NH<sub>3</sub>. Thus, for example, rice straw, sycamore tree leaves and the sawdust of pine trees release (600-1.200°C) more NH<sub>3</sub> in fuel tests than soy bean slurry, although they contain less nitrogen than soy beans [29].
- In terms of water content: the water content of biomass can provide hydrogen radicals and therefore favour NH<sub>4</sub> formation [27] [35].

Power plant sites, with the opportunity of separating or mixing diverse fuels, have the potential to reduce corrosivity at the cold end of the boiler with respect to the listed parameters. This requires, first of all, knowledge about the substance properties if various fuels are come into play (e.g. paper sludge, rejects, adhesives and glue in composite materials etc.). Some of these properties are to be tested analytically, others can be referred to in data sheets. The requirement of turning the fuel into the right piece size often requires special machinery. Basically, the operator can influence the result in numerous ways.

Primary NO<sub>x</sub> reduction in the 1. pass, i.e. through a reaction with the ammonia formed during combustion, only seems possible to a limited extent or at least, it is not proven that the entire reaction occurs. The NH<sub>3</sub> from the combustion is formed at temperatures of around 600-850°C, according to the above mentioned literature, and can be oxidised (burned) if temperatures continue to rise. During DENOX by means of SNCR, through the injection of liquid urea or an ammonia solution, NO<sub>x</sub> is efficiently reduced by NH<sub>3</sub> at temperatures of approx. 1,000°C, see Figure 14. Usually, the SNCR-ammonia is not fully consumed as it can be detected through gas measurements (slip) and also as desublimates, together with HCl in the form of NH<sub>4</sub>Cl.

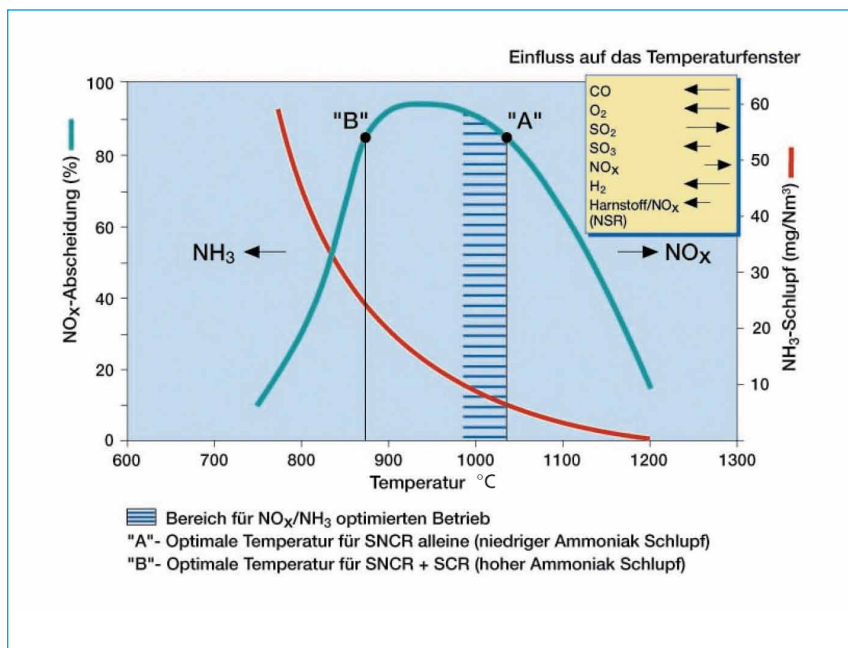


Figure 14: NO<sub>x</sub> separation during the SNCR process as a function of temperature, with notes regarding the impact when temperatures are beyond the optimum range of temperatures. Source: [1]

### 3 Case Studies regarding Renewable Fuels

In the course of assessing the damage on economizers in biomass power plants, which are fired by renewable fuels from the natural wood market, corrosion phenomena have been found repeatedly which cannot be explained by erosion alone. These damage cases have in common that they occur, in particular, at feed water inlet temperatures in the ECO from slightly above 100°C to around 120°C.

At such power plants, SNCR equipment is not used.

Analytical tests with regard to temperatures below the sulphuric acid dew point and therefore resulting in corrosion, or with regard to erosion corrosion, came to the result that - under deposit layers dominated by sulphates - chlorides are concentrated directly at the corrosion front.

The results are, in addition to chemical analyses of the fouling and to mineral phase analyses by means of X-ray diffractometry, also based on the spatially-resolved microanalytical findings on the prepared metallographic sections, which were produced including the depositions. Figure 15 displays examples of such findings.

Figure 15: Top and middle rows: Degraded ECO tubes from different sites (partially cleaned) as well as a prepared metallographic section with remainders of the deposit in the degraded pittings. Bottom row: Light-microscopical evaluation of the corrosion front (salts and corrosion products with droplets formed) and a grey-scale picture taken with scanning electron microscopy. The marked area contains exclusively chlorides, no sulphur compounds. Next to it an image of chlorine, displaying the distribution of the elements which are concentrated directly at the corrosion front (concentration increases from black to red to light yellow).

In the deposit layers with some distance from the ECO tube surface, calcium carbonate („lime“) and calcium oxide are detected, in addition to inert siliceous ash parts, sulphates and chlorides of calcium and potassium. Calcium oxide and calcium carbonate can neutralise the condensing sulphuric acid (buffering effect) until they have been fully consumed. This full consumption was mainly found at special positions. At the same time and due to the locally increased humidity, deliquescent calcium chloride possibly increases the tendency to form



sulphuric acid with the  $\text{SO}_3$  from the gaseous phase. During this, the present chlorides can be converted into sulphates and again release  $\text{HCl}$ .

The degradations of the tube, from shallow pittings to canyon-like structures, contain sulphates of calcium and potassium as well as chlorides (predominantly potassium chloride and, to a lesser extent, calcium chloride), in addition to swelling iron oxides and hydroxides. It is to be emphasized that mere chloridic seams regularly occur directly at the corrosion front, with no cationic partners (e.g. K or Ca) for chlorine to be proven by any common methods of proof. The cations are therefore supposed to consist of elements, which cannot be detected by these methods (e.g. N and H).

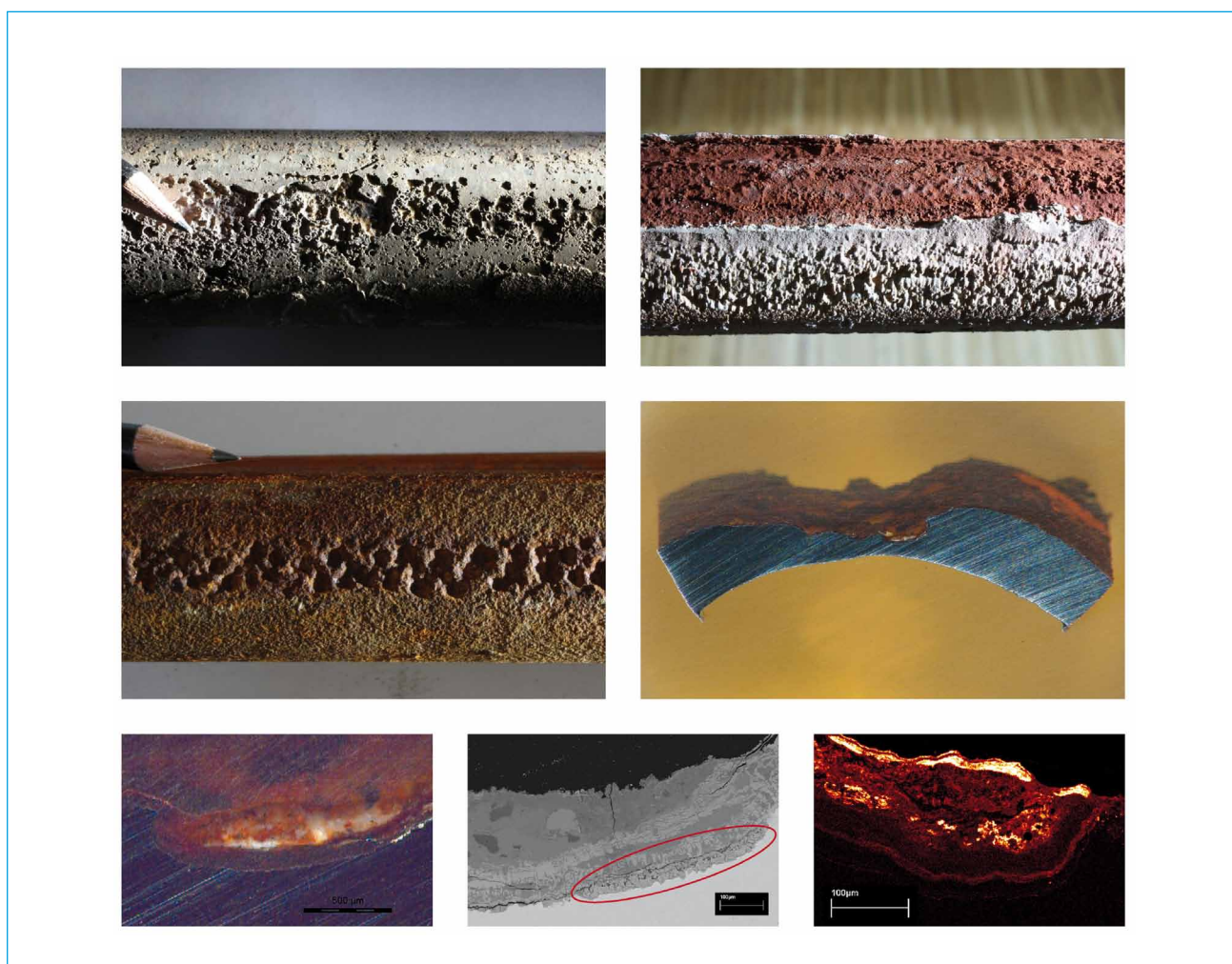


Figure 15: Top and middle rows: Degraded ECO tubes from different sites (partially cleaned) as well as a prepared metallographic section with remainders of the deposit in the degraded pittings. Bottom row: Light-microscopical evaluation of the corrosion front (salts and corrosion products with droplets formed) and a grey-scale picture taken with scanning electron microscopy. The marked area contains exclusively chlorides, no sulphur compounds. Next to it an image of chlorine, displaying the distribution of the elements which are concentrated directly at the corrosion front (concentration increases from black to red to light yellow).

Deposit monitors were deployed for further tests during operation in order to assess the mechanisms and causes of corrosion. The deposit monitors are explained in Chapter 2.3.1. With respect to the surface morphology

of the deposit monitors, a first assessment is made as to whether a local corrosion attack occurred during testing in the boiler. Figure 16 displays the surface morphology of cleaned deposit monitors (diverse materials) after operations in the preheater area of a biomass power plant.

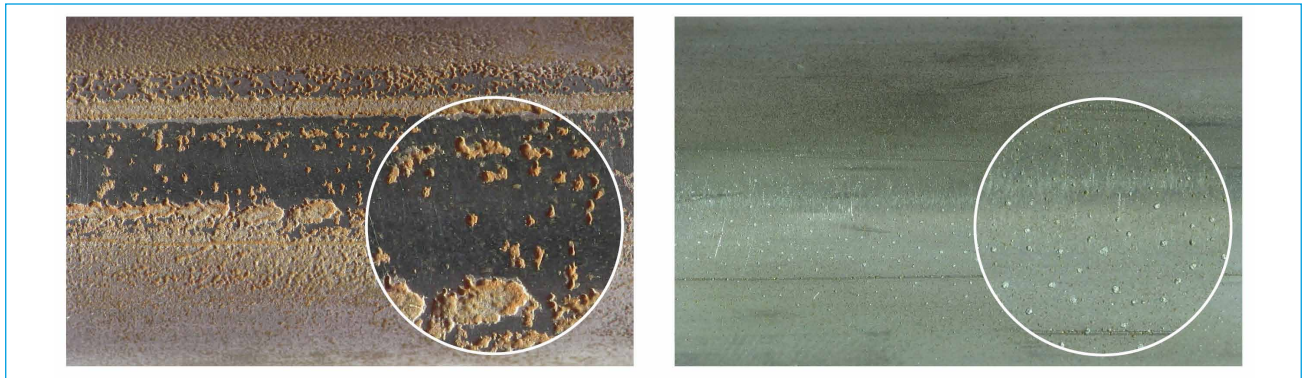


Figure 16: Surface morphology of the deposit monitors after testing of diverse materials in the preheater area; left: ferritic material; right: austenitic material.

The fouling on the deposit monitors is analyzed, e.g. chemically (chloride content) and through phase analysis for the substances contained. With the help of X-ray diffractometric phase analysis, proof of the participation of ammonium salts - particularly ammonium chloride and ammonium-iron-chloride - can be provided. On the metallographic sections the typical corrosion phenomena are visible under the microscope. On the deposit monitors, clod-type or cloudy and diffuse (not flaky) red-brownish corrosion products are formed and - in the pittings below - swelling corrosion products. Detailed spatially-resolving microanalytical tests provide proof of the chlorine concentrations and characterize their bonding form.

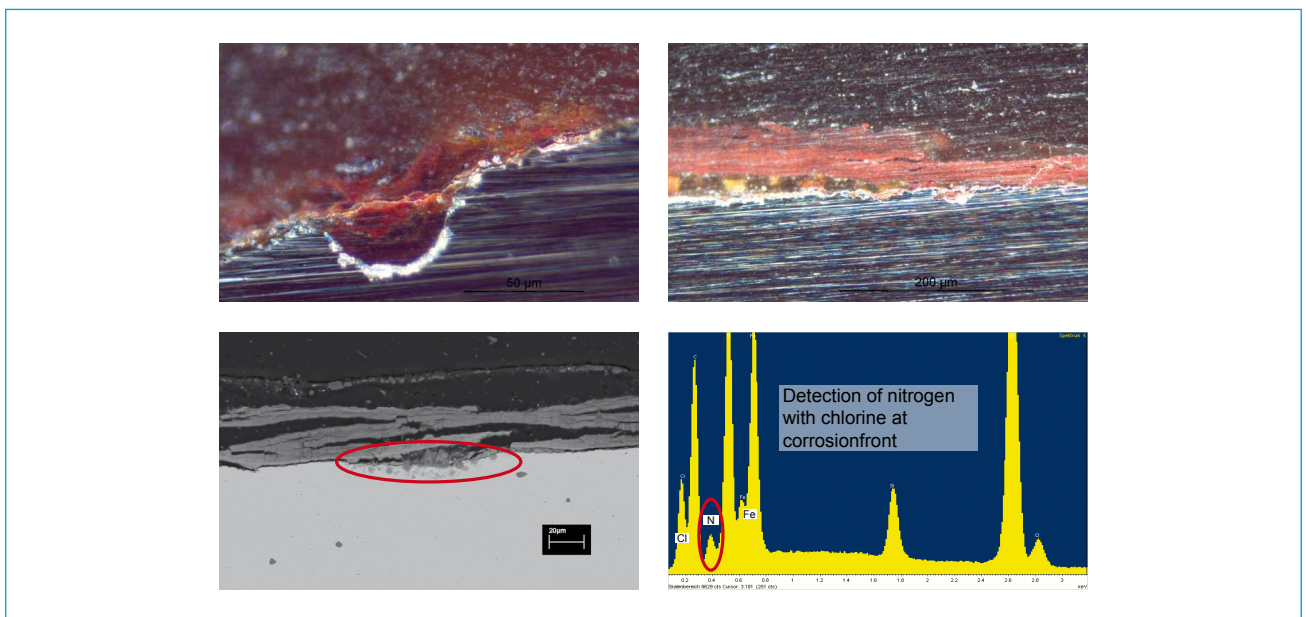


Figure 17: Cross-section results from the deposit monitors under temperatures ranging from 100 to 120°C, and spectrum with the detected nitrogen next to chlorine directly at the corrosion front.



Figure 17 shows examples of cross section results from these deposit monitors, under temperatures ranging from 100°C to 120°C after few weeks of application in the ECO range (findings by microscopy and scanning electron microscopy). On the bottom right the spectrum is presented, with the detected nitrogen next to chlorine directly at the corrosion front (spatially-resolved proof of ammonium chloride or ammonium-iron-chloride).

#### 4 Case Studies on Waste Fuels

DENOX in waste-fired power plants is carried out either in the firing system with the SNCR method (by adding a reduction agent in the 1. pass) or during flue gas cleaning with the SCR method (by adding a catalyst). In the following two examples of corrosive damage in the ECO range are presented, one from a power plant with SNCR, the other one with SCR. In the latter case, with “SCR”, this means that the firing system is the source of NH<sub>3</sub>. The previously listed parameters for the formation of NH<sub>3</sub> in relation to biomass fuels are assumed to be largely transferable to waste (to which extent such assumption is permitted needs to be further examined).

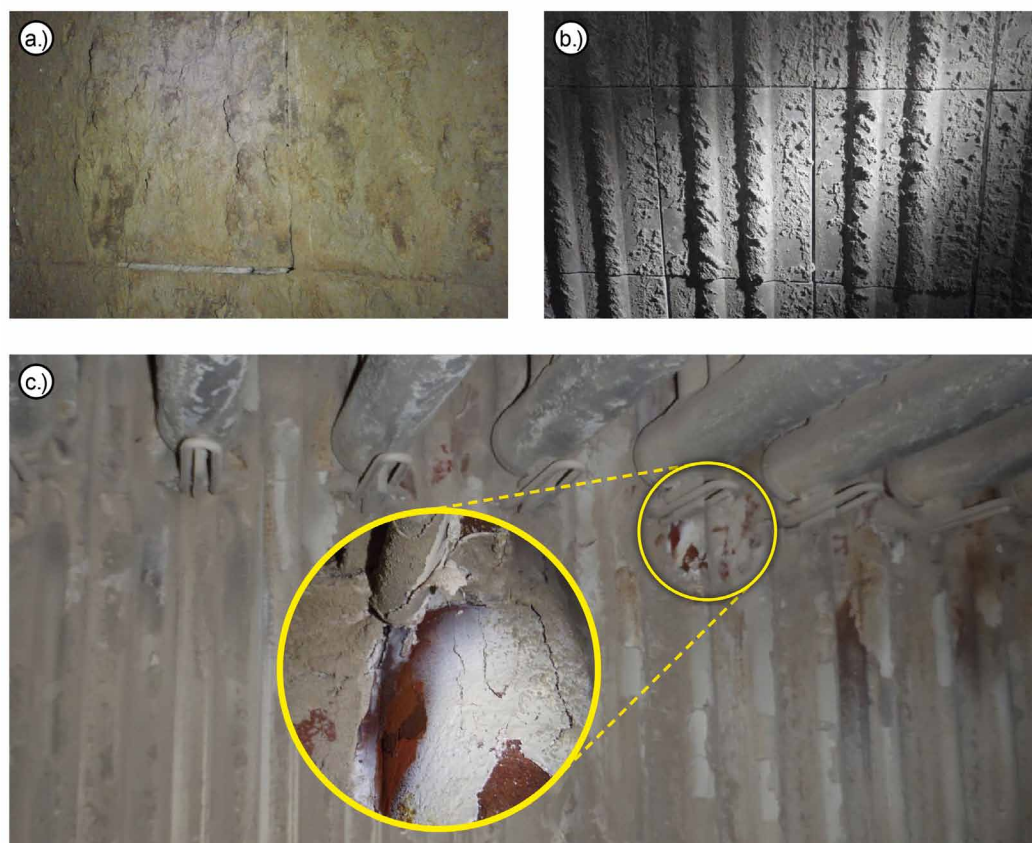


Figure 18: SNCR slip at a waste-to-energy plant. a and b: Photos from two combustion lines, same height, rear wall of the 1. pass: Cornices grow towards the flue gas stream, which comes from the top (backflow), reaching up to the height of the SNCR injection nozzles. c: Deliquescence corrosion through ammonium chloride at cold traps (side walls in the ECO range).



The simplest case of  $\text{NH}_3$  availability is such of a poorly adjusted SNCR injection or an injection negatively affected by the operating conditions or flue gas imbalances with insufficiently constant temperatures as a result of streaks near the SNCR nozzles that are too cold or too hot. Figure 18 gives an example for this. The findings are:

- At the rear wall of the 1. pass, loose conical cornices growing from the top down, covering the wall from the top to the bottom, due to the backflowing flue gas.
- On the front wall opposite, a “hot streak” can be measured during prolonged operating periods and is proven by hard sintered cornices.
- A comparatively low efficiency of  $\text{DENO}_x$ , presumably as a result of poor mixing in the 1. pass, and proven by corresponding loads of  $\text{NO}_x$ .
- In addition, at the boiler end thin-leaved layers of red corrosion products are visible, with and without white salts. The corrosion layers easily disintegrate into powdery, fine particles, in contrast to the often rigid scale layers from high temperature corrosion in the hot passes and on superheaters. The steel surface below is coloured beige-brown and may have black stains (as from splashing drops). With common X-ray fluorescence analysis (XFA) hardly any other elements can be detected in the white salts, apart from chlorine and iron. With suitable equipment also nitrogen is revealed qualitatively through scanning electron microscopical analysis.

Conclusion for this case: An ammonia slip is the consequence of a poor mixing of the SNCR injection, leading in combination with  $\text{HCl}$  to corrosion at the cold end of the boiler. The corrosive agent is ammonium chloride, forming a liquid electrolyte with sufficiently humid flue gas.

#### 4.1 Case Study: Power Plant with SNCR and with Ammonia Slip

Figure 19 to Figure 22 display a case examined in detail. After decades of operation the surprising finding was: pittings at the flue gas outlet of the first ECO, i.e. on the lee sides of the coldest tubes. In the passes, no imbalances in the flue gas can be observed/ measured, implying that thorough mixing of the SNCR injection and the flue gas is to be assumed. Besides, no time reference to an operating period with a deviating mode of operation or an unusual fuel – i.e. to a possible anomaly of operations – could be established. The detected corrosion led to a discussion between the operator and the manufacturer of the boiler regarding the stoichiometrically required volumes of SNCR injection. In order to verify the suspected corrosion caused by the ammonia slip, further examinations were carried out.

##### Examination and sampling during revision:

- Comparative sampling of the fouling on the ECO tubes in corroded and not corroded areas. Chemical analysis (X-ray fluorescence analysis) and phase analysis (X-ray diffractometry) of the samples.
- Sampling of corrosion products from the pittings, Figure 20. Examination of the samples by scanning electronic microscope for quantitative analysis (in the periodic table from sodium upward) and qualitative analysis of nitrogen.
- Washing of the tube surfaces with distilled water, Figure 19. The filtered washing water was tested for its pH-value and ammonium.

### Temperature measurement and sampling during operation:

- Continuous temperature measurements of the ECO surface temperature in the boiler, Figure 21. Thermocouples were mounted on the upside and downside of the tubes during revision. Data were recorded from the time when the operational control system was commissioned.
- Assembly of a deposit monitor, Figure 22. Explanations on the deposit monitors are given in Chapter 2.3.1.

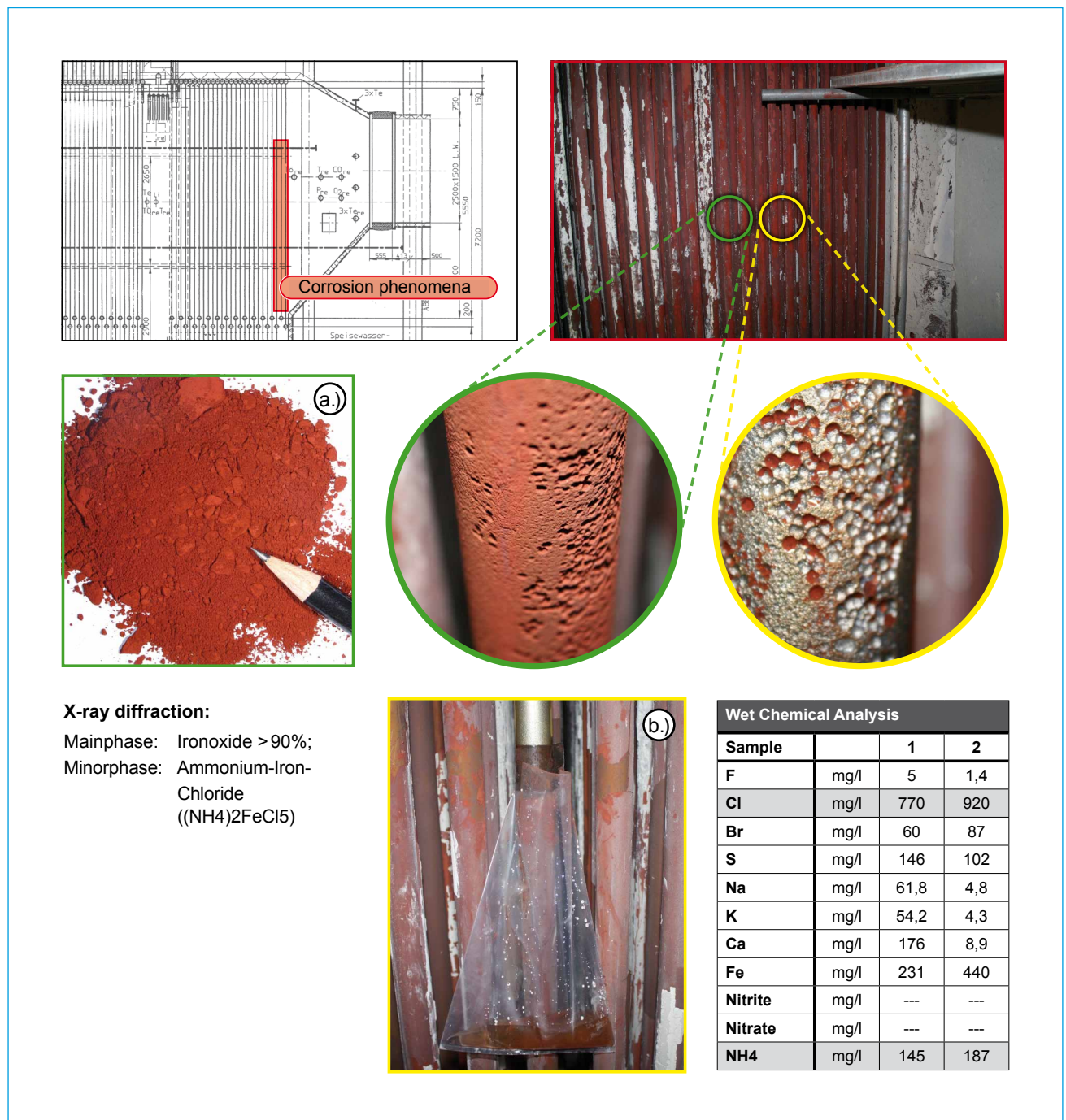


Figure 19: Pittings on the lee-sides of ECO tubes at a WTE plant. a) X-ray diffractometry of the fouling: Detected ammonium iron chloride >90% iron oxides. b) Wet chemical analysis: Detected ammonium (NH<sub>4</sub><sup>+</sup>).

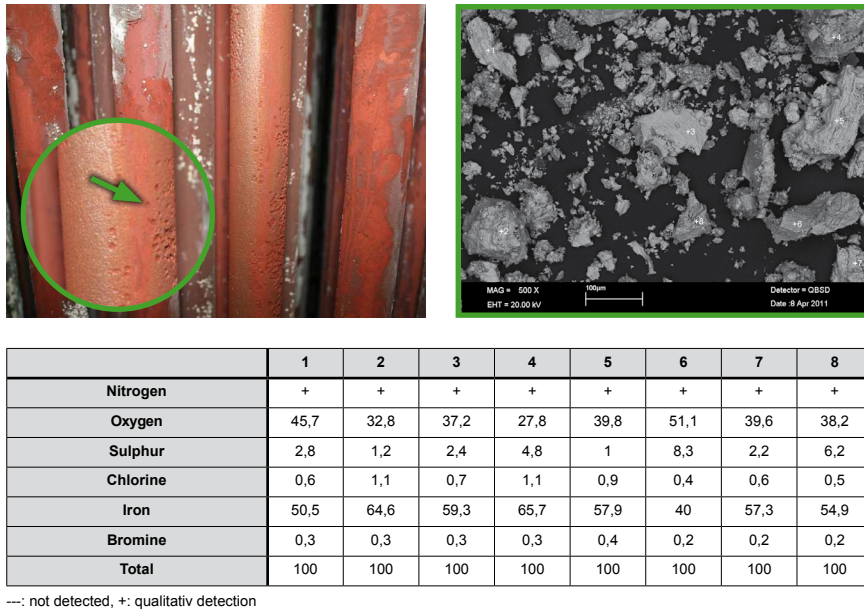


Figure 20: Same position as in Figure 19. Fouling with pittings. Results of the SEM-EDX analysis: Qualitative proof of nitrogen (Symbols "+"). Corresponding to the result of X-ray diffractometry, Figure 19, the chlorine proportion of the ammonium-iron-chloride is relatively small. In this case, X-ray diffractometry is the preferable method of proof.

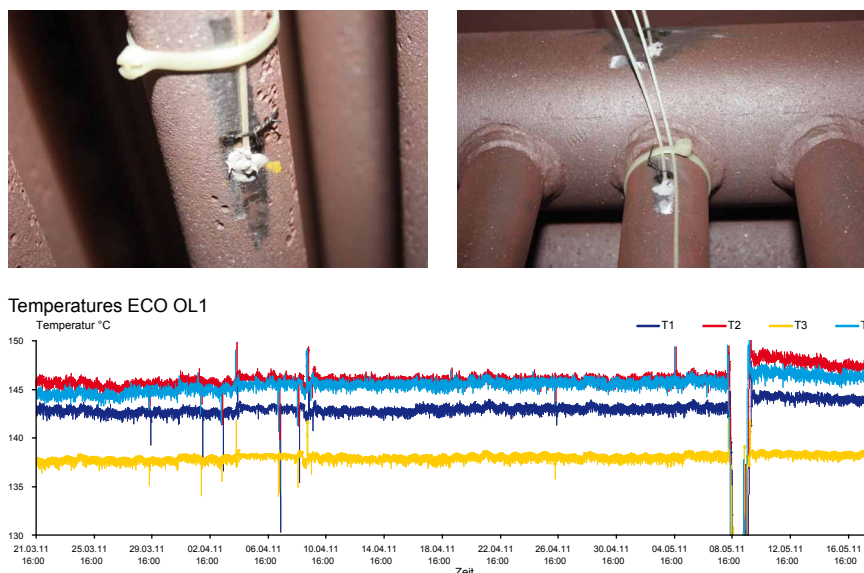


Figure 21: Photos) Thermocouples on the ECO tubes. Diagram) Continuous temperature measurements by T1 (surface temperature ECO tube, bottom = ECO inlet), T2 (surface temperature ECO tube, top), T3 (feed water before the ECO) and T4 (surface temperature on the header), no startup operations. Anomalies during operation are not observed.

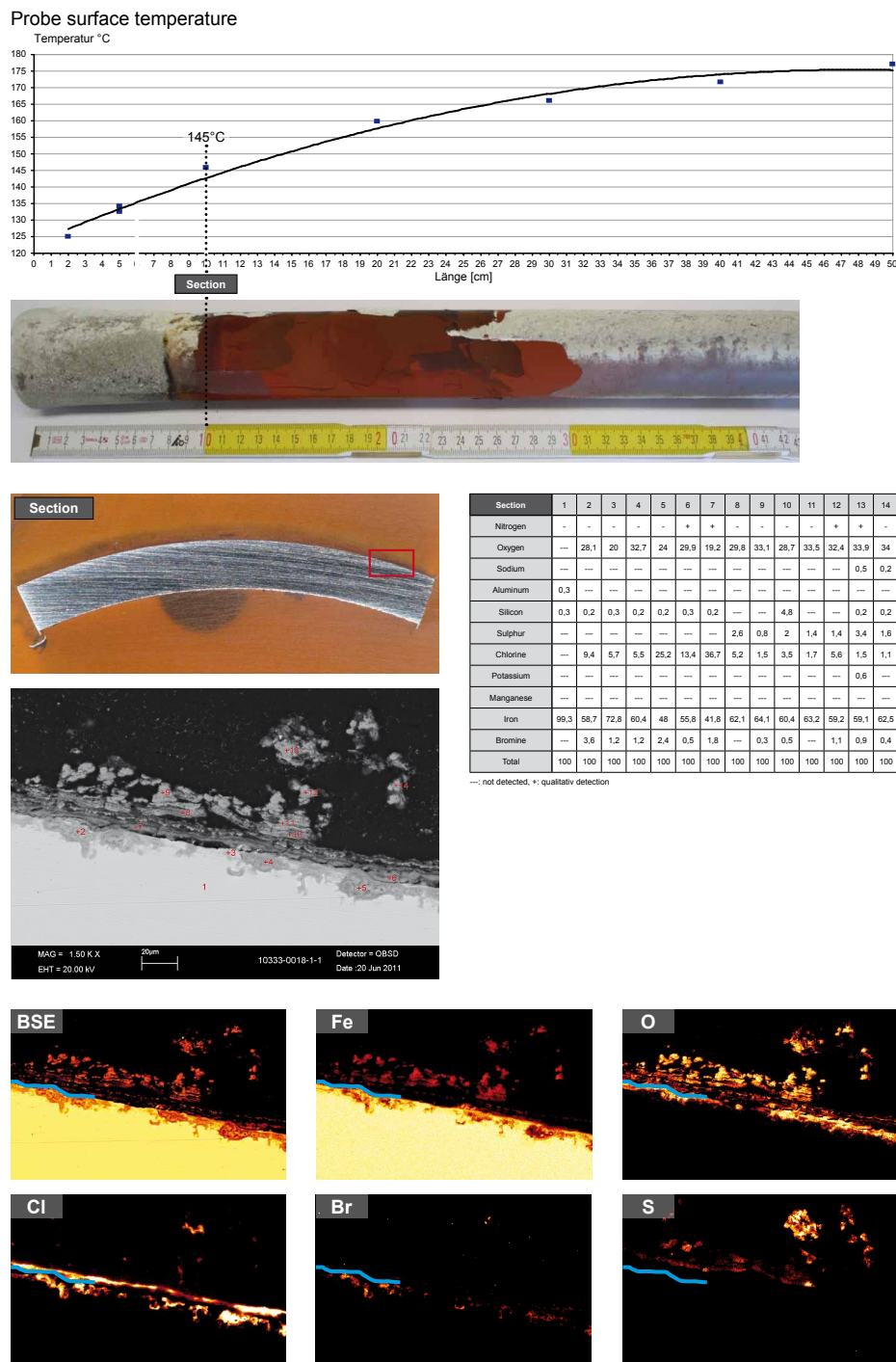


Figure 22: Deposit monitor with the set temperature gradient. Test of the 145°C position. The metallographic section was analysed with SEM-EDX. Table: Results from point measurements with qualitative proof of nitrogen. Coloured: BSE image and element distribution images (Fe), oxygen (O), chlorine (Cl), bromine (Br) and sulphur (S). Significant proof of chlorine at the surface of the deposit monitor. Detection of nitrogen at the same position, see table. Apart from chlorine also bromine is found. The outer layers contain sulphates (images of S and O).



**Measurement results:**

- Continuous temperature measurements did not lead to findings. Surface temperatures remain at the intended level from the time when the boiler was started, Figure 21.
- After the start-up, the deposit monitor was assembled during operations and operated for a month. At temperatures of about 145 to 165°C flaky corrosion can be observed. At the steel surface, the main substances are nitrogen, chlorine and iron, i.e. iron-ammonium-chloride. The oxygen content listed in the table is calculated as a function of given stoichiometries (common method at the SEM) and, for the most part, stems from the H<sub>2</sub>O or OH which are bound in the salts and corrosion products. Further elements (<2 weight %) are sodium, potassium, calcium, aluminium, silicon, chrome and zinc as well as bromine.
- In the samples taken during boiler stop concentrated chlorine on the corroded lee sides is apparent. By means of X-ray diffractometry iron-ammonium-chloride was detected (confirming the findings of the deposit monitors), in addition to a major share of iron oxide (approx. 90% hematite). The ammonium ion was also verified by the washing water. The corrosion products in the pittings confirm the findings on the deposit monitors. The relatively high sulphur content can be explained by the sulphatization of the fouling or by deposited sulphates. The metallographic section from the deposit monitor also indicates this (element distribution images), Figure 22.

The conclusion for this case study: As a consequence of the found deliquescence corrosion through ammonium chloride, an investment was made in continuous ammonia slip measurements. With the aid of measurements of the slip, emissions and other operating data, the SNCR settings are currently optimized to keep the slip as low as possible. This includes optimizing the startup process. Further examinations are carried out with the deposit monitor.

**4.2 Case Study: Waste-to-Energy Plant with SCR, NH<sub>3</sub> Formation in the Firing System**

In this case study DENO<sub>x</sub> is not effected by means of SNCR in the 1. pass; an ammonia slip is therefore excluded. As described in the introductory chapter, fuels and the firing system can produce NH<sub>3</sub> amounts in the flue gas. Figure 23 shows the corrosion of steel sheets at mandooors in the ECO tube range.

Note: In this case, the present corrosion and the damage involved neither pose a risk to availability, nor do they significantly raise expenses and costs for maintenance – in contrast to the preceding case study. But such damage impedes other work at the narrowest place of revision, the access to the boiler.

**Examination and sampling during revision:**

- The box between the ECO case and the mandoor is rather long and thus constitutes a dead spot with a cold trap for the passing flue gas.
- The frontmost edge of the box at the ECO case, about 10 cm thick, is covered by some centimetres of thick, greyish-white layer of ash and salts. The steel sheet below hardly corrodes.
- The floor of the box is only slightly hit by corrosion. Centimetres of piled up ashes and salts lie here during operation.
- The surroundings of the mandoor, part of which sticks into the box, are covered by fouling during operation, with hardly any corrosion underneath.

- The corroded area is limited to the sidewalls and the ceiling of the box - surfaces that are only covered by little fouling during operation. The strongest degradation with holes in the box is close to the manhole, the coldest spot which is, at the same time, covered least by the fouling; arrows in Figure 23. These were the findings after removing the fouling layer by layer:
  - The outermost layer next to the flue gas consists of a dark, brown-violet coloured hard layer, composed of iron oxides with adhering ash and salts.
  - Underneath, several adjoining flaky red layers loosely adhere to the steel sheet wall. They disintegrate into red powder in the sampling bag. Between the flakes are some white layers of fibrous salts.
  - The photo in Figure 23 clearly shows layers peeling off again and again during operation, to be newly formed thereafter.
- In the steel sheets are pits and troughs. At the metal surface, the contours of both are round and thus penetrate in round form into the steel sheet. Larger pittings become troughs with a steep wall and a flat floor; at the surface of the steel sheet they have a diameter of up to 2 cm. The pits are united and it seems as if the thickness of the wall has been degraded extensively. Along the edges of the steel sheet, where the box was assembled, as well as right across the sheets, not only roundish but also longish pit-shaped holes occur. It is likely that, during grinding or transport the mill scale of the steel sheets was harmed, allowing the corrosive agent to reach the steel surface, punctually at the holes and along scratches and scrub marks. Swollen corrosion products are stuck in the pits and troughs, literally like plugs; detail in Figure 23. The plugs jump out when removed as the corrosion products are under tension due to the increase in volume.
- The plugs cover up the pits and troughs while the layers fall off during operation and are formed anew.
- Samples of the ash-salt-deposits are taken from the ECO tubes. They are not visibly corroded under the fouling. The tube surfaces are brown. The colour typical of corrosion caused by ammonium chloride would be red, as aforementioned.

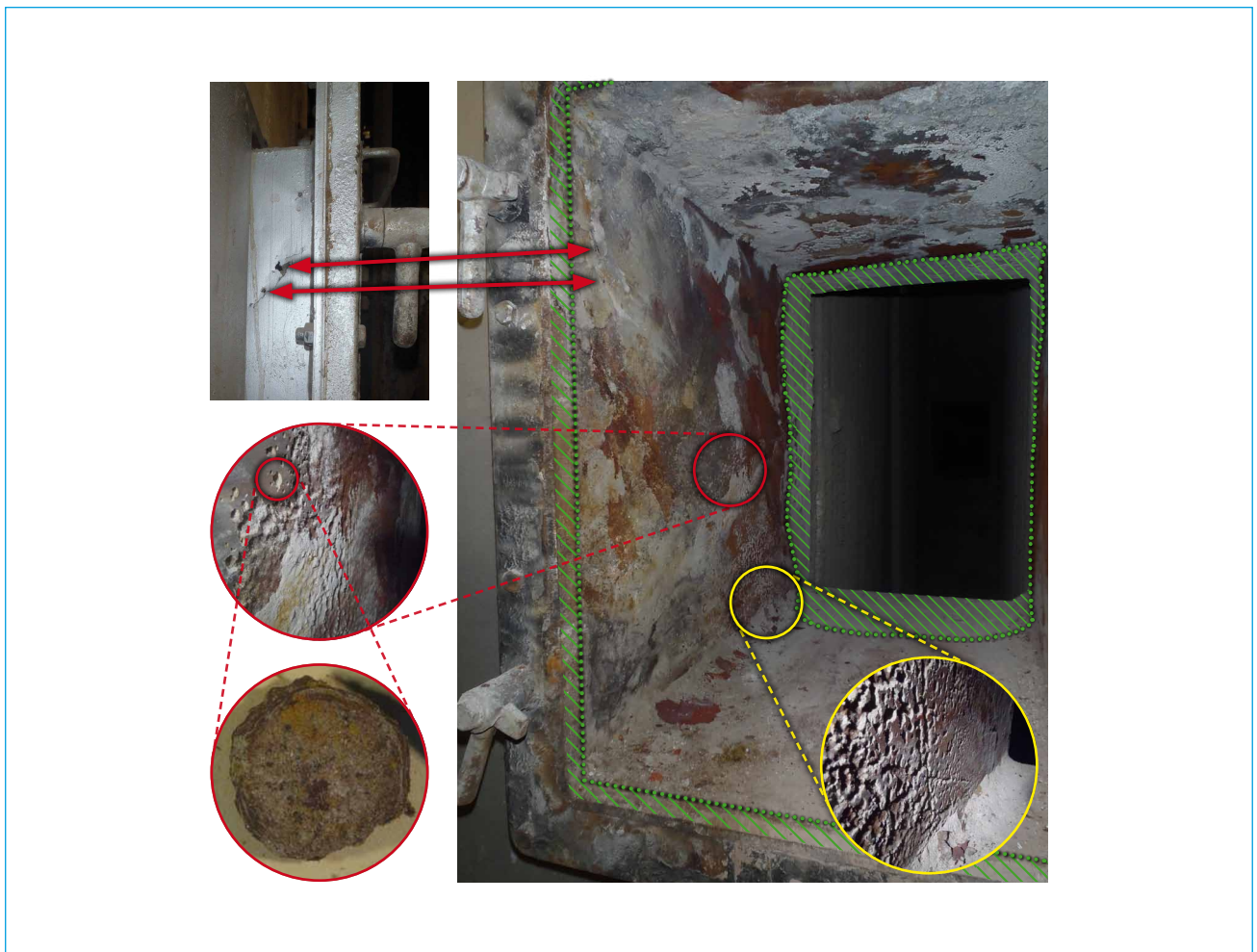
**Measurement results:**

- Hard, brown-violet covering layer with greyish-white layers of ash and salts: they are iron oxides, salts (chlorides, sulphates etc.) and ash. These are the usual findings and the salt content is relatively similar to that which forms the fouling on the ECO tubes. Ammonium compounds were not detected.
- Flaky, red intermediate layers: They contain ammonium compounds such as ammonium chloride. The red layers consist of fine scales of hematite.
- Plugs in the pits and troughs: They are iron oxides, e.g. hematite. No ammonium compounds are detected or no longer detectable. Chlorine and bromine are present. Thus ammonium chloride cannot be detected directly, either due to artefacts (is highly unstable and may disintegrate through air humidity, see chapter on Fundamentals). Or the ammonium chloride in the plugs of the pits and troughs has been “consumed” (has “delivered” chlorine to the iron) or has scattered so far that the concentrations are beyond the detection thresholds of the analytical methods applied.
- Black stains in the steel sheet surface and on the floor of pits: As for the plugs, not ammonium but chlorine and bromine are detectable in a matrix of iron oxides.
- Sealing by plugs or the falling off/new formation of the layers: The sealing of the pits and troughs by the plugs might be reason why the corrosion mechanism comes to a standstill and wall thickness is not penet-

rated. The very poor mechanical stability of the flaky layers is a problem because the surfaces keep being attacked again and again. Presumably the corrosion attack would come to a standstill under a mechanically stable layer, as is the case under the plug.

- Thin deposit layer: Taking the distribution of corrosion into account and the falling off/new formation of the layers as described in the previous paragraph, a crucial criterion for this corrosion attack is that the steel surfaces have to be more or less “clean”. In other words: the smaller the deposit layer or the more often the metal is without protection, the easier it is for corrosion to “work”. This also demonstrates that, for a continued corrosion attack, the presence of flue gas is necessary, i.e. flue gas humidity for the deliquescent salts.

Conclusion for this case study: Ammonia can be produced from fuel (waste) and the firing and then bond with flue gas-HCl to form ammonium chloride. The turbulence in the dead spot of the relatively deep box to the man-door seems to be an ideal position for the mixing. Regarding this, short-term help can be provided by a steel sheet circumventing the dead spot.



*Figure 23: Deliquescence corrosion through ammonium chloride in the box of a relatively long built mandoor. Green hachures: There is fouling all around the opening and on the border to the boiler, as well as on the floor; hardly any corrosion occurs at these positions. Top left, seen from the outside: Holes in the box. The holes occur at the coldest spot of the box. Further explanations are given in the text.*



## 5 Summary

The described corrosion mechanism caused by deliquescent salts, e.g. deliquescence corrosion through ammonium chloride, is dependent from both, the depositing of such salts and flue gas humidity. Both depend on temperature.

If deliquescent salts and, simultaneously, other solid matter (oxides, silicates, sulphates) are deposited so that a relatively thick layer is formed, the corrosion attack will be stopped.

Ammonia may be present as one of the flue gas components, resulting from the slip of a SNCR injection or the interaction of fuel (waste or biomass) and firing (grate or fluidized bed).

In practice, ammonium chloride is formed at the cold end of the boiler. Below temperatures of approximately 160-180°C, this phase was proven by various analytical methods to be a constituent of the fouling and/ or the corrosion products. The immediate mixing of the gas stream (turbulences) can contribute to the formation and deposition.

Basically,  $\text{NH}_3$  and  $\text{HCl}$  do not form a condensate (liquid), but solid matter crystallizes directly from the gaseous phase. In the strict sense, this is no process of desublimation, but the formation of a complex by two gases; these are not true “desublimation points” of a chemical compound. This means that, by referring to literature, it cannot be confirmed whether an ammonium chloride gaseous phase is formed. However, such a gaseous phase is indicated by the growth of needle-like layers of ammonium chloride, several millimetres thick; this structure proves the desublimation of an existing  $\text{NH}_4\text{Cl}$  gaseous phase.

Other deliquescent salts that absorb humidity, thus deliquescing into a saturated salt solution, include, for example, calcium chloride and zinc chloride. The mineral and chemical composition of the corrosion products should each provide sufficient information as to which salt was the corrosive agent. Ambiguous findings are to be expected as different salts may be deposited during operation, simultaneously and subsequently.

Ammonium chloride/ -bromide may pass through the fabric filter and cause corrosion on the clean gas or recirculation side.

Hygroscopic and deliquescent salts may have a negative impact on operations, not only due to their corrosiveness. Other effects reducing availability and efficiency are, among others, the covering of heat transfer surfaces, the loss of pressure at the fabric filter and impediments to the discharging of dust from hoppers and silos.

The deposition of deliquescent salts and their corrosive impact can be examined in situ with deposit monitors. With wide temperature gradients along the monitors they allow to record the dew points and “desublimation points” of deliquescent salts which are present within this temperature range. Deposit monitors can be used during test combustions or continuously during operation.

Generally speaking, the deposit monitors should be applied and accompanied by measuring the relevant material surface temperatures to the effect that different operating phases can be recorded and assessed (startup, boiler stop, unsteady operations, slip etc.). Measurements of flue gas or clean gas humidity are helpful for an evaluation of the operating conditions.

The deposit monitors also allow the simulation of planned changes to the operating parameters (e.g. decreasing the temperature of feed water) in advance.

The relevant corrosion mechanisms can be weighted in qualitative and quantitative terms with laboratory equipment. For this, the deliquescent salts or electrolyte salt solutions detected in the boiler interact, at online-measured flue gas humidities, with test coupons (original or alternative materials, coatings included), under material

temperatures and in oxygen concentrations which correspond to those in the boiler.

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