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Corrosion as a Result of Dew Points and Deliquescent Salts in the 
Boiler and the Flue Gas Treatment System.

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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 and even on the evaporator tubes or 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 SO₃ 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 DENOX (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 or from the deposition of these salts as solid particles; it is only afterwards that, with sufficient humidity in the flue gas and appropriate temperatures, 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 to a lesser extent sodium and potassium, but elements such as calcium, magnesium, zinc etc. as well as ammonium. As to ammonium chloride (NH₄Cl), the focus is shifted to ammonia (NH₃). 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 factor contributing to 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 of 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).

2. Dew Point Corrosion

If gas temperature falls, the solubility of the gaseous matter dissolved therein decreases; the dissolved matter becomes saturated. Using the example of water this means that relative humidity (rH) increases. Liquid drops condense at the dew point or condense even earlier on relatively colder surfaces, when the gas is hitting these surfaces.

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.
The corrosion mechanism with sulphuric acid causes rather extensively degraded structures, so it can be visually distinguished from the pitting corrosion caused by other electrolytes. 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.

### 3. Corrosion by Deliquescent Salts – Deliquescence Corrosion

Many salts, mostly chlorine salts (chlorides), have the property of absorbing moisture from the surrounding atmosphere: their reaction is hygroscopic. This self-wetting with moisture is very strong among some salts, e.g. calcium chloride. Calcium chloride takes up so much water that it dissolves in the absorbed moisture and forms an aqueous solution. This behaviour is known as deliquescence, calcium chloride deliquesces in the absorbed water.

![Figure 1: Correlation of relative humidity (rH for a flue gas with a 15 and 25 Vol.-% water content) and deliquescence relative humidity (DRH) of calcium chloride. When the relative humidity of the flue gas increases above approx. 18 %, the deliquescence of calcium chloride is possible. (1) At approx. 25 Vol.-% flue gas moisture the DRH of CaCl₂ is reached at approx. 110 °C. (2) At approx. 15 Vol.-% flue gas moisture this occurs at approx. 95 °C.](image)

Data from:

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In contrast to dew point corrosion, where droplets are formed directly from the flue gas, deliquescence corrosion starts with the deposition of solid salts on material surfaces. Aerosols are formed in the flue gas by saturation and deposit on surfaces, or solids from hotter flue gas temperatures crystallize on colder surfaces (cold trap effect), which is called desublimation (transfer from the gaseous state to the solid state). In a second step, when moisture is available to the solid salts, they start to deliquesce and form a corrosive electrolyte even above the dew point of water and the dew point of sulphuric acid.

Therefore deliquescence corrosion includes two steps, Figure 1:

- Step 1: Deposition of solid salts or desublimation of gaseous species to solid salts.
- Step 2: When the relative humidity of the flue gas (rH) increases above the deliquescence relative humidity (DRH) of the salt, enough moisture for wetting is available and deliquescence can occur.

The electrolyte causes wet pitting corrosion, Figures 3 to 9. While the initial solution is concentrated, ongoing deliquescence reduces the concentration of the electrolyte.

Further deliquescent salts are for example ammonium species such as ammonium chloride, ammonium bromide, their mixed salt ammonium chloride/bromide, and ammonium sulphate and nitrate. Corrosion damage from ammonium zinc chloride is described in [10]. Deliquescent chlorine salts are e.g. magnesium and zinc chloride. The list can be continued with every salt which has strong hygroscopic behaviour and high solubility in water, e.g. zinc-potassium-chloride or lead-potassium-chloride. Data on the relative deliquescence humidity (DRH) of these salts are rarely published in literature.

4. Fouling and Deliquescence Corrosion by Ammonium Chloride and Bromide

While calcium chloride is well known, ammonium chloride, for example, seems to be relatively new in the scene of boilers firing difficult fuels (biomass, waste and waste derived fuels).

Ammonium chloride (NH₄Cl; sublimation point at approx. 340 °C) is a naturally occurring mineral and, as a white and mostly granular salt, also known under the name of salammoniac. In power plant technology, the problems caused by the sometimes massive fouling or build-up of ammonium chloride are familiar, Figure 2. In [3] 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 °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 [2, 4]. In this context it is discussed that NH₄Cl is formed in the fabric filter or that the particles are so minute that the fabric filter does not constitute a barrier to the salt [4, 5]; deliquescent corrosion behind the fabric filter is displayed in Figures 3 to 9.

- Ammonium bromide (NH₄Br; sublimation point at approx. 450 °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 in combination with ammonium chloride in boilers, i.e. as a NH₄Br-NH₄Cl mixed crystal. The problems caused are similar to those listed above.

On the one hand, ammonium chloride grows on ECO tubes mostly in the form of fine needles, all close to each other; Figure 2. 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 NH₄Cl gaseous phase through desublimation:
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1) \( \text{NH}_4\text{Cl} \) (gas) → \( \text{NH}_4\text{Cl} \) (solid)

On the other hand it is well-known that gaseous hydrochloric acid and ammonia form white crystals of ammonium chloride, thus skipping the liquid state:

2) \( \text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl} \) reaction of pure, saturated gases

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.

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 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 °C [6] or at temperatures of < 140 °C in connection with significant HCl-concentrations and an ammonia slip [7, 8].

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 HCl [9]. 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 are easily and quickly lost, unless the desublimates are stable and well-crystallized as displayed in Figure 2.

Figure 2: Massive ammonium chloride layer. Its needle-like growth gives evidence of the crystallization of solid NHCl, from a NH Cl gaseous phase. Sample from an ECO tube, biomass power plant with SNCR DENOX, waste wood classes AIII 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.
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. Turbulences can favour the mixing of the gas, increasing the probability of reactions of 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.

The formation of ammonium chloride and bromide requires the presence of HCl/HBr and ammonia NH₃ in the flue gas. While the sources of HCl and HBr are commonly known, the source of ammonia is very often a slip from the SNCR injection. But ammonia can also be found in biomass and waste fired boilers without a Denox unit or a properly working SNCR.

Pathways and favourable operation conditions for ammonia generation are published online in [10].

5. Case Studies on Biomass

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 3 displays examples of such findings.

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 specific 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 SO₃ from the gaseous phase. During this, the present chlorides can be converted into sulphates and again release 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).
Deposit monitors\(^1\) were deployed for further tests during operation in order to assess the mechanisms and causes of corrosion. 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 4 displays the surface morphology of cleaned deposit monitors (diverse materials) after operation in the preheater area of a biomass power plant.

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\(^1\) Deposit monitors are probes with a cooled surface, which can be operated up to several months or during specific test periods inside the boiler, from high temperature conditions in the 2\(^{nd}\) pass down to low temperatures inside the flue gas cleaning. The surface temperatures can be set to a relatively wide temperature range. Therefore it is possible to accumulate the original deposits online at different material temperatures on only one probe. The probes are analyzed with respect to the deposits and their in situ corrosion mechanisms, depending on the tested fuel, firing condition, heat transfer etc. Detailed information provides [41].
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 5 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.
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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). Other examples explained in detail are published online by [10].

6. Case Studies on Waste Fuels

The following case study on a waste fired boiler describes the formation of corrosive ammonia chloride due to an ammonia slip from the SNCR unit. An example of a boiler without SNCR, therefore without ammonia slip, is published online in [10].

Figures 6 to 9 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

![Figure 6: 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 (NH₄⁺).](image)

<table>
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<th>X-ray diffraction:</th>
<th>Wet Chemical Analysis</th>
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<tr>
<td><strong>Mainphase:</strong> Iron oxide &gt; 90 %; Ammonium-Iron-Chloride (((\text{NH}_4)_2\text{FeCl}_5))</td>
<td>**Sample</td>
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<tr>
<td><strong>Minorphase:</strong> Ammonium-Iron-Chloride</td>
<td><strong>F</strong> mg/l</td>
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<tr>
<td></td>
<td><strong>Cl</strong> mg/l</td>
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<td></td>
<td><strong>Br</strong> mg/l</td>
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<td></td>
<td><strong>S</strong> mg/l</td>
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<tr>
<td></td>
<td><strong>Na</strong> mg/l</td>
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<td></td>
<td><strong>K</strong> mg/l</td>
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<td></td>
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<tr>
<td></td>
<td><strong>Nitrite</strong> mg/l</td>
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<td></td>
<td><strong>Nitrate</strong> mg/l</td>
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<tr>
<td></td>
<td><strong>NH₄⁺</strong> mg/l</td>
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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 on 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 7. 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 6. The filtered washing water was tested for its pH-value and ammonium.

<table>
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<th>3</th>
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<td>+</td>
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<td>+</td>
<td>+</td>
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<td>4,8</td>
<td>1</td>
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---: not detected, +: qualitative detection

Figure 7: Same position as in Figure 6. Fouling with pittings. Results of the SEM-EDX analysis: Qualitative proof of nitrogen (Symbols +). Corresponding to the result of X-ray diffractometry in Figure 6 the chlorine proportion of the ammonium–iron–chloride is relatively small. In this case, X-ray diffractometry is the preferable method of proof.

Temperature measurement and sampling during operation:

- Continuous temperature measurements of the ECO surface temperature in the boiler, Figure 8. 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.
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Assembly of a deposit monitor, Figure 9. Explanations on the deposit monitors are given in footnote 1.

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 8.

- After the start-up, the deposit monitor was assembled during operation 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 H₂O or OH which are bound in the salts and corrosion products. Further elements (<2 weight %) are sodium, potassium, calcium, aluminium, silicium, 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 9.
Figure 9: 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).
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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.

7. 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, NH₃ and 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 NH₄Cl 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 operation, 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.

8. Literature

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