Extended heat utilization of the flue gas after the boiler

Causes of corrosion and possible countermeasures

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1 What is flue gas after the boiler?

Flue gas after the boiler is generally understood to be the flue gas at the end of the convective heating surfaces, starting at the inlet to the flue gas cleaning system. It starts with a temperature level of approx. 200 to 250 °C until it leaves the system via the stack. A basic distinction is made between raw and clean gas, the state within the flue gas cleaning area is not defined in more detail. The local chemical composition of the flue gas (gaseous species and solids) differs greatly along the cooling path and reaction section from the end of the boiler to the stack, and essentially depends on the following factors:

- fuel
- firing technology
- measures in the boiler (e.g. selective non-catalytic reduction (SNCR), additives, on-line cleaning)
- selection of flue gas cleaning units
- local reference:
  before flue gas cleaning (raw gas)
  on the way through the flue gas cleaning system
  after flue gas cleaning (clean gas)

The interaction of the flue gas with the given components (e.g. heat exchanger surfaces, sheet metals, flue gas cleaning units) leads to locally different fouling and corrosion conditions (see exemplary findings from boiler inspections in Figure 1). In addition to the chemical composition of the flue gas, the local flue gas temperatures also play a decisive role in the dynamics of such processes in combination with the local material temperatures.

Probes can be used to fully analyse the chemical composition of the exhaust gas [13]. These are additional measurements that are not carried out as standard. However, in the German market, selected emission-relevant parameters are available and must be published in accordance with legal requirements according to 17th BImSchV (i.e. the 17th Ordinance on the Implementation of the Federal Immission Control Act). Table 1 compares the annual emission values for three different plants (two waste incineration plants and one biomass plant) with the daily limit values from the 17th BImSchV. These data already show a large variance in the chemical composition of the clean gas in relation to different fuels and flue gas cleaning technologies.

2 Corrosion-relevant species in the exhaust gas

Corrosion-relevant species are gases and molecular groups that can actively oxidize

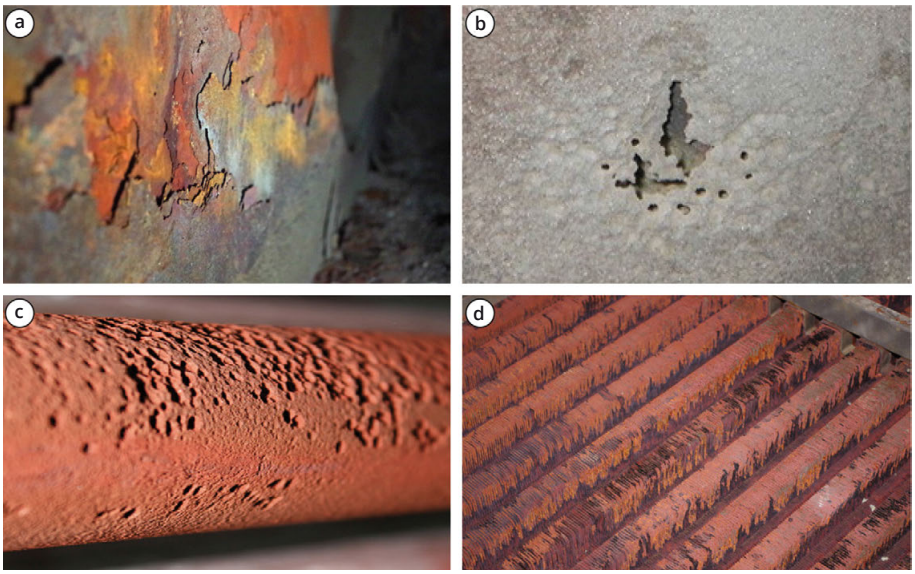

Fig. 1. Examples of corrosively damaged components in the flue gas system after the boiler. (a) Sheet-like corrosion layers with embedded salts on a sheet metal wall. (b) Pitting corrosion on a sheet metal triggered by localized cooling via an externally welded T-beam. (c) Pits caused by aqueous electrolytes after deliquescent corrosion on a heat exchanger tube. (d) Corrosion on a finned tube heat exchanger upstream of the stack.

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Tab. 1. Exemplary emission measurement results for two waste incineration sites and one biomass site in comparison with the limit values from the 17th BImSchV. n.d: not detected [1. 2. 3. 8. 11].

Emission-relevant elements	Daily average limit value WTE-plant [mg/m³] *	WTE-plant 1	WTE-plant 2	Biomass plant 1
		Flue gas cleaning units		
	Existing system	SNCR. addition of $Ca(OH)_2$. spray absorber. addition of HOK. addition of $NaHCO_3$. fabric filte	E-filter. HCl scrubber. SO_2 scrubber. SCR. addition of HOK. fabric filter	SNCR. cyclone. addition of lime and HOK. fabric filter
		Annual averages [mg/m³]*		
CO	50	18.7	14.28	39.1
NOx	150	141.6	66.94	125.3
SO_2	40	8.6	1.44	20.98
NH_3	10	1.5	0.1	2.44
HF	0.9	0.1	0.2	n.d.
HCl	8	6.7	1.25	6.33
C tot.	10	0.1	0.15	1.12
Dust	5	0.2	0.05	2.30
Hg	0.01	0.001	n.d.	0.001
Total Cd/Tl	0.05	n.d.	0.009	0.002
Total Sb. As. Pb. Cr. Co. Cu. Mn. Ni. V. Sn	0.5	0.0023	0.018	0.127
Total As. benz(a) pyrene. Cd. Co. Cr	0.05	0.0005	0.0032	0.013
Dioxins/furans [ng/m³]*	0.1	0.0024	n.d.	0.001

* Volume flow measured in cubic metres per hour (m^3/h) and in relation to the flue gas volume in the standard state (temperature 273.15 Kelvin (K). pressure 101.3 kilopascals (kPa)) after deduction of the moisture content of water vapour. The emission limit values refer to a reference oxygen content of 11 per cent. [2].

through dissociation. These species are in particular halogen salts, primarily chlorides of the cations Na^+, K^+, Ca^{2+}, Zn^{2+} and Pb^{x+}, but also SO_3 groups and their acids. The halogens I and Br and possibly F can also play a role, as can NH^{3+} and Mg^{2+} on the cationic side. We have chosen the term 'corrosion-relevant species in flue gas' to briefly describe this very heterogeneous group of molecules, which also cannot be characterised by uniform phase states like gaseous, liquid and solid. As described in the chapter above, there are large differences in the flue gas composition and the local temperature levels at individual components along the flue gas path. As this also applies to the presence of corrosion-relevant species, the following chapters (3 to 5) are categorised according to raw and clean gas and the area of flue gas cleaning.

Whether and where corrosive species are deposited also depends on whether surface cleaning has a localized and direct influence on materials, as can be the case with compressed air cleaning, for example. These processes can repeatedly produce 'clean' and therefore 'cold' material surfaces on which selective accumulations of corrosive species can occur. On the other side, cleaning aggregates may be necessary to prevent deposits from accumulating, growing and hardening that could limit the availability of the operation.

The initial deposit formation during start-up after an overhaul can also have a decisive influence on corrosion processes. If, for example, the radiation pass and the convective heating surfaces are not cleaned during a shutdown, salts can be transported a long way through the flue gas path until they first encounter 'cold' surfaces, deposit and accumulate there selectively and thus start corrosion processes.

3 Corrosion-relevant species in the raw gas

The deposition sites from the end of the boiler to the entry into the flue gas cleaning system are regarded in this chapter. The relevant components include sheet metals in flue gas ducts, expansion joints, manholes and installations on the raw gas side of filters. At the end of the boiler, a large proportion of the salts are already present as solids. In addition, inert ash particles and gaseous species can be detected. The humidity varies greatly depending on the fuel and whether temporary online cleaning technology is used in the process (e.g. shower cleaning).

3.1 Deliquescent salts

Deliquescent salts are species that can – under the given environmental conditions (humidity and temperature) – liquefy themselves above the respective water dew point. If these salts are chlorides, they form a chloride electrolyte (= saturated, acidic solution) during liquefaction, which may cause corrosion in contact with metallic components. Calcium chlorides, ammonium chlorides and possibly also zinc chlorides are often found in the raw gas environment, in some cases the bromides of these cations are also present. In addition to the halogen salts, e.g. KOH, NaOH, KCO_3 and some sulphates can also have a hygroscopic effect and thus lead to moist conditions in the vicinity of the deposits. This can cause the chloride salts to liquefy, even above their specific deliquescence temperatures and thus become electrolytically corrosive. This may be particularly important for ammonium chloride, as its deliquescence temperature is only just above the water dew point.

Figure 2 illustrates the specific behaviour of different salts using laboratory tests as an example.

On the other hand, deliquescent chlorides can interact with each other. $CaCl_2$ for example, is already deliquescent at higher temperatures compared to ammonium chloride. $CaCl_2$ is therefore able to liquefy ammonium chloride above its relative deliquescence temperature [4]. Furthermore, it is known that salt mixtures can react deliquescent at higher temperatures and in a stronger way than would be the case for the respective individual salts [6].

Which of the above-mentioned salt is deposited, strongly depends on the prevailing conditions. Calcium chloride is preferably found in the raw gas of plants incinerating waste paper, paper residues or high proportions of plastic. Calcium chloride often has its origin in finely particulate calcium carbonates in the fuel, which react with HCl [12]. Ammonium chloride, on the other hand, is formed from the reaction of NH_3 with HCl and is therefore particularly evident at sites where a larger amount of NH_3 is present in the flue gas. This can result from the use of an SNCR or also from the interaction of fuel and firing conditions. Zinc chloride is particularly evident at sites that receive material flows from metal recycling. KOH is likely to deposit when biomass is burnt and the proportion of HCl and SO_2 in the flue gas is relatively low [4, 9]. NaOH can be relevant when waste is incinerated.

Especially for ammonium chloride, local temperature conditions are decisive (on the subject of salt saturation, see the comments in [5]). If the heat exchangers are operated at sufficiently high temperatures and if there are no local cold traps, on sheet metal ducts or expansion joints etc., this species passes through this area in gaseous form. It will only become saturated at lower temperature conditions further down the flue gas path, in the flue gas cleaning area or even in the clean gas, where it desublimates as a solid. From a corrosion point of view, this spe-

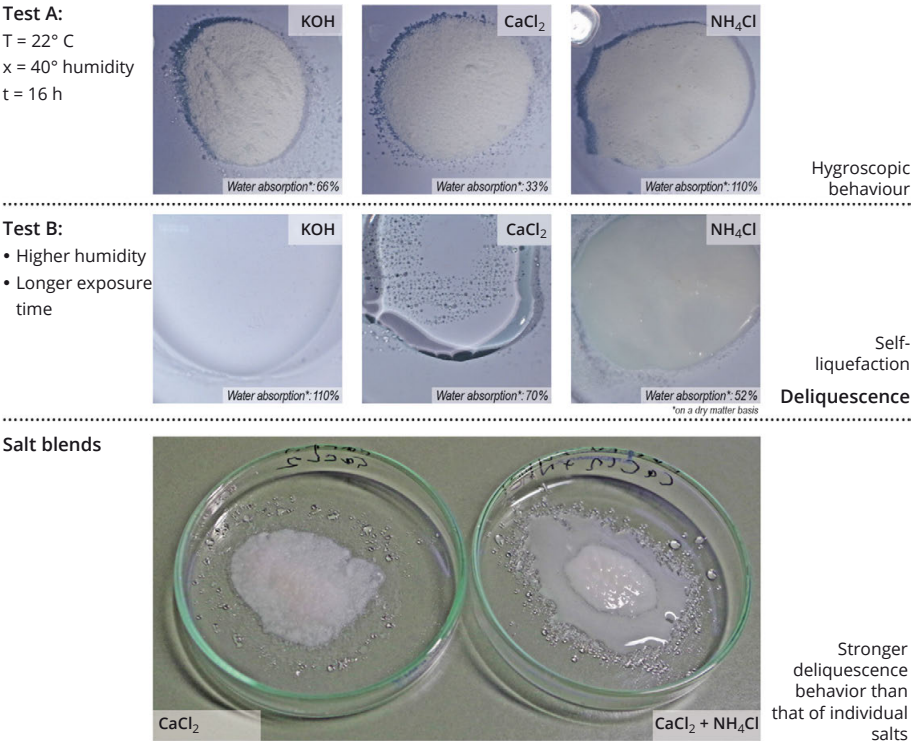

Fig. 2. Hygroscopic and deliquescent behaviour of selected salts in relation to changing water vapour concentrations at room temperature, and the influence of mixing the salts with each other.

cies is not critical in the gaseous dissolved state.

3.2 Acids

It is known from the combustion of fossil fuels such as coal or heavy oil, that sulphuric acid can occur. Depending on the SO_3 load and moisture content in the flue gas, the acid dew point lies in the temperature range between 100 °C and >150 °C [14]. In the case of fuels with a high proportion of chloride salts, however, the sulphuric acid dew point usually plays a subordinate role. SO_3, which is also produced during the combustion of e.g. waste, RDF or waste wood, reacts with chlorides within the process to form sulphates (keyword: sulphation) and is therefore only present in low loads at the end of the boiler. As SO_3 is essential for the formation of sulphuric acid, the sulphuric acid load is typically low for such fuels.

Sewage sludge should be emphasized in this consideration, provided it is a sludge with a high sulphur content, i.e. high SO_2 and SO_3 loads occur in the flue gas during incineration. If this is the case, there may be relevant amounts of sulphuric acid in the flue gas (see the following example in Figure 3). The sulphuric acid can have a corrosive effect on its own, but can also serve as a liquefier for chloride salts and thus convert them into a chloride electrolyte, which also has a corrosive effect. Other acids, such as HCl and HBr, whose dew points are close to the water dew point, are not relevant at material temperatures significantly > 80 °C on metallic surfaces with raw gas contact [14, 16].

3.3 Case Study

Figure 3 shows an example of a corrosive attack on unalloyed sheet metal in a raw gas environment of a sewage sludge incineration after dust separation. In the flue gas duct of the reactor before the addition of the additive, there is a massive corrosion attack on the sheet metal. A temperature range probe was used for an operating time of 1,000 hours to determine the cause of the corrosion and to establish the threshold temperature for the corrosion attack. The probe serves as a temporary material surface and can be destructively investigated after use. Within the deposits formed on the probe surface, it can be seen that in addition to a layer of NH_4Cl/NH_4Br, there is also a layer of $FeSO_4$. This is proof that ammonium salts and sulphuric acid were both active in the corrosion attack. The material loss determined in the temperature range of approx. 95 °C is 1 mm / 1,000 hours.

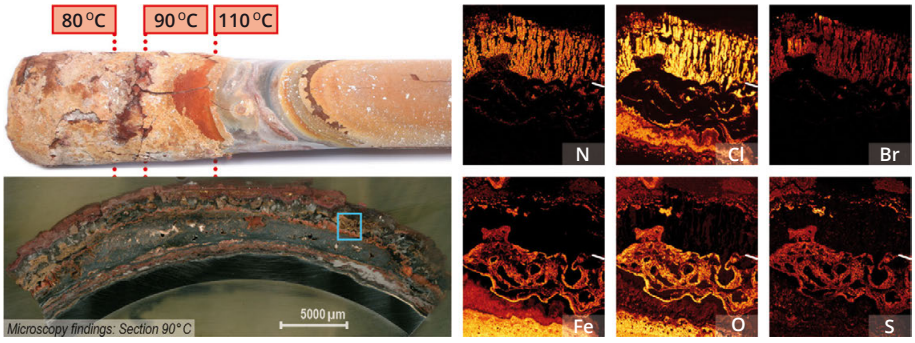

Fig. 3. Application of a temperature range probe of unalloyed steel in the raw gas of a sewage sludge incineration plant after dust separation, flue gas temperature 180 °C. Macroscopic, microscopic and microanalytical (element maps) findings are shown.

4 Corrosion-relevant species in the area of flue gas cleaning

Whether and where a corrosive attack occurs in the area of flue gas cleaning heavily depends on the selection and the sequence of the individual cleaning units, as well as the selection of the additives used.

4.1 Deliquescent salts

Deliquescent salts also play a decisive role in the area of the flue gas cleaning. Calcium chloride is formed during the reaction of lime additives with gaseous HCl. This is an intended reaction to separate the acidic pollutant gas. If the surface temperatures of the materials (e.g. metal sheets or metallic components in filters) with which calcium chloride comes into contact are sufficiently high, no corrosive attack can be assumed. However, if localized cold traps occur, this species can have a large corrosive effect. In addition, ammonium chloride or ammonium bromide may also be present. These species are particularly relevant where selective accumulations are possible. This is the case, for example, when ammonium salts can pass through the first filter stage (fabric filter, ESP, cyclone) for the separation of fly ash as a gas species, and the local temperature levels allow this species to desublimate (phase transition from gaseous to solid) in some places. Furthermore, ammonium salts can be present after selective catalytic reduction (SCR), provided that ammonia reaches this area to a significant amount and that no separation of HCl from the flue gas has taken place prior to this position. For example, a few ppm of bromine in the fuel can be locally enriched to several percent bromide in deposits. Bromine has its origin, e.g. in brominated flame retardants in plastics or wastewater of waste, RDF or sewage sludge, or geogenically in biomass with marine influence [7, 10, 15]. Studies have shown that ammonium bromide in particular has a highly corrosive effect.

4.2 Acids

If a SCR is installed after dust removal and before the separation of SO_2, a further corrosive process can occur. In addition to the

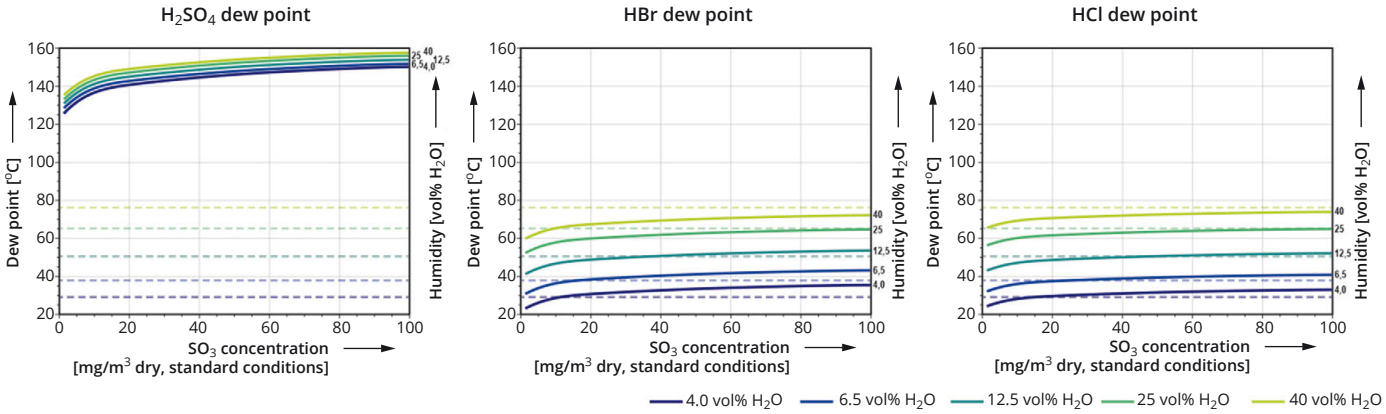

Fig. 4. Comparative presentation of acid dew points in relation to the respective concentration of the aggressor and as a function of the humidity in the flue gas.

intended reduction of nitrogen oxides, the SCR can cause SO_2 to oxidise to SO_3. With a certain amount of SO_3, the formation of sulphuric acid is possible below the corresponding dew point temperature, which results in corrosive processes on the metal sheet, heat exchangers and flue gas cleaning units. Whether other acids such as HCl or HBr become effective depends on the local conditions (temperature, humidity) which may or may not allow these acids to condensate. As the acid dew points of these species are close to the water dew point, it is possible, for example, that cleaning with cold compressed air can lead to the condensation of these species in the flue gas cleaning area [14]. Selected species are shown in Figure 4.

5 Corrosion-relevant species in the clean gas

The possible selective enrichments categorized in Chapter 4 play a particularly important role in clean gas. This is due to the fact that the particle load in the clean gas is significantly reduced. If there are areas where salts become saturated, they will be only slightly diluted by other species and can therefore develop their corrosive effect particularly well. In addition, the flue gas temperature in this area is relatively low and therefore heat exchanger surfaces are also operated at low medium temperatures. Additionally, potential cold traps on housings are also very effective.

5.1 Deliquescent salts

A comparison of the saturation properties of specific salts shows that ammonium salts (NH_4Cl, NH_4Br, NH_4I), in contrast to calcium, alkali or heavy metal salts, only reach saturation late in the process, i.e. at low temperatures well below 200 °C. This means that these salts can pass through the flue gas cleaning system as gaseous species or fine aerosols. Furthermore, surface temperatures may be close to the water dew point at a high humidity. This promotes the deliquescent behaviour of the salts mentioned. A high flue gas humidity results, for example, from the combustion of bark, from location- and climate-related factors (e.g. tropics) or from flue gas cleaning, where water may be added to the process.

5.2 Acids

Like salts, acids can also be locally concentrated, as the diluting components of the fly ash is only present to a very small extent in this area. If the flue gas is cooled far below the water dew point, which is the case with flue gas condensation, the water can act as a diluting component. Whether acids become effective depends strongly on the extent to which the upstream flue gas cleaning eliminates relevant species such as SO_3, which material temperatures are present and whether this may lead to dilution of the acids.

5.3 Case Study

Figure 5 shows an example of a finding from a probe application (temperature range probe) in a biomass plant in which chicken manure is incinerated. The limited temperature range in which a strong corrosion attack occurs is striking. In addition to chlorine, iodine also contributes to the attack. This is shown by the microchemical detection of chlorine and iodine at the active corrosion front. The chemical bonding of these elements to ammonium is likely, as both ammonium iodide and ammonium chloride can be transported into the clean gas as gas species due to their saturation properties. Only in contact with cold surfaces does the phase transition to solid particles occur and thus the potential for corrosion attack, see diagram in Figure 5. In the temperature range below approx. 80 °C, water, HCl and HI may also be below the dew point (the flue gas humidity is not known to CheMin).

6 Preventing corrosion by adapting the material?

Whether corrosion can be prevented by material adaptation cannot be answered in general terms. Extensive experiences from high-temperature heat exchanger applications indicate that alternative materials or protective coatings typically lead to a reduction but not a complete elimination of corrosion. The efficiency of a corrosion protection measure varies between different systems and therefore reported results can often be contradictory. There are also different observations in the 'cold' area of the boiler. As described in the chapters above, this is due to the different conditions (chemical components in the flue gas, temperatures, mois-

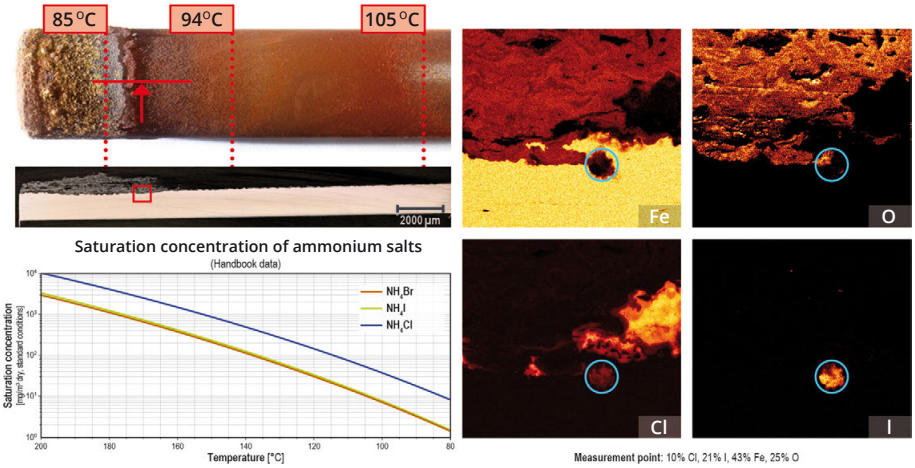

Fig. 5. Application of a temperature-range probe of a carbon steel material in the clean gas of a biomass combustion plant upstream of the stack. Macroscopic, microscopic and microanalytical findings (element maps) are shown as well as saturation curves of selected ammonium salts.

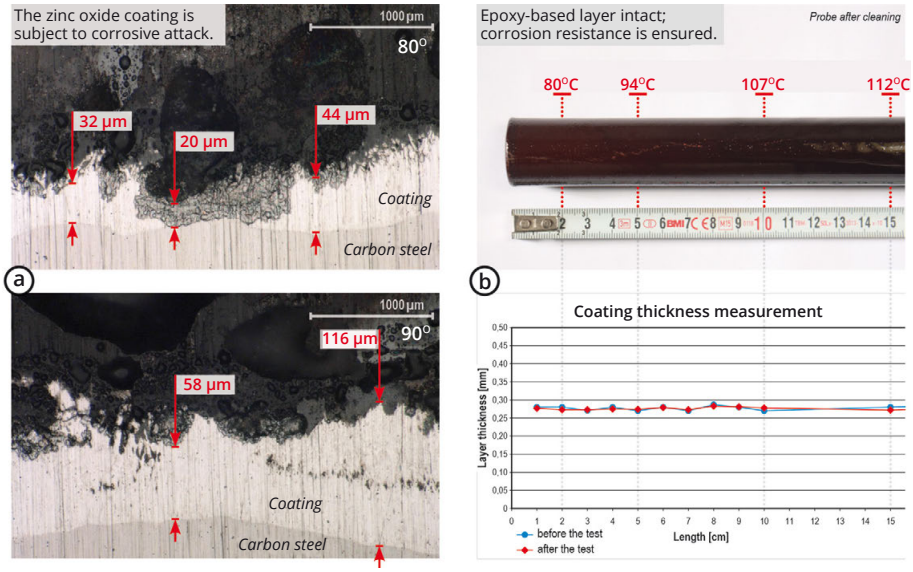

Fig. 6. Findings from material tests in the clean gas upstream of the stack of a biomass plant. Two protective coatings were tested using temperature range probes (TRP), each applied with an exposure time of 2,300 operating hours. a) microscopic findings on polished sections; b) macroscopic findings and thickness measurements on the probe body of the TRP.

ture content, etc.) at the respective corrosion positions. The material can be adapted by replacing with higher quality solid material or by applying a protective coating. As solid materials, metals such as stainless steels and nickel-based alloys, as well as polymers such as PPS graphite, GRP and glass can be used. Applied protective coating comprise e.g. zinc oxide coatings, synthetic resin-based layers and PTFE (Teflon) films.

The example, Figure 6, shows findings from a test with two different protective coatings, each of which was tested using temperature range probes. At the plant, where mainly chicken manure is incinerated, it can be seen that the two coatings exhibit different corrosion resistance after an exposure time of 2,300 h in the flue gas. The zinc oxide layer on the left (a) is severely corroded, whereas the epoxy resin-based layer on the right (b) shows no damage.

7 Potential for energy utilisation of the flue gas after the boiler

There are various answers to how a reduction in the exhaust gas temperature at the end of the boiler can be achieved while still maintaining an acceptable availability of the plant. Temperature range probes can be used for determining temperature thresholds for corrosive attack or for material testing. They can be operated as a temporary boiler component at the area in question and can be removed for destructive testing after the application. As the temperature thresholds for corrosion are typically very narrow (in the order of a few Kelvin), experimental investigations are often required to define operating conditions just above the critical threshold. Such tests should take account of seasonal variations as well as transient conditions, including load fluctuations, start-up and shutdown conditions, which may shift the corrosion threshold. This should be considered when designing the test.

As described in the chapters above, an operation with only little corrosion may be ensured by adapting the used material even at lower flue gas temperatures. Which material is suitable for a given application must be evaluated on a case-by-case basis. Apart from material solutions, there are operational options to reduce corrosion at lower flue gas temperatures at the end of the boiler. Where possible, reducing the moisture in the exhaust gas can potentially help to lower surface temperatures without a higher corrosive effect. Additionally, consistently good insulation without cold traps or retrofitting of flue gas cleaning components may also be a sensible step.

8 Conclusion

Operation with lower flue gas temperatures is possible at many locations, often by necessary adjustments to the general conditions. Since the conditions in boilers vary greatly depending on the fuel, firing technology, flue gas cleaning units and the local reference in the flue gas path, it is essential to regard each individual case separately. In particular, the assumption that clean gas is ‘clean’ applies to emission-related considerations, but not necessarily for the corrosive point of view. This especially applies for the situation, when an enrichment of corrosive species occurs in the clean gas area over time. In this case, the used material can be subject to strong corrosive attack. In order to have certainty, it is recommended to create transparency in the given case before the decision to lower the flue gas temperature is made.

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Kurzfassung

Erweiterte Wärmenutzung des Rauchgases nach dem Kessel

Ursachen für Korrosion und mögliche Gegenmaßnahmen

Aktuelle Entwicklungen im Markt der Kraftwerkstechnik zur Verbrennung schwieriger Brennstoffe, wie z.B. Müll, EBS, Biomasse, Klärschlamm und Papierreststoffe führen dazu, dass das Abgas nach dem Kessel in Bestandsanlagen zukünftig weiter abgekühlt wird. Zu nennen ist hier z.B., dass an vielen Standorten, im Rahmen von kommunalen Wärmeplanungen, eine erweiterte Wärmenutzung diskutiert wird. Im Rahmen des vorliegenden Beitrages werden Unterschiede in der Abgaszusammensetzung im Kontext zu Brennstoff, unterschiedlichem Anlagendesign und mit Bezug zur Position entlang des Rauchgasweges nach Kessel diskutiert. Die Übersicht ergibt sich hierbei aus Erfahrungen, die seitens CheMin in den letzten Jahren beobachtet wurden. Des Weiteren erfolgt eine Übersicht möglicher korrosiver Spezies, ergänzt um Beispiele aus der Praxis, sowie ein Überblick und Befunde zu unterschiedlichen werkstofflichen Schutzmaßnahmen. Abschließend erfolgt eine Bewertung mit Bezug auf mögliche Stellschrauben, die eine weitere Absenkung der Rauchgastemperaturen zur erweiterten Wärmenutzung an Bestandsanlagen möglich machen.