Corrosion in Boilers with Difficult Fuels

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ABSTRACT
Waste-to-energy (WTE) plants may be considered power plants with "difficult fuels". The waste, biomass and processed waste, i.e. biogenic fuels, used by these plants present great challenges to process engineering due to the corrosion damage on heat transfer surfaces hit by the flue gas. The corrosion processes, which are generally influenced by the fuel properties, the firing system and the heat transfer in the boiler, have a direct impact on investment and maintenance costs, availability, and achievable energy efficiency in WTE plants. This contribution reviews the causes and mechanisms of this corrosion, giving a survey of the current research aimed at maximising energy efficiency and availability in WTE plants.

EXPERIENCE WITH CORROSION IN WASTE-TO-ENERGY BOILERS
This article does not deal with fossil fuels in power plants, but with waste, biomass and processed waste, i.e. biogenic fuels. These fuels present, in terms of corrosion on heat transfer surfaces hit by the flue gas, enormous challenges to process engineering and the fuels used. This article gives a survey of the current state of the research aiming to maximise energy efficiency and availability despite a high corrosion potential in power plants with "difficult fuels".

Particularly waste-to-energy (WTE) plants have, to a material extent and in various ways, been shaped by the consequences of corrosion damage which has occurred during past decades. This concerns primarily the limitation of the medium temperatures in the saturated steam and live steam. These temperatures are clearly below those parameters reached in conventional power plants. In addition, the extensive use of cost-intensive protective coatings on heat transfer surfaces has become common for evaporators and superheaters. Thus corrosion processes have had a direct impact on investment and maintenance costs, availability as well as achievable energy efficiency.

Corrosion processes are generally influenced by the fuel properties, the firing system and the heat transfer in the boiler. Unfavourable properties of the fuel and unfavourable properties of the firing may reinforce each other in their effect on corrosion processes. The same applies to the interaction of the firing system and heat transfer.

The effect of corrosion, culminating in corrosion damage, is characterised by degradation processes which clearly exceed the expected scope and usually occur on the heated side of the boiler tube, under the fouling (Figure 1).

Of all types of corrosive damage cases, flue-gas side corrosive attacks have by far the largest economic impact. Assuming an expected 10-year service time of boiler tubes and considering 2 mm of the usual 5 mm of a tube wall as an availability buffer, degradation rates of approximately 0.025 mm per 1000 operating hours are the result. The maximum degradation rates found on evaporator and superheater walls amount to 1 mm per 1000 operating hours, that is a 40 times faster degradation.

The nature of corrosion is:
• Even a corrosive attack that is confined to a very small area can, when opening into an uncontrollable tube crack, destroy the entire boiler, thereby involving not only extremely high property and financial losses, but even personal injury due to its unpredictable consequences. Therefore, corrosion has a high potential to cause damage.
• The heated tube surface cannot be entirely monitored during operation, neither visually nor by any other means. An evaluation of accessible areas is only possible during scheduled inspections. Hidden tube surfaces, e.g. behind refractory materials, cannot be inspected at all. Thus corrosion can be monitored only to a limited extent.

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for corrosion protection has been going on for decades and will continue in the medium term.

The market of corrosion protection suppliers has not yet seen a "breakthrough". There is no "solution to all corrosion problems". Instead, every investor or operator seeks the individual optimum between the extent of corrosion protection and the economic benefit derived therefrom. There are rather different objectives and solution concepts to be employed at various sites. Correspondingly, different solution concepts have been developed successively. The solutions that work for some plants can be employed at other – even comparable - plants only to a limited extent [1–3].

Corrosion can also be reduced by exerting influence on process design and process control. For this purpose it is helpful to get as much information as possible on the process behaviour and process course, which requires more sensory information on operational activity:

- Space-resolved information can be obtained during phases of planned outages (concept of foresighted maintenance) [4,5].
- Time-resolved information can be obtained during operation through specific measurements, using sensors and monitors (heat flux sensors, deposit sensors, deposit monitors, ash-salt-proportion monitoring, HCl-flue gas measurement, SO₂-flue gas measurement) [6,7].

The use of these sensory measures from the start of the plant’s service time, i.e. the accompanying search for a minimum corrosion load during operation, is called “early recognition of corrosion” [8].

Maximum degradation rates are typically reached through the process of high-temperature chloride corrosion, which applies to evaporator and convective surfaces. Calculating the average of several thousand operating hours, up to 1 mm per 1,000 operating hours is reached. During the first 100 operating hours after an inspection (cleaning or new tubes), degradation rates of up to 2 mm per 1,000 operating hours (projected) have been proven. Due to the maturing of the deposit layers, the process of high-temperature chloride corrosion probably develops in a non-linear degressive way, starting with high degradation rates that decrease gradually.

This is the reason why corrosion, corrosion protection and corrosion avoidance play such an essential role, particularly in waste-to-energy plants and biomass plants.

Contemporaneously with an increasing exposure to corrosion, numerous protective measures against corrosion have been developed and established, in particular protective coatings (ceramics, cladding, thermal spray coating). This race between ever more specialised technical requirements for plants and ever more specific solutions...
The selected pressure stage of the saturated steam (drum pressure) generally influences the potential and dynamics of corrosion processes to a significant extent. Most experiences have been gained regarding 40 bar plants. Individual plants are operated at 80 bar or above. So far, pressure stages of < 30 bar have rarely been affected by serious corrosion in the evaporator section. These rankings of corrosion potential based on pressure stages can vary, depending on the properties of the fuels used. For example, an increased percentage of heavy metals in the fuel can lead to increased degradation rates, even in the range of < 30 bar.

Superheater components are affected by corrosion from a steam temperature of about 350 °C. At an approximate steam temperature of 400 °C, i.e. tube temperature, the degradation rates of unprotected tubes in waste-to-energy boilers range from one to two tenths of millimetres per 1000 operating hours, translating into service times of 2 to 4 years. With an increasing steam temperature, the service time of the component declines. At the same time, the flue gas temperature directly affects the dynamics of corrosion through the temperature gradient in the deposit and its decisive impact on the maturing processes in the deposits. Here, too, the following is true in most cases: an increase in flue gas temperature results in a decline in the service time of the component. It is therefore important to cool down the flue gas sufficiently in the radiative part in order to protect the convective surfaces from corrosion. Flue gas temperatures at the beginning of the convective part should be < 650 °C, even better < 600 °C.

The trend of the past years toward larger-scale power plants (> 60 MW thermal), in particular refuse-derived fuel plants, has led to "limit experiences", which also have an impact on the relevance of corrosion. Hardly avoidable imbalances of energy distribution within the flue gas stream in the 1st pass are to be mentioned here.

These parameters are directly or indirectly influenced by the properties of the
- fuel,
- firing, and
- heat transfer in the flue gas.

Corrosion-relevant properties of fuel are:
- load of chemical substances
- bonding forms of chemical substances
- proportions of specific chemical substances to each other (generally and locally)
- proportions of specific chemical substances to energy content (generally and locally)
- shape and size of the fuel pieces
- humidity
- lower heating value (LHV)
- ignitability, pyrolysis and volatilisation, burn and burnout behaviour

Corrosion-relevant properties of the combustion are:
- stoichiometry and air distribution in the primary combustion (primary air, recirculated flue gas, if any)
- the excess air factor (lambda) and thorough mixing in the secondary combustion (secondary air, tertiary air, etc., if any; recirculated gas, if any)
- burnout behaviour of the flue gas
- loads of dissolved or solid/liquid substances in the flue gas
- position and length of the fire
- energy release in the combustion area
- combustion chamber geometry and conduction of the flow

Many of these combustion properties are closely connected with available degrees of freedom for process management and with the quality of information regarding high control standards.

Corrosion-relevant properties of the heat transfer in the flue gas are:
- pressure stage, superheater temperature
- temperature profile of the flue gas in the radiative part and in the convective part
- temperature profiles in the individual wall build-up
- natural circulation behaviour per component and per boiler tube

CAUSES OF CORROSION

Corrosion processes and corrosion damage in waste-to-energy plants are usually multi-causal, i.e. the damage incurred cannot be attributed to just one parameter. Parameters can be categorised into conditional and adequately conditional, always reinforcing and temporarily reinforcing, avoidable and unavoidable, predictable and unpredictable, temporary and permanent, etc.

A parameter can always be classified as a
- thermal,
- chemical, or
- mechanical influence.
- online cleaning procedures
- deflections, obstacles in the flue gas flow
- flue gas velocities
- flue gas retention times before the convective part

From these complex interactions, certain patterns can be derived, according to which given parameters often interact in a similar way and thus cause a corrosion mechanism which is to be considered as important regarding the number of plants concerned, the extent or intensity. Corrosion on heat transfer surfaces does not cover a large surface or occur in linear progression, but rather forms shallow pits, notches, and holes and is locally accelerated — in an unpredictable way.

Boiler steel is — like many solid materials — a mixture of crystals that can belong to one or more crystalline phases. Type, form, size and relative position of the crystals to each other shape the so-called microstructure of steel.

The microstructure is responsible for many of the properties of the material. In a first approximation, the resistance of steel to thermal, chemical and mechanical influences can be equated with the steel’s ability to maintain its microstructure, i.e. the type, form, size and relative position of the crystals to each other. Basically, the same is true for metallic and ceramic protective coatings (Figure 2).

The path of metallic iron back into an oxidised state — through corrosion — releases again some part of the energy which was consumed during steel making, and this goes on continuously if adequate reacting agents are available and temperatures are sufficiently high. The dynamics of this reaction mainly depend on
- the transport processes of the substances involved in this reaction and
- the temperature.

Gaseous reaction partners are, due to their high mobility, better suited for this oxidation process than liquid or solid reaction partners. Depending on the composition of the gaseous reaction partner, i.e. the type and specific volume of the gas species (partial pressure), metallic iron is converted into iron oxide (with oxygen), into iron sulphide or sulphate (with a gaseous sulphur species or sulphur dioxide/oxygen), into iron chloride (with a gaseous chlorine species), etc. The reaction between metallic iron and the specific gas phase starts on the material surface and then penetrates gradually into the material, e.g. into the intercrystalline space along the grain boundaries. The reaction products can form a buffer layer between the metal and the gas phases, so that — the deeper the reaction in the material — the reaction rate may be strongly reduced.

The presence of oxygen in the flue gas provoked by the process, on an uncoated and unprotected tube surface, leads to the formation of iron oxides (scaling). This is the
unavoidable, always occurring "first corrosion attack" on uncoated steel surfaces. An oxide layer of some 10 µm thickness is built up once. This corrosion process quickly ends, because iron oxides form a buffer layer against the gas space and impede the fresh supply of oxygen to the metal surface. According to this, scaling is to be seen as a corrosive process which, in itself, does not result in technically relevant degradation. The reaction of metal and oxygen is generally an unavoidable and harmless process resulting in only thin oxide layers, which can also act as a barrier against the penetration of other flue gas substances (usually described as passivation, and usually intended).

This situation radically changes as soon as substances transported by the flue gas start to deposit on the tube surface, i.e. a deposit layer is formed (i.e. fouling) (Figure 3).

This applies to almost all heat transfer surfaces in boilers which are fired with solid matter. The gas space at the tube surface under a deposit layer no longer corresponds to a flowing flue gas, but to a more or less static gas. The components of this gas are no longer determined by the combustion, but by the evaporation of the substances in the deposit layer, amongst others. A self-sufficient, decoupled microclimate develops [9,11–13] (Figure 4).

Depending on the condition of the deposit (in particular: permeability, thickness, heat flux density; influenced by the location relative to the flue gas), the microclimate can also vary on a small spatial scale, i.e. measured in centimetres of tube surface. The microclimate is determined by:

- Chemical parameters
  composition of the mineral phases and their respective aggregate states, as well as the proportions of the mineral phases to each other
- Mechanical parameters
  physical properties of the deposit (thickness, porosity, gas permeability, thermophoresis)
- Thermal parameters
  temperature levels and temperature gradient in the deposit (with the gradient depending on heat flux density).

These parameters are not static in their behaviour. Instead, driven by changing temperature levels or the input and output of matter, changes in the condition occur per share of volume in the deposit, e.g. minerals grow and the microstructure densifies ("maturing of the deposit"). Very different parameters dynamically influence the properties of the micro gas space. This diversity in the properties of the deposit constitutes the major driver for the diversity as well as the spatially limited scale of corrosion phenomena [14,15].

The following chemical parameters tend to influence the processes at the corrosion front, under the fouling in the micro gas space:
deposit itself. This includes a mechanical influence on the deposit in terms of momentum cleaning procedures (steam or water) during operation, which is the periodic removal of entire deposit layers. In contrast to this, rappings (vibrations) and explosion cleaning (blast waves) as well as some momentum cleaning procedures do not have a cleaning effect in terms of entirely removing the fouling. Instead, diffuse effects such as partial cleaning and/or the cracking and shattering of the deposit layers occur, leading to sudden changes in the temperature levels of the deposit, the penetration of flue gas into the deposit (along cracks) and thus to the penetration of salts and oxygen-containing gas species, too. So the conditions in the microgas space at the corrosion front can become more aggressive.

In addition, the mechanical influence of the fouling on corrosive processes can manifest itself in the strength of the deposit layers, their brittleness, gas permeability as well as porosity. In older, thicker fouling (after some 100 operating hours, some mm in thickness) at least 3 layers can be distinguished. Firstly, close to the tube, the layer of corrosion products (iron chloride, iron sulphide, iron oxide - depending on the chemical environment), then a very dense layer with few pores and rich in salts, and finally the (hotter) outer layer containing more pores and less salts.

- type and volume of chloride salts in the deposit and their temperature level (the first deposit layer close to the material surface has a major impact here)
- diffusion of an oxygen-containing gas species from the flue gas to the deposit (via pores or cracks). Water steam is to be included here, with a usual percentage of 10 to 20 % in the flue gas.

The dynamics of this chemical reaction of the oxidation of metallic iron, indirectly via iron chloride, are influenced by

- the gaseous state of the main reaction partners (reactants and products; with the exception of steel) and
- the diffusion properties of the gases involved.

The effect of mechanical parameters on corrosion occurs by mechanical influences on the deposit or within the

The geometric conditions (tube walls or single tubes), interacting with reversible thermal expansions of the material and the fouling, also constitute a mechanical influence, i.e. stress develops which can lead to cracks, spalling, etc. in the fouling. Through temperature changes in the flue gas (e.g. load fluctuations) phase transitions may occur in addition to the effects of thermal expansion, i.e. melts solidify and embrittle the deposit structure. The strongest effect of this expansion stress is provoked during start-up and shutdown procedures, when different temperature gradients of cooling (or heating) affect both material and deposit layers.

Thermal parameters of corrosion fall into two categories:

The first category refers to events that have a relatively short-term and mostly one-off effect, with a high energy input. This includes, for example, so-called heat-affected zones with respect to joint-welding or cladding.
The original microstructure of steel is largely dissolved and newly formed involving, as a rule, reduced corrosion resistance. This comprises the overheating of steel, i.e. its heating beyond the “upper application temperature”, resulting in the liquation of the microstructure and in mineral reactions within the microstructure. Thus, creep-resistant properties can be destroyed and corrosion resistance be reduced. The overheating of evaporator and superheater walls is caused by the lack or the absence of a cooling agent (water for evaporator walls or water steam for superheater walls).

The second category refers to the connection (Arrhenius) between the oxidation rate and material temperature in the presence of an oxygen-containing gas phase on the steel surface (scaling). The oxidation rate is doubled at approximately every 20 K [12]. There are also thermal parameters as a result of the temperature level and the temperature gradients in the flue gas and in the fouling, or in a combination of ceramic and/or metallic protective coatings and overlying deposits [14]. As a rule, the heat conductivity of most deposit layers – contrary to the metallic and ceramic protective coatings – is very low and, therefore, steep temperature gradients arise related to the thickness of the deposit. A temperature difference of 100 K is actually possible per millimetre of deposit thickness. The driving force for thermodynamic processes of the substances involved in the build-up of the deposit is correspondingly high. The closer the chloride salts within this solid matter get to the surface of the tube, the higher the corrosive effect of these salts, amongst others.

These temperature conditions are primarily caused by heat flux density. High heat flux density generates steep temperature gradients in the flue gas, enabling chloride salts to get in a position close to the material surface (i.e. potential of high-temperature chlorine corrosion) or directly on the material surface (i.e. potential of salt melt corrosion) (Figure 5).

This contributes to increased degradation rates. Taking the example of imbalances in the 1st pass, the associated difference in heat flux densities is to be correlated with the degradation rates of evaporator walls [14].

The contribution of these thermal parameters to degradation is always to be evaluated in connection with the given specific chemical and mechanical parameters. They are interdependent, to some extent, i.e. it is only under specific temperature conditions in the fouling that degradation is caused by the chemical or mechanical parameters, and vice versa. In other words: the fouling acts as a heated chemical reactor.

Besides, temperature conditions – levels and gradients – in the flue gas also exert through the thermodynamic properties of salts, i.e. their solubility in the flue gas, a major influence on the properties of the fouling and thus on corrosive processes. The high temperature levels in the flue gas after the firing (mostly > 1000 °C) favour the solubility of high loads of salts, in particular chloride salts (up to several 100 mg·m⁻³ STP).

Depending on the salt species, the cooling flue gas becomes saturated at a specific temperature, i.e. the dissolved salt turns into solid or liquid form (Figure 6). Below the saturation temperature or saturation concentration, the salt also exists as solid matter (crystals) or in molten form and can thus contribute to building up the deposit and, by reevaporating in the deposit, to providing the micro gas environment there with a chlorine gas species, as explained above.

If, in practice, salt in the flue gas reaches a specific saturation temperature, this rarely leads to a spontaneous phase transition from the dissolved into the solid or liquid state of the salt. There are, in fact, many influencing fac-
tors, such as the lack of nucleus (supersaturation) and an inhomogeneous distribution of the load and temperature in partial volumes of the flue gas which encourage a phase transition on surfaces (= nucleus), and in partial volumes of the flue gas that are close to the wall and have cooled more quickly (formation of turbulence and interference of colder partial volumes).

This supports the deposition of salts on the fouling, thus raising the corrosion potential. Flue gas flowing with sufficient retention time – meaning rather slowly – and with little turbulence along the margins as possible can cope with the saturated state of the respective salt more easily, so that the share of salts absorbed by the fouling does not become disproportionate.

The cooled tube surfaces have, through convective heat transfer, a basically cooling effect on the margins of the flue gas stream and thus act as a "cold trap" for the salt species dissolved in the flue gas [14]. The growth of very thick deposit layers (in the range of centimetres) reduces this effect significantly.

MECHANISMS OF EROSION CORROSION

The highly complex conditions and environments of metallic materials in the boiler can be characterised by three principal mechanisms or processes of degradation. They are:

- high-temperature chlorine corrosion,
- salt melt corrosion, and
- erosion or, in combination, erosion corrosion.

Scaling is to be included.

High-Temperature Chlorine Corrosion

Chlorine corrosion solubilises the ferrous material – this is why this corrosion process is also called "active oxidation" or "chlorine-induced corrosion". This mechanism is responsible for most corrosion processes on evaporator walls [6,9–11,12,13,16–26]. It often provokes corrosion on superheaters, too.

The core reactions of chlorine corrosion are:

- \( \text{Fe (solid, material)} + \text{Cl}_2 \text{ (gas)} \rightarrow \text{Fe(II)Cl}_2 \text{ (gaseous, solid, liquid)} \)
- \( \text{Fe (solid, material)} + 1\frac{1}{2}\text{Cl}_2 \text{ (gas)} \rightarrow \text{Fe(III)Cl}_3 \text{ (gaseous, solid, liquid)} \)

The iron chlorides develop in the grain structure of the material surface. They often form thin layers on the material surface. On them lie or on them grow layers of magnetite, depending on the availability of oxygen on that side of the iron chloride layer which is facing away from the boiler tube. These layers of magnetite can grow on evaporator walls and turn into layers of several millimetres of thickness, resembling puff pastry. The particles deposited from the flue gas adhere to them, in the form of fouling. In the convective part, particle surfaces are often covered by tiny haematite pigments, thereby documenting how deep the iron chloride, which evaporated at the corrosion front, had penetrated into the fouling, before sufficient oxygen was available for its oxidation (Figure 7).

The high-temperature chlorine corrosion process attacks the steel grains with a chlorine gas species. Iron chloride is formed. Depending on the conditions of the chemical environment, bivalent and/or trivalent iron chloride is formed. The latter, in particular, occurs in a gaseous state under evaporator temperatures and, to an even greater extent, under superheater temperatures, i.e. the corrosion products evaporate. This is important because a network of hollow spaces gradually develops in the upper layer of the material (some 10 \( \mu \text{m} \)), encouraging the penetration.
and the distribution of the chlorine gas species. This corrosion process is therefore not decelerated, with corrosion products being formed and blocking the supply lines for the corrodent. This blockage occurs when oxygen provokes the corrosive attack. Iron oxides that have been formed remain lying at the place of corrosion, blocking the penetration of oxygen to the corrosive front (= scaling).

As long as adequate environmental conditions exist for this chlorine corrosion, this process is – merely due to the specific removal of the corrosion products – highly efficient, dynamic and infinitely effective. Metaphorically speaking, steel dissolves into a gaseous state, the boiler tube evaporates.

Adequate environmental conditions for this process are mainly provided by

- the presence of a chlorine gas species and by
- the absence of oxygen

in those parts of the fouling which are close to the corrosion front (in the first 10 μm).

These two conditional states are supported by other optional states that particularly impact the duration and dynamics of this corrosion process:

- Conditional
  The presence of a chlorine gas species at the corrosion front. The higher its proportion in the gas mixture of the microporous volume close to the material’s surface in the fouling, the larger the volumes of steel that can oxidise to iron chloride. The chlorine gas species comes from two sources. One is fed by the evaporation of chlorine salts in the fouling and the other is the reaction of iron chloride vapour with oxygen (e.g. bound in H₂O). Chlorine gas species is released here, too. The latter process means that the same chlorine can dissolve steel several times (chlorine cycle). It is also possible that a chlorine gas species from the flue gas contributes to its presence in the microporous volume (diffusion through the fouling, if general porosity is given).

- Conditional
  The absence of oxygen at the corrosion front. As long as oxygen occurs in the gas mixture of the microporous volume (even in tiny amounts), the also present chlorine gas species remains ineffective. The state of scaling persists, with a small extent of degradation. However, as soon as the gaseous fraction of oxygen is fixed in crystalline form through reactions with solid particles, e.g. through the oxidation of the steel, it can no longer be “fed back”. This means that when the supply of oxygen or oxygen-containing gases is blocked by thick layers in the fouling, oxygen is inevitably and entirely consumed through oxidation in the microporous volume of the deposit layer close to the material’s surface. As soon as this state occurs, iron chloride can develop – in the presence of a chlorine gas species.

- Intensifying
  For a continuously high proportion of chlorine gas species in the microporous volume, a high content of chloride salts in the fouling is favourable, particularly salts with a high steam pressure at the specifically given temperature. For deposit layers on evaporators, these are mainly mixed salts of lead chloride and potassium chloride (and zinc chloride). For deposit layers on superheaters, these are mixed salts of sodium chloride and potassium chloride (and possibly also calcium chloride). The steam pressure levels of these salts are...
controlled by the temperature. As already mentioned above, relatively high temperatures in the fouling rather close to the material's surface are "favourable" for a high corrosion potential (i.e. a high heat flux density).

- **Intensifying**
  The chlorine cycle is supported if iron chloride, which evaporates at the corrosion front, hits within a small distance an oxygen-containing microporous volume in the fouling (e.g. of some 10 or 100 µm thickness). Conditions are particularly "favourable" if just the necessary amount of oxygen-containing gas species is supplied by the flue gas via the porosity of the fouling (diffused) so that the evaporating iron chloride can quantitatively be converted into iron oxide.

- **Intensifying**
  All microstructure effects in the fouling which limit – but do not entirely block – the diffusion of gases. This includes, amongst others, microstructure conditions of salt-rich layers or sintered deposit layer volumes due to the formation of mixed salts with salt melts (eutectics) or the formation of caverns by corrosion products which resemble layers of puff pastry (iron oxides).

**Corrosion Caused by Sulphur-Containing Gas Species**

The participation of sulphurous phases as a corrosive species, i.e. the sulphidation (degrading or through cracks), is – contrary to in coal-fired power plants – more or less rare with regard to waste fuels and biomass. Such findings are possible for, for example, the protective coatings of cladded nickel-base alloys on evaporator walls with a very high heat flux level or on analogously protected superheater tubes. The frequency of this corrosion mechanism will rise in line with the growing number of waste-to-energy (WTE) plants with increased steam parameters.

**Oxygen-Deficiency Corrosion**

What is known as oxygen-deficiency corrosion or CO corrosion is characterised by the destruction of the scale layer through the reduction of iron oxide in the absence of oxygen in the flue gas (e.g. locally by the fractions of not entirely burnt out flue gases or through visible/adjacent flames). With the presence of oxygen in the flue gas always changing, constantly repeated scaling can have a degrading effect. The assumption that these corrosive pro-

- **Salt Melt Corrosion**
  For salt melt corrosion – in contrast to high-temperature chlorine corrosion – the direct contact between the corrosive and the steel material is the conditional and thus determining condition. The volumes of elements from the steel material, soluble in the salt melt, depend on the chemical composition, temperature and melt volume. The mass gradient in the melt promotes a dynamic system of dissolving and precipitating solid particles, which intensifies the degrading effect. In most cases, however, locally limited corrosive attacks occur, indicating that the salt melt quickly "suffocates", i.e. solidifies, from the absorbed steel elements (Figure 8).

Typical salt melts are mixtures of salts containing chlorides and sulphates. Depending on the ratio of the mixture and the salts involved, melting temperatures range from approximately 230 °C to more than 1 000 °C. Very low melting temperatures are achieved with zinc chloride mixtures (down to approx. 230 °C). Pure zinc chloride melts at approx. 320 °C.

**Figure 8:**
Examples illustrating the effect of salt melt corrosion on heat transfer surfaces. Isolated, funnel-shaped degradation phenomena prevail. There are also effects covering extensive areas (on the bottom right: stain-like distribution on cladded nickel-base alloy).
Although salt melt corrosion on unprotected boiler tubes is subordinate to high-temperature chlorine corrosion, it also can overlap the latter, i.e. the phenomena of both corrosion mechanisms can be found at the same place. However, salt melt corrosion on protective coatings of nickel-base alloys (cladded or thermally sprayed) is a rather frequent phenomenon. A corrosive attack triggered by salt melts can infiltrate existing scale layers, thus detaching them and even dissolving them chemically.

Until the 1990s salt melt corrosion was considered the attack of sulphurous melts, i.e. pyrosulphates. They melt from temperatures of above approx. 400 °C if sufficient SO₃ is present. As salt melt corrosion also occurs at lower temperatures and the presence of SO₃ in the flue gas is very limited due to the sulphate reaction of the chloride salts, pyrosulphates do not seem to be relevant in this context.

**Erosion Corrosion**

The degradation process of erosion requires that the boiler tube is not covered by fouling for at least some time (and that no protective coatings have been applied or that existing protective coatings have been destroyed). As soon as the tube is covered by permanent fouling, no direct mechanical influence on the boiler steel can be exerted. In many cases, any mechanical influence can only be exerted if, in a preceding process, the fouling was removed. When the fouling is systematically removed, e.g. by means of soot blowers, water cannons or other online cleaning procedures, the cleaning itself may contribute to erosion in two ways. First, the cleaning procedure might take longer than necessary for the removal of the fouling. Then those particles in the flue gas which were also accelerated by the cleaning agent might have an erosive effect on the boiler tube. Second, in the period between the cleaning and the growth of a new deposit layer, the particles transported by the flue gas might cause erosion on the boiler tube.

If, after the cleaning and while new deposit layers are being formed, a corrosion phase starts, such as scaling, this results in an interaction of cleaning and corrosion, in addition to the erosive effect of cleaning. The simultaneous or phase-shifted effect of erosive and corrosive parameters is called erosion corrosion (Figure 9).

![Figure 9: Examples illustrating erosion corrosion in the convective part of the boiler at WTE plants. The locations of degradation are clearly geometrically related to the range of a soot blower.](image)

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THE AUTHORS

Wolfgang Spiegel (Ph.D., Geosciences, Ludwig Maximilian University of Munich, Germany) has been the owner and managing director of CheMin GmbH since 1996. He is an officially appointed and sworn expert by the Swabian Chamber of Industry and Commerce in the field of non-metallic, refractory raw materials and refractory materials.

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