Müller, W.; Schneider, D.; Kaiser, M.; Brell, J.; Spiegel, W.; Pohl, M. (ENVERUM GmbH) (2014):

"Fuel leaflets" for the prevention of negative impact on the boiler from minor fuel constituents.

In: VGB PowerTech, Ausgabe 7/2014, S. 76-81



Creating Fuel Leaflets for the prevention of negative impact on the boiler from minor fuel components

Brennstoff-Beipackzettel: Vorbeugen gegen Belastungen des Kessels bedingt durch Nebenkomponenten des Brennstoffs

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Kurzfassung englisch

For solid fuels, like biomass, lignite, black coal and peat, used in power plants, a proximate and elementary analysis do not provide sufficient information if problematic processes like corrosion and fouling in the power plant are to be minimised. It is of high relevance to know the mineralogy of the fuel components and the successive steps of reaction and transformation during firing and cooling in the power plant. Typically minor components and even traces in the fuel can cause corrosion and fouling. Based on damage investigations the importance of minor fuel compounds is known. These compounds include, among others, chlorine, bromine, sulphur, ammonium, aluminium, calcium, potassium, sodium, magnesium, lead and zinc. Even gaseous fuels like hydrogen may contain minor components with relevance for corrosion, i.e. due to hygroscopic salts.

Minor components are able to cause major problems in terms of corrosion and fouling. Transfer of diagnostic measures derived at waste fired power plants during the last decades should enable focusing on the important characteristics of fossil fuels, biomass and cofiring in relation to corrosion and fouling. These measures include mainly mineralogical investigations and online sampling by probes.

These measures support creating a fuel leaflet for each specific fuel, including advice for operational thresholds, risks for corrosion and fouling, etc. Minor components should be of major interest.

Kurzfassung deutsch

Die Kurz- und Elementaranalyse von Biomassen und fossilen Brennstoffen, die in Kraftwerken verfeuert werden, sind keine ausreichenden Informationsgrundlagen, um problematische Prozesse im Kraftwerk, wie Korrosion und Verschmutzung, zu charakterisieren und zu minimieren. Vielmehr ist es relevant, die mineralogische Zusammensetzung des Brennstoffs zu erfassen, sowie die sukzessiven Reaktions- und Transformationsschritte, die im Zuge von Feuerung und Rauchgasabkühlung stattfinden. Typischerweise sind es die Brennstoff-Nebenkomponenten bis hin zu Spurenbestandteilen, die für Korrosion und Verschmutzung verantwortlich sind.

Aus vielen Schadensuntersuchungen ist die Bedeutung der Brennstoff-Nebenkomponenten bekannt. Unter anderem gehören hierzu Brennstoff-Bestandteile, die Chlor, Brom, Schwefel, Ammonium, Aluminium, Calcium, Kalium, Natrium, Magnesium, Blei und Zink enthalten. Sogar gasförmige Brennstoffe, wie z.B. Wasserstoff, können Nebenkomponenten enthalten, die für Korrosion relevant sind, z.B. durch die Wirkung hygroskopischer Salze.

Brennstoff-Nebenkomponenten können in Bezug auf Korrosion und Verschmutzung erhebliche negative Auswirkungen entwickeln. In den Anlagen zur thermischen Abfallbehandlung wurden in den letzten Jahrzehnten diagnostische Methoden entwickelt, um diese negativen Auswirkungen zu minimieren. Ein Transfer dieser Methoden auf fossile Brennstoffe, Biomassen und Mitverbrennung sollte helfen, die wesentlichen Merkmale dieser Brennstoffe in Bezug auf Korrosion und Verschmutzung zu erfassen und zu verstehen. Diese Methoden beziehen sich vor allem auf mineralogische Untersuchungen und spezielle online Sonden.

Für jeden spezifischen Brennstoff lässt sich mit diesen Methoden ein Brennstoff-Beipackzettel erstellen, der anhand der Nebenkomponenten die kritischen Schwellenwerte und Risiken für Korrosion und Verschmutzung benennt, analog zu einem Medikamenten-Beipackzettel.

Minor fuel components

Minor components of fuels have potential to cause major negative effects in almost all parts of power plant processes, including firing, boiler, flue gas cleaning and treatment of residues.

Design of modern power plants for solid or gaseous fuels has benefited from the experience of decades of operation and efforts to minimize any negative impact from minor fuel components. In the case of solid fossil fuels (peat, lignite, black coal), these components include, for example, sulphur mineral phases, chloride mineral phases, alkali mineral phases and silicates. Long lasting stable conditions for a power plant, e.g. the same black coal and the same firing conditions, make it unnecessary to focus continuously on the minor fuel components.

But fuels with less quality requirements cause more unexpected negative effects due to differing minor fuel components in terms of reaction products, phases and load. Even black coal, whose origins, such as continent or mine, or blends, may vary widely nowadays and may cause similar unexpected negative effects in power plants. Even greater impact by minor components is caused by cofiring of biomass.

The German "Energiewende" and other influences on a more global scale push power plants to accept discontinuities in terms of operation periods, steam load and fuel quality. Black coal from other parts of the world, cofiring of biomass, and even firing of pure biomass are main trends for existing power plants. This situation pushes operators and manufacturers of power plants to learn more about fuel components which are not of interest in terms of energy (reduced phases containing carbon, hydrogen, etc.), but which are part of the fuel as well.

The thermal process of firing acts like a separator, a "distillation process", to form new phases of the minor fuel components or at least to transfer these components from solid to liquid or even to gaseous states. In the latter case condensation and desublimation have an important impact on particle size, distribution and even strong local enrichment of specific phases, e.g. salts, along the flue gas path.

Fuels derived from solid waste and from specific biomass (e.g. demolition wood) are a worst case scenario in terms of differing kind, load and reactivity of minor components. Waste to energy (WTE) plants had to learn in the past to understand and to handle the negative impact of minor components on the process of firing, heat extraction, flue gas cleaning and residue treatment. In many cases this negative impact is connected with fouling, corrosion and erosion. The especially heterogeneous and varying thermo-chemical processes in WTE plants cause unpredictable reactions.

Solid waste and related biomass need specific focus on their minor components to minimize negative impacts in WTE plants. During the last decades in WTE plants were developed various diagnostics and technical solutions to handle this situation. Power plants fired with fossil fuels or cofired with biomass should make use of this knowledge.

There is one big advantage for the fossil and/or biomass fired power plants in relation to WTE plants: to a certain degree the fuel can be designed to minimize the heterogeneity of the fuel. This has the advantage of more or less stable phases, load and reactivity of minor components. Compared to solid waste, fossil and biomass fuels are relatively simple in terms of their minor components. Thus, it would be beneficial to take the effort to learn more about the thermo-chemical effects caused by the minor components of a certain fuel. This learning curve should take place before the specific fuel is fired continuously in a power plant or at least during the first phase of continuous use. Having done this, fossil and biomass fired power plants should use the experience derived from WTE plants.

Measures for characterisation

To describe and understand the thermo-chemical effects arising from minor components, e.g. corrosion, fouling and erosion, first it is necessary to identify the fuel itself (before firing) in terms of mineralogical and chemical parameters. Second, the combined effect of fuel and firing has to be considered. This step needs access to the boiler by probes to sample the relevant chemical information in the flue gas and to determine the phases, load and reactivity

of the components. The latter includes the reactions of the chemical components in the flue gas (derived from minor components of the fuel) with the tube material and/or the protective layer (metallic or ceramic). This can be achieved by specific probes as well. To get samples of this very specific mineralogical and chemical information out from the flue gas, CheMin developed and patented several probes. These "CheMin-Probes" are listed in table 1. More detailed information about the design and use of these probes are given in [1 to 3].

CheMin-Probes	Type of test	Suitable for
Temperature-range probe	Corrosion	Temperature threshold for
		 High temperature chlorine corrosion Salt melt corrosion Dew point corrosion Deliquescence corrosion
		Cause and mechanism of corrosion
		Corrosion rates
	Fouling	Characteristics of fouling
		 Texture, porosity Salt-enrichment at cooling traps Solid mineral reactions Eutectic melts Layering
	Material	Testing different materials Tube material Protective layers
Particle probe	Short-range collection (grid probe)	Chemistry and mineralogy of flue gas components along flue gas path Characteristics of
		 Salt aerosols (desublimation) Particles (size, shape, solid-liquid) Compounds
	Long-range collection (ash-salt-proportion, ASP)	Chemistry and mineralogy of flue gas components at the end of boiler Characteristics of
		Load of particlesElementary composition of particles

The features of the "temperature-range probe" are (figure 1):

• The probe corresponds to a real boiler component in terms of size (e.g. boiler tube), material and, optionally, corrosion protection (e.g. ceramics, weld overlay, spray coating).

- The temperature range on the probe surface is freely selectable and is kept at a constant level by a temperature control. This allows the temperature range to be observed simultaneously on the material surface.
- The probe can be applied at different flue gas temperatures (from secondary combustion chamber to flue gas cleaning).
- The probe can be used for a time period which is freely chosen (from hours to months) and can be inserted or removed at any time. This specifically allows for the investigation of special operating conditions.
- The heat flux can be measured on the basis of the amount of cooling air and its outlet temperature.
- The application of different materials on the probes allows evaluation with regard to their resistance to corrosion.
- Following the operational application of the probe, laboratory tests have to be started with regard to the given issue, e.g. cause and mechanism of corrosion, dependence of corrosion or fouling on temperature, corrosion resistance of various materials, etc.

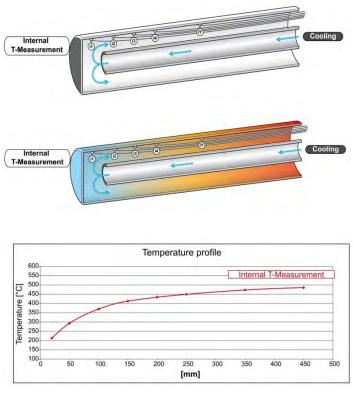


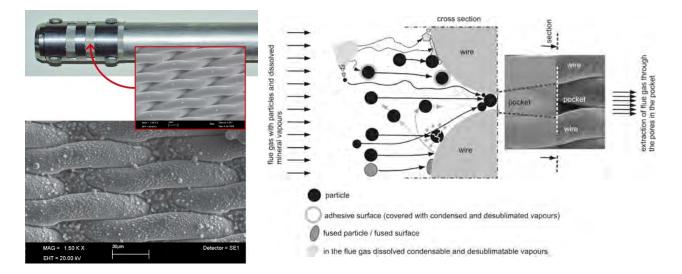
Figure 1: Principal function of the temperature-range probe (patented). Cooling air is transported in the inner tube to the head of the outer tube and flows back through the space between the inner and outer tube. Several thermo couples on the inner surface of the outer tube record the temperature range along the tube (e.g. medium temperature). A control unit keeps the temperature profile constant. Design of the inner tube and amount of cooling air makes it possible to select a starting temperature at the head of outer tube and a specific the temperature profile along the outer tube, e.g. from 200 to 350 °C (for water wall conditions), or 350 to 500 °C (for super heater conditions) or 80 to 200 °C (for economizer conditions). The temperature-range probe can be

used with the characteristics of a corrosion probe, a fouling probe and/or a material probe, depending on what the probe is designed to do.

The features of the particle probe "grid probe" are (figure 2):

- The cooled or uncooled probe is inserted briefly into the flue gas stream at different flue gas temperatures.
- The flue gas is drawn through a grid with a mesh size in micrometer range.

- Particles already existing in the flue gas are deflected into the meshes. Salts, which are saturated under the given flue gas conditions, condense on the wire surface. In this way, the beginning formation of fouling can be recorded.
- The analysis (Scanning-Electron-Microscope SEM e.g. with EDX-Analysis) of the particles and salts provide information on the potential of corrosion and fouling. Furthermore, the fluegas particles can be described in terms of size, shape and elemental composition [4].



Particle probe (grid probe)

Figure 2: Principal function of the particle probe (grid probe), patented. Suitable for shortrange collection of flue gas components along flue gas path in order to identify, e.g. salt aerosols, size and shape of particles, compounds. The right side sketch indicates the possible kinds of behaviour of particles during the deposition in relation to their chemical and mechanical characteristics. For further comments, see text immediately above and below.

CheMin first developed its chemical and mineralogical know-how about the negative effects of minor fuel components while working in the field of WTE plants. There, corrosion and fouling especially limit the potential to achieve evolved energy efficiency and/or availability. The objective to apply these probes into the flue gas of WTE plants first tends towards improvements in firing conditions and/or protective layers (e.g. nickel base alloys) and only second towards improvement of the fuel itself (because waste is unpredictable and only to a limited extent designable). But, of course, for fossil fuels, biomass and cofiring, the focus on the minor fuel components is of relevance and therefore the use of these probes for this purpose, as well. The general attempt for this strategy may be called "creating a fuel leaflet".

Creating a fuel leaflet

The purpose of a "fuel leaflet" about the minor components of a specific fuel (specific coal, specific biomass, specific blend, cofiring) basically is to avoid future negative impacts for a

specific power plant by employing the following measures in the very first stage of usage of the specific fuel. These efforts include three options:

- (1) Mineralogical investigation of the specific fuel (before firing)
- (2) Test firing of the specific fuel in a batch reactor or a combustion chamber (technicum scale)
- (3) Chemical and mineralogical investigation of particles in the flue gas of power plants firing the specific fuel (test firing or first stage of regular firing)

At least option (1) and (3) should be included for a "fuel leaflet" of minor components.

Fuel itself is not "suitable" or "not suitable". The fuel always has to be regarded in relation to the given process of firing (pulverized combustion, fluidized bed or grate firing) and boiler design.

Option (2) is a good chance to preselect fuels in terms of their potentials to cause negative impacts, e.g. fouling, corrosion or erosion. Option (2) was developed in cooperation with the Technical University of Dresden and was funded by the DBU (Deutsche Bundesstiftung Umwelt) [5 to 12]. During this research the focus was set on a strong linkage between options (2) and (3). This mainly could be achieved by downscaling the size of the CheMin-Probes to be suitable for an application in a technicum scale Batch reactor. The investigated fuel was biomass for cofiring. Regarding the method as used for coal combustion see [13 to 15].

The following examples should give an idea how these three measures are performed, which probes are used and which methods for analysis are applied to create a "fuel leaflet" for a specific fuel. The examples are given anonymously and cover several types of fuels.

Three examples

First example: Mineralogical investigation of a specific lignite, reference to option (1)

<u>Procedure:</u> Sampling of lignite at different locations along the sequence of handling from opencast mining towards the boiler. Sampling at different locations in the opencast mine.

<u>Methods applied:</u> Mineralogical preparation of samples (embedding, polishing etc.), light microscopy, SEM-EDX.

<u>Findings about minor components</u> (figure 3): The primary sulphur species of this lignite is pyrite (iron sulfide). During oxidising conditions (opencast mining, ground water level) pyrite partly changes to gypsum/anhydrite (calcium sulfate).

<u>Contribution to "fuel leaflet"</u>: During firing of this lignite, the transformation rate of solid sulphur mineral phases towards gaseous components (SO_2) strongly depend on the ratio of sulphur as pyrite or as gypsum/anhydrite in the lignite. The consequence will be a differing amount of SO₂ in the flue gas which influences the dew point at the cold end of the boiler (SO_3) , the flue gas cleaning (capacity, costs for additive) and also the sulphation reaction of chlorides in the fouling.

Option (2) and option (3) would quantify this behaviour (interaction of the firing with the differing sulphur species). In addition, option (3) is an instrument for testing slagging behaviour of ash, induced by different reactive calcium and iron mineral phases with their specific influence on melting point and on the chemical mechanisms of building up foulings.

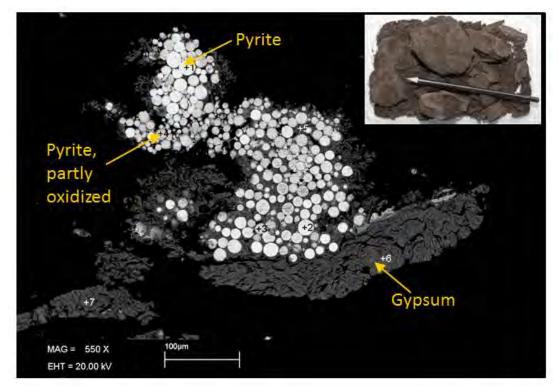


Figure 3: Mineralogical phase relations of iron, sulphur and calcium (SEM-EDX) of a specific lignite.

Second example: Test firing of biomass in a batch reactor, reference to option (2)

<u>Procedure:</u> Preheating of the batch reactor and firing of about 10 kg of biomass (wood pellets blended with different kind of chlorine compound).

<u>Methods applied:</u> CheMin-Probes (temperature-range probe and grid probe) are positioned along the flue gas path of the batch reactor during biomass firing. Chemical analysis (SEM-EDX) of probe material after removal from the batch reactor (figure 4).

<u>Findings about minor components:</u> Potassium fixed in biomass and chlorine fixed, e.g. in organic compounds (in this case: PVC (organical chlorine) & NaCl (anorganical chlorine) mixed into the biomass) have potential to form gaseous salt compounds during firing. Desublimation of these salts along the flue gas path – due to cooling of the flue gas and due to cooling trap conditions at heat exchange surfaces – induce strong and local enrichment of chlorides in the fouling at specific parts of the process.

<u>Contribution to "fuel leaflet"</u>: The compounds of alkalies, alkaline earths, chlorine and sulphur in a biomass, in terms of amount, proportions and mineral phases, interact during firing and subsequent cooling of the flue gas, according to the characteristic firing and cooling conditions of a given power plant, not predictable but specific and reproducible. Test firing in a batch reactor demonstrates the general direction of this interaction for the given biomass. This information is of importance for, e.g. design of a firing process, design of a boiler or design of a fuel (i.e., blends). To point out the real interaction of the components of alkalies, alkaline earths, chlorine and sulphur in a given power plant process, to complete the fuel leaflet, needs application of option (3).

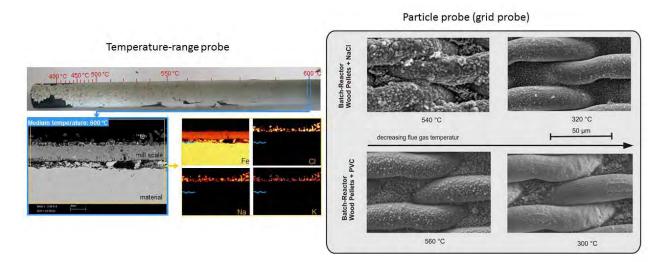


Figure 4: Left side: Temperature-range probe used to characterize fouling. Temperature profile from 400 to 600°C. Residence time in the batch reactor about 40 minutes. Preparation at the 600°C position (embedding, polishing) with element maps (SEM-EDX) for iron (Fe), chlorine (Cl), sodium (Na) and potassium (K). Finding: Chlorine, sodium and potassium form common compounds. Right side: Particle probe (gride probe). Finding: Strong difference in deposition of chlorides at wire position depending on fuel (organic and anorganic chlorine) and flue gas temperature.

Third example: Chemical and mineralogical investigation of particles in the flue gas of power plants firing biomass, reference to option (3)

<u>Procedure:</u> Definition of specific and stable operational conditions (of interest) for a given time period (e.g. hours, days). Application of CheMin-Probes in the boiler during this time period (radiative and/or convective part, positions depending on the questions of interest).

<u>Methods applied:</u> CheMin-Probes (temperature-range probe and grid probe) are positioned along the flue gas path. Chemical analysis (SEM-EDX) of probe material after removal from the power plant.

<u>Findings about minor components (figure 5, figure 6, figure 7)</u>: Evidence of the degree of formation of gaseous chloride salts (alkalies, alkaline earths, heavy metals) and evidence of the zones along the flue gas path affected by subsequent desublimation of chlorides at different temperature levels (according to flue gas temperature and/or surface temperature). Additional, evidence is given for reactivity of chlorides in the fouling (sulphation, formation of solid solutions, eutectic melts).

<u>Contribution to "fuel leaflet":</u> The specific and stable operational conditions will be modified step by step (each step accompanied by CheMin-Probes) in order to find an optimum of operational conditions for the given fuel in terms of minimised impact of corrosion and fouling. Such high quality information, anchors the given biomass fuel for the given power plant process in the fuel leaflet.

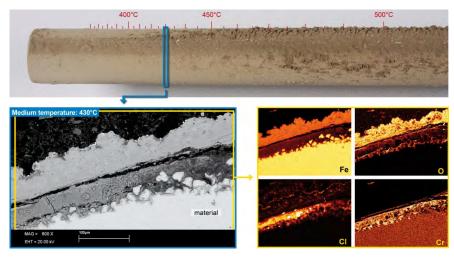


Figure 5: Temperaturerange probe used for high temperature corrosion. Temperature profile from 360 to 500°C. Time in the boiler 400 hours at superheater position. Preparation of the 430°C position (embedding, polishing) and element maps (SEM-EDX) for iron (Fe), oxygen (O),

chlorine (CI) and chromium (Cr). Finding: Formation of iron chloride at the corrosion front. Intercrystalline attack of the alloy.

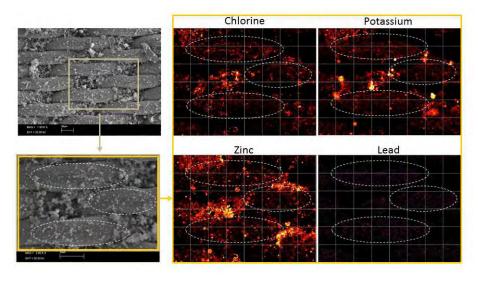


Figure 6: Particle probe (grid probe). SEM-EDX with of element maps some wire and mesh positions (dotted white lines indicate areas with wire surface where aerosols are dominant; in between, at mesh positions, the "larger" particles are dominant). Findings: Aerosols formed at

wire positions indicate the presence of gaseous potassium zinc chloride. Some traces of lead are visible as well. Zinc, potassium and chlorine also form "larger" particles (at mesh positions), but typically not in common compounds.

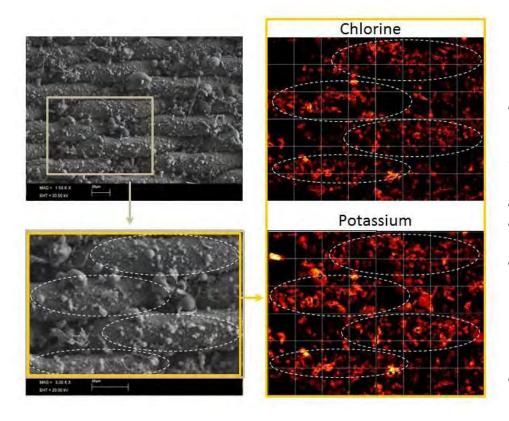


Figure 7: Particle probe (grid probe). SEM-EDX with element maps of some wire and mesh positions (dotted white lines indicate areas with surface wire where aerosols are dominant; in between. at mesh positions, the "larger" particles are dominant). Findings: Aerosols of potassium chloride at wire positions. The larger particles visible in mesh contain no chlorides. Some of the larger particles contain potassium (e.g. feldspar).

Summary

The usual characterisation of a fuel to be fired in power plants includes investigation in relation to its firing behaviour (volatile matter, fixed carbon, ash content, water, i.e. proximate analysis) and its chemical composition (elementary analysis), including minor components. But the message of this paper is to point out that elementary analysis does not provide sufficient diagnostic information if problematic processes like corrosion and fouling in the power plant are of interest. It is of high relevance to know the mineralogy of the fuel components, its proportions in relation to other compounds and the successive steps of reaction and transformation during firing and cooling in the power plant. Typically, minor components and even traces in the fuel can cause corrosion and fouling. Based on damage investigations the importance of minor fuel compounds is known. These compounds include, among others, chlorine, bromine, sulphur, ammonium, aluminium, calcium, potassium, sodium, magnesium, lead and zinc. Even gaseous fuels like hydrogen may contain minor components with relevance for corrosion, i.e. due to hygroscopic salts (deliquescence corrosion) [16 to 18], see figure 8.

Minor components are able to cause major problems in terms of corrosion and fouling. Transfer of diagnostic measures derived at waste fired power plants during the last decades should enable focusing on the important characteristics of fossil fuels, biomass and cofiring in relation to corrosion and fouling. These measures include mainly mineralogical investigations and online sampling by probes. CheMin developed several probes for this purpose.

These measures support creating a fuel leaflet for each specific fuel including advice for operational thresholds, risks for corrosion and fouling, etc. Minor components should be of major interest.

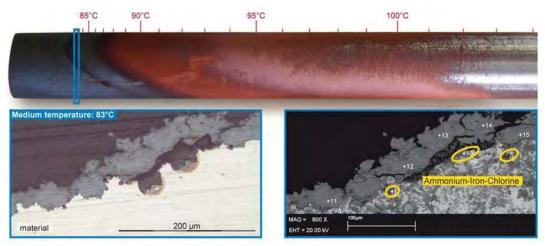


Figure 8: Temperature-range probe used for dew point corrosion and deliquescence corrosion. Fuel: hydrogen. Temperature profile from 80 to 104°C. Time in the boiler 15 hours at economiser position. Findings: Different type of corrosive attack above water dew point with thresholds at about 85°C and 100°C. In this case almost no corrosive attack above 100°C. Preparation of the 83°C position (embedding, polishing) and SEM-EDX analysis. Finding: Ammonium chloride is the corrosive agent (deliquescence corrosion).

We gratefully acknowledge the TU Dresden for the collaborative research as well as the Deutsche Bundesstiftung Umwelt (DBU) funding for a part of the work presented in this paper.

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