Corrosion of 15Mo3 carbon steel superheater tubes in waste incineration plants: A comparison between a field-returned tube and laboratory tests

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Funding information
Bundesministerium für Bildung und Forschung, Grant/Award Number: Vokos/03X3589

1 INTRODUCTION

Since the early 60s of the last century, when the demand for clean and energy-efficient waste management grew, interest in the understanding of the corrosion mechanism in waste incineration boilers has also increased, as demonstrated by numerous publications.[1–5]

Previously, chlorine has already been identified as a potent corrosive agent, for example, by Kautz et al.[6] and Miller et al.[4] Both these groups are among the first ones who provided scientific reports on failed tubes, corrosion scales, and deposits from waste-to-energy (WTE) incineration plants. They identified about 20 different chemical compounds, most of them in the deposits. They found, in particular, that the deposits consist of alkali and earth alkaline sulfates and chlorides. Furthermore, they found Pb and Zn and different oxides such as silica, alumina, and iron (III) oxides. Especially, heavy-metal chloride salt mixtures have been considered as the most critical deposit components. They can melt at low temperatures, for example, 48ZnCl2–52KCl at 250°C, and thus attack the metal tubes strongly.[5,7,8] Kautz et al. observed a gradient, especially of potassium, within the deposit, being enriched at the interface to the corrosion scale. The potassium enrichment at the corrosion scale interface is related to its high mobility, as was found by Kawahara.[9] However, Nakagawa and Matunaga[10] showed that chlorine-containing deposits have a much higher corrosive effect only in conjunction with reducing atmospheres.

The corrosion scale beneath the deposits was described by Miller et al.[4] as a mixed oxide scale of hematite Fe2O3 (outer layer) and magnetite Fe3O4 (inner...
layer). Beneath this oxide scale, an FeS scale can occur depending on local conditions, such as tube temperature or gas flow direction. At the metal surface, a layer of FeCl₂ was found. Miller et al. additionally, noted that a thin powder layer of α-Fe₂O₃ is formed at the interface between FeCl₂ and the oxide scale. Comparable results were reported by Reichel¹¹ in his work, nearly 20 years later. However, there are some discrepancies in the description of the FeCl₂ and the thin α-Fe₂O₃ scales. Reichel observed iron chloride in the form of a hydrate or as an amorphous iron compound; also, the content of chlorine was varying. Furthermore, in the same region where Miller et al. identified a thin layer of powdery α-Fe₂O₃, Reichel found fine crystalline corrosion products with high sulfur content as well as big crystals with a shape typical for magnetite. The magnetite crystals were also found at a greater distance from the tube surface but with some alteration, which led the author to the conclusion that an oxidation process from magnetite to hematite had taken place.

As represented by the square in the phase stability diagram of Fe–O–Cl in Figure 2, which represents an average atmosphere of the flue gas in the region of superheater tubes, iron chlorides are not stable under such conditions. This can, of course, change with the deposits on the superheater tube. For instance, Bramhoff et al.¹² showed for low-alloyed steels that chlorine can penetrate through the pores and cracks of the oxide scale to the tube surface where the oxygen activity is low enough for chloride formation. After the chloride is formed, it can become volatile and diffuse outward into the combustion atmosphere. On its way through the oxide scale, with increasing oxygen activity, volatile chlorides are converted into solid metal oxides. Here the released chlorine can either escape into the atmosphere or diffuse back to the metal/oxide scale interface to react again, forming new volatile metal chlorides. This general cycling reaction was first proposed by McNallan et al.¹³ and is well known as “active oxidation.”

Krumm and Galetz¹⁴ showed in their work, in line with Jacobson¹⁵ and Pasten,¹⁶ that in chlorine-containing gas with high oxygen content, such as flue gases in WTE, only metal oxides were found and the corrosive attack was not accelerated. In general, a question arises: If chlorine can penetrate through cracks and pores of a deposit, why this is not possible for oxygen so that the partial pressure decreases within the deposit—not within the oxide scales as usual for oxidation. Even after more than 50 years of research, the mechanisms responsible for the destruction of a protective oxide scale are still not clear.

In general, the chemical and physical processes that lead to the described layered sequences of the corrosion products are hardly discussed in the literature.

The aim of this study is to help understand the processes occurring within and below the deposits. For this purpose, a field-tested tube was investigated and compared to laboratory tests, which were designed to simulate the field conditions and replicate the observed corrosion products.

## 2 | EXPERIMENTAL SECTION

### 2.1 | Examination of a 16Mo3 field‐returned superheater tube after use in a WTE boiler

The analyzed superheater tube was removed after 2 years of operation from a waste incineration boiler. It had been manufactured from carbon steel 16Mo3 (composition given in Table 1) with an average wall thickness before exposure around 5.9 mm. The tube was located in the third gas pass parallel to the gas steam direction close to the back panel. During operation, the temperature of the tube surface was estimated at around 430°C while the steam temperature was around 550°C. After the removal of the tube, a section was cut out and then transported in a desiccator to prevent moisture adsorption.

Investigation of deposit and corrosion products was performed using a layer by layer method following Okoro et al.¹⁷ Here the deposit and corrosion products were removed layer by layer by a scalpel or by dry grinding and subsequently analyzed after each scale removing step. Thus, the different scales became accessible for a plan-view investigation. The different scales were analyzed by scanning electron microscopy (SEM) and X‐ray diffraction (XRD). For the XRD analysis, Co-Kα radiation was used to limit Fe fluorescence.

Furthermore, a cross-section of a tube section was prepared. For this purpose, the sample was mounted in epoxy under vacuum to prevent spallation during further treatment. In the next step, a tube segment was cut, before it was sectioned again in four further pieces, as shown in

| TABLE 1 Chemical composition of carbon steel 16Mo3 (1.5415) |
|------------------------------------------------------------|
| **Element (mass%)** | **Fe** | **C** | **Ni** | **Mn** | **Cr** | **Mo** | **Si** | **Al** |
| Nominal | Balance | 0.12–0.2 | ≤0.3 | 0.4–0.9 | ≤0.3 | 0.25–0.35 | ≤0.35 | ≤0.04 |
| Actual | – | 0.17 | 0.09 | 0.69 | 0.19 | 0.28 | 0.27 | 0.02 |
Figure 1. The residual wall thickness was measured using macrophotographs and image processing.

Each of the pieces was embedded in epoxy. All crosssections were metallographically prepared water-free, as described by Rahts et al.\[18\] and finally analyzed by light optical microscopy (LOM), SEM, energy-dispersive spectroscopy (EDS), Raman spectroscopy, and electron probe microanalysis (EPMA). To avoid charging during EPMA and SEM analysis, the samples were coated with carbon.

2.2 | Laboratory tests

16Mo3 samples provided by a commercial supplier (Quick-Metall GmbH) were exposed to a synthetic plant atmosphere containing 0.1 vol% HCl + 0.01 vol% SO2 + 8 vol% O2 + 17 vol% H2O + 10 vol% CO2 + N2 balance at 440°C. After exposure for 300 hr without any interruption, the gas flow was switched to an atmosphere with the composition 0.1 vol % HCl + 0.01 vol % SO2 + 15 ppm O2 + N2 balance, and the test was continued for another 300 hr. The experimental conditions are shown in Figure 2. In addition, tests for 300 and 900 hr without interruption were carried out in the synthetic plant atmosphere only.

The samples had a cylindrical shape with a diameter of 8 mm and a length of 15 mm. Before exposure, all samples were ground by using a 400 grit abrasive paper and finally cleaned in an ultrasonic bath with ethanol. The nominal and actual chemical compositions of the steel as a mean of five measurements by an Optic spark emission spectrometer (OES; SPECTROMAXx) are given in Table 1. In addition to the specified elements, only Cu was present in a significant amount of 0.16% (all others were <0.01%).

After exposure, the samples were prepared for metallographic examination. The preparation of all crosssections was water-free, as described above, for the actual tube. Finally, these samples were also analyzed by LOM and EPMA.

3 | RESULTS AND DISCUSSION

3.1 | Field-returned tube

Figure 1 shows clearly that material degradation was not uniform. This was also confirmed by quantitative measurements. While around three-quarters of the sample shows a high material loss of up to 2.8 mm, the rest of the sample is much less corroded. There, the maximum wall thickness loss was below 1 mm after 2 years in service. Deposits and corrosion products stuck together, but the corrosion products showed bad adhesion to the tube surface and could easily be removed for further investigation. On the tube side with high corrosion, the scale in contact with the tube surface was greyish-green with some yellow spots. It was very brittle, showing many blisters. EPMA investigations revealed a chemical composition of iron, chlorine, and oxide with the average Fe to Cl to O ratio of about 1:1.7:1.2 (see Figure 11a). Above this iron-chlorine-rich scale, a dark needle-shaped scale follows (which is indicated as FeS in Figure 3a), according to the EDS measurements summarized in Table 2, Regions 1–3.

The FeS layer was followed by a thick oxide scale with three different iron oxide modifications, as revealed by LOM investigation using polarized light. Without polarized light, there were only two different colors of the oxide scale. The inner layer was gray, and the outer one

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**FIGURE 1** Cross-section of an embedded field-returned superheater tube (16Mo3) including deposit and corrosion products [Color figure can be viewed at wileyonlinelibrary.com]
was red. It should be mentioned that the greater the local material loss, the thicker the oxide scales. The XRD results shown in Figure 4 suggests that the gray layer mainly consists of magnetite and the red one of hematite.

In contrast to magnetite with a more or less compact scale, hematite seems to consist of many wavy layers. The space between such layers increases with the distance from the metal, as can be observed in Figure 5, which represents the morphology of the different scales on the tube surface.

Some thin hematite threads were even found in the ash deposits at a distance of up to 2.5 mm from the tube surface. The deposit at the boundary to the corrosion products was red, due to the growth of hematite into the ash layer, while the rest of the deposit had a bright brown color. XRD measurements identified CaSO₄ and K₂Ca₂(SO₄)₃ as the main components (see Figure 4). Interestingly, the amount of other compounds in the ash was too small to be visible in the XRD pattern. A combination of SEM–EDS measurements and EPMA (see Figure 6) revealed further components, such as aluminum- and silicon-rich oxides, sulfates, and chlorides of mainly sodium and potassium as well as some traces of phosphorus, zinc, and lead.

In addition, the analyses of the cross-section showed an increase in chlorine concentration toward the iron-rich corrosion scale. Also, the sodium and zinc content was higher at the interface to the red scale, where chlorides and sulfates were locally enclosed by hematite.

Plan-view investigations using LOM and SEM revealed another discontinuous layer between the oxide scale and the FeS scale. It consists of octahedral crystals with a size between 10 and 100 μm, which were also observed by Reichel. The cubic crystal structure indicates magnetite, but EDS measurements summarized in Table 3 yield an iron to oxide ratio of 1:1.5 or even higher oxygen content. Such crystallites and their related EDS results are shown for example in Figure 7. With the higher oxygen content along with the cubic crystal structure, the metastable γ-Fe₂O₃, also known as maghemite, seems likely to have formed. To verify this assumption, Raman spectroscopy was carried out.

**TABLE 2** Elemental composition of selected regions within the corrosion scale (see Figure 3) determined by EDS

| Element (atm%) | Fe | S  | O   | Cl  | K  | Ca |
|---------------|----|----|------|-----|----|----|
| Region 1      | 49.03 | 48.92 | 1.87  | 0.18 | –  | –  |
| Region 2      | 49.95 | 49.81 | 0.19  | 0.05 | –  | –  |
| Region 3      | 49.49 | 49.38 | 1.02  | 0.11 | –  | –  |
| Region 4      | 38.10 | –   | 61.90 | –   | –  | –  |
| Region 5      | 38.26 | 1.02 | 60.19 | 0.53 | 0.29 | 0.34 |
| Region 6      | 37.90 | –   | 62.10 | –   | –  | –  |

Abbreviation: EDS, energy-dispersive spectroscopy.
additionally, but the spectroscopic test identified these crystals as magnetite. One reason might be that, as Egger and Feitknecht\cite{20} showed in their work, the conversion from magnetite to hematite via maghemite proceeds only up to a maximum particle size of 0.5 µm. At higher particle size, the conversion occurs directly. As the crystals found in this study are larger than 10 µm, no maghemite could be found.

Furthermore, rather unusual, features of the scale include cavities, which were found in the magnetite scale along with loose particles. The cavities were mainly distributed at the interface of the magnetite/hematite scale. In general, at this interface, the magnetite scale appeared to be dissolved into loose, needle-like particles, which could also be plated depending on the point of view. Comparable observations were made by Boettger and Umland.\cite{21} These last described observations are represented in Figure 3. The EDS results of the particles given in Table 2 (Regions 4–6) yielded an iron to oxygen ratio of 1:1.5, which is typical for hematite. Surprisingly, further investigation of the whole gray scale by quantitative EPMA analysis showed that approximately the upper half (toward the hematite scale) of the gray magnetite scale was enriched with oxide. The ratio of iron to oxygen in this region reached, again, 1:1.5. This region correlates with the area that was revealed by the polarized beam during LOM investigations as a third iron oxide modification. The details of this quantitative analysis, as well as the LOM image of the corresponding analyzed area, are shown in Figure 9a, b, respectively. Furthermore, Figure 9a clearly shows the difference in structure between the “classical” magnetite, which is widely compact, and the oxidized magnetite, which is more porous. Also, in this case, Raman measurements did not confirm maghemite, as shown in Figure 10.

A schematic composition of the corrosion products, including the deposit identified in this study, is summarized in Figure 8.

In general, at the tube side with the lower corrosive attack, besides thinner corrosion layer thicknesses, some major differences were observed. First of all, the pronounced FeS layer was missing, even though some regions with FeS were found in the oxide scale at the interface to the chlorine-rich scale. Furthermore, the cubic iron oxide crystals were not found on this side of the tube. The chlorine-rich scale was different as well and the chlorine content found in the layer next to the substrate was lower in comparison to that found on the tube side with high material wastage.

The average ratio of iron to chlorine was reduced to 1:1, and the ratio of iron to oxygen increased to 1:2. Thus, the chlorine content is half and the oxygen content is double in comparison to the tube side with a stronger corrosion attack. A comparison of the chlorine-enriched corrosion scales of the tube areas with different corrosion intensities is presented in Figure 11. From the results shown in Figure 11a, it can be assumed that at the tube side...
side with a strong corrosion attack, FeCl₂ was the main compound of the scale next to the tube surface. The small oxygen signal might be derived from absorbed water due to its hygroscopic characteristics. However, the results shown in Figure 11b indicate FeOCl as the formed corrosion product at the tube side with a lower corrosion attack. Hence, we propose that the state of the chlorine-rich scale found at the tube surface also depends on the moment of the tube’s investigation. If the oxygen partial pressure is already strongly reduced and at the same time the chlorine partial pressure is increased due to reaction within the deposit described in Section 4, a pronounced FeCl₂ scale can be formed, as was postulated by Fruehan [24] and shown by Foroulis [25] in his work. But in the case of higher oxygen partial pressure, intermediate products such as FeOCl will occur. These suggestions are in line with the phase stability diagram shown in Figure 2.

Inside the deposit, another difference was observed. Above the iron oxide-rich scales, zinc and oxide were present, followed by lead and chlorine. In general, the deposit was not the uniform layer by layer grown scale, as may be expected, but it had a villus-like shape. Generally, the deposit appeared less compact, and, in some regions, thinner in comparison to the deposited layer on the tube side showing high metal wastage.

### 3.2 Laboratory tests

Figure 12 shows a cross-section of 16Mo3, including the formed corrosion products and its related quantitative linescan determined using EPMA, after exposure in synthetic plant atmosphere at 440°C for 300 hr. These results reveal that the corrosion products consist of iron oxides with an Fe to O ratio of 1:1.3 at the inner

### Table 3 Elemental composition of selected regions within the crystalline scale (see Figure 7) determined by EDS

| Element (atm%) | Fe  | O   | S   |
|----------------|-----|-----|-----|
| Region 1       | 40.37 | 59.07 | 0.56 |
| Region 2       | 28.28 | 71.72 | –   |

Abbreviation: EDS, energy-dispersive spectroscopy.
scale and 1:1.5 at the top of the scale, as exemplified in Figure 12b for 300 hr. Such scales are typically observed as a result of “classical” oxidation. No chlorine- or sulfur-containing scales can be found. The scale shows bad adhesion, but after another 600 hr of exposure in synthetic plant atmosphere, an inherent scale (see Figure 13a) with similar corrosion products as after 300 hr formed (shown in Figure 13b). However, the corrosion scale thickness of approximately 10 µm after 300 hr of exposure remains nearly constant even after 900 hr.

After switching from synthetic plant atmosphere with a high oxygen content of 8% to the low oxygen atmosphere with 0.1 vol% HCl + 0.01 vol% SO$_2$ + 5 ppm O$_2$ + N$_2$ balance, a significant attack on the substrate as well as on the oxide scale was observed as shown in Figure 14a. From the EPMA results (Figure 14b), it can be assumed that FeOCl was formed at the surface of the iron oxide scale. The ratio of iron to oxygen is mainly 1:1.3, but in some regions, a ratio of 1:1.5 or even higher was found, mainly close to the substrate surface. The corrosion scale thickness doubled in comparison to the exposure in the synthetic plant atmosphere. Moreover, in some regions, the corrosion scale consisted of several iron oxide layers, showing small void formation between them. At other regions of the sample, even huge cavities were detected, as shown in Figure 15. Another interesting observation was the discovery of crystals that had formed at the crucible wall as shown in Figure 16. They had a comparable crystal structure to that found on the investigated field-returned superheater tube described in this study. Also, in this case, the crystals were identified as oxygen-enriched magnetite by EDS and Raman spectroscopy. At the surface of such crystals, needle-shaped compounds, containing sulfur on their surface, were found. In Table 4, the elemental composition of the regions denoted in Figure 16 is summarized.

4 | CORROSION MECHANISMS

In general, the findings confirm those reported in the literature,[4,11] but several new aspects arise from the study of the field-returned superheater tube from the...
incineration plant, such as the oxide-enriched magnetite scales as well as the crystals found at the crucible wall. As Gat\textsuperscript{[26]} and later Mann\textsuperscript{[27]} reported in their studies about chlorination of uranium oxide and iron oxides, respectively, chlorine has the potential to catalyze the oxidation of low oxygen-containing oxides, for example, from wüstite to magnetite and further on to hematite at low p(O\textsubscript{2}). In addition, chlorine has a higher electronegativity than oxygen, and thus chlorine can displace oxygen from its lattice site, especially when it is present in its elemental form, favored by the Deacon equation\textsuperscript{[28]}

\begin{equation}
\text{Fe}^{3+} + \text{Cl}^- + \text{O}^{2-} \leftrightarrow \text{FeOCl}.
\end{equation}

**FIGURE 9**  (a) Light optical microscopy image of the corrosion scale found on the field-returned superheater tube (16Mo3). (b) Concentration profile of the iron oxide scale determined using electron probe microanalysis. The corresponding analysis path is denoted in (a)

**FIGURE 10**  Raman spectra of corrosion scale at the hematite/magnetite interface found on field-returned superheater tube. The wavenumbers are given in references Ohtsuka et al.\textsuperscript{[22]} and Thibeau et al\textsuperscript{[23]}

**FIGURE 11**  Quantitative electron probe microanalysis linescan of the chlorine-rich scale next to the substrate (a) of the tube side with strong corrosion attack and (b) tube side with lower corrosion attack
Thus, after metals have reached their highest oxidation stage, chlorine can attack this metal oxide directly by forming volatile metal oxide chlorides as described by Mann\cite{27} and shown in Reaction (1). Such oxychlorides have a stability range of partial pressures according to Egger et al.\cite{20} (see also Figure 2).

Thus, in some regions, on the one hand, magnetite can locally transform into hematite, for example, in some regions

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{(a) Cross-section of a 16Mo3 sample after 300 hr exposure at 440°C in synthetic plant atmosphere and the formed corrosion scale. (b) Quantitative linescan of the corrosion scale shown in (a) determined using electron probe microanalysis}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13.png}
\caption{(a) Cross-section of a 16Mo3 sample after 900 hr exposure at 440°C in synthetic plant atmosphere showing the formed corrosion scale. (b) Quantitative linescan of the corrosion scale shown in (a) determined using electron probe microanalysis}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{(a) Cross-section of a preoxidized 16Mo3 sample after 300 hr exposure in 0.1 vol% HCl + 0.01 vol% SO\textsubscript{2} + 5 ppm O\textsubscript{2} + N\textsubscript{2} balance atmosphere at 440°C. (b) Quantitative linescan of the corrosion scale shown in (a) determined using electron probe microanalysis}
\end{figure}
with cavities or at the interface to the red hematite scale shown in Figure 3. The transformation of magnetite to hematite results in the change of the crystal structure from cubic to trigonal, which can cause scale flaws due to the resulting stress in the crystal lattice. Finally, only loose and not protective hematite plates remain at the tube surface. In this way, microcracks could be formed in the scale, which can serve as paths for corrosive species such as HCl, Cl2, or SO2. These transformation reactions can also explain the porosity and the severe spallation of the oxide scale often reported in the literature, for example, in connection with chlorine-induced corrosion by the destruction of the oxygen scale by chlorine, for example, as discussed in the study of Asteman and Spiegel. They found that the spallation of oxides did not occur, as expected, at the metal/scale interface but within the oxides. Furthermore, they could detect Cl at the fracture surface using Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) analysis.

On the other hand, hematite scales can again be attacked by chlorine to form oxychlorides, as can be seen in Figure 14. A comparison with Krumm and Galetz confirms the findings of the laboratory tests, which indicate that a significant attack on the oxide scale is only possible when the partial pressure of oxygen is decreased in comparison to the average combustion plant atmosphere.

Different authors, such as Hohmann and Born, Reichel, or Spiegel et al., attributes an oxygen-reducing property to the WTE deposit. Sulfation of alkali chlorides is one of the possible oxygen-consuming reactions in the deposit, with chlorine release occurring at the same time. The reaction, which analogously applies to KCl, can be described as follows:

\[
2\text{NaCl} + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}. \tag{2}
\]

Furthermore, NaCl and KCl, which were found in high concentrations at the oxide scale/deposit interface, are known as fluxing agents in metallurgy to protect metal melts from oxidation. The impact of deposit on the corrosion intensity beneath the deposit can also be seen on the actual field-returned superheater tube. At its side with higher material wastage, the deposit is more compact in comparison to the side with a lower corrosion attack. It can be assumed that the stronger the deposit is baked together, the lower the gas exchange between the plant atmosphere and the atmosphere at the tube surface and thus the lower the p(O2). A decreasing p(O2) in a chlorine-containing atmosphere leads to an increased corrosion rate. For example, in the work of Ihara et al., the corrosion rate reaches its maximum rate at a p(Cl2) to p(O2) ratio of 1:3 at a temperature of 400°C. In addition, they showed that the corrosion rate decreases again at further reduction of p(O2), which again demonstrates the strong interaction between oxygen and chlorine. In the case of a fully suppressed gas exchange, the corrosion attack can also be strongly reduced despite the high chloride contents in the deposit adjacent to the corrosion scale.

Comparing the sides with high and low material wastage provides a hint concerning the formation of the FeS layer. In the plant flue gas atmosphere, sulfides are not thermodynamically stable. Similarly, in the temperature below 700°C, SO3 is thermodynamically stable. However as the oxygen partial pressure drops within the deposit, SO2 becomes favorable and is therefore used in the following discussion of the reactions close to the surface.
As Grabke et al.\cite{36} reported, SO\(_2\) is also not able to penetrate the oxide scale in large amounts and build sulfur-containing corrosion products beneath the oxide scale. This only becomes possible after chlorine is introduced. The formation of cracks in oxide scales enhanced by chlorine at low p(O\(_2\)), as described above, allows SO\(_2\) to penetrate the oxide scale, where the p(O\(_2\)) is low enough for its dissociation. Afterward, sulfur and oxygen react separately with Fe, whereby oxygen is the stronger oxidizing agent. Similarly, the FeS grown on the oxide crystals in the laboratory tests (see Figure 16) suggest a direct transformation of FeCl\(_2\) to sulfide and magnetite by one of the following reactions:

\[
4\text{FeCl}_2 + \text{SO}_2 + \text{O}_2 \leftrightarrow \text{FeS} + \text{Fe}_3\text{O}_4 + 4\text{Cl}_2, \quad (3)
\]

\[
5\text{FeCl}_2 + 2\text{SO}_2 \leftrightarrow 2\text{FeS} + \text{Fe}_3\text{O}_4 + 5\text{Cl}_2. \quad (4)
\]

Thus, the FeS layer can only form at an advanced stage of chlorine attack and after a sufficient reduction of p(O\(_2\)). In Figure 17, the different stages of scale formation and the corresponding corrosion mechanisms are schematically summarized.

5 | CONCLUSION

Taking into account the present results in addition to the scientific findings described in the literature, the picture for the processes occurring in a superheater tube made of carbon steel and applied in a waste incineration plant becomes clearer.
At the beginning of the exposure, the tubes are exposed to an oxidizing atmosphere with a negligible impact of chlorine, as was shown by laboratory test results.\textsuperscript{[14]}

Even after some alkali chlorides have been sublimated at the tube surface, an uncritical corrosion rate can be assumed, as was proposed by Nakagawa et al.\textsuperscript{[10]} With further sublimation of particles from the combustion atmosphere at the tube surface, the oxygen partial pressure will be reduced due to various reactions such as sulfation or caking of deposit, while the chlorine activity will be enhanced. Thus, the chlorine will start to attack the oxide scale by dissolution, at the same time enhancing the oxidation of iron oxides. Through the cracks and pores formed in the oxide scale, critical species such as HCl, Cl\textsubscript{2}, or SO\textsubscript{2}/SO\textsubscript{3} can penetrate even faster to the substrate surface. Finally, an accelerated corrosion attack according to the “active oxidation” model will occur at the tube surface, as indicated by the chemical vapor deposited crystals, for example, on crucible walls in the laboratory test and by similar crystals found in the deposit of the field‐returned tube.

With further deposit growth and caking together of the deposit, further p(O\textsubscript{2}) decrease and p(Cl\textsubscript{2}) increase will be induced. Such a strong reduction in oxygen partial pressure accompanied by increased corrosion attack is confirmed by the observed FeS formation at the side of the tube showing the high material loss.

Finally, when the caking deposit has built a barrier for the gas exchange, and a sufficient chlorine pressure has been reached at the tube surface, a distinct layer of FeCl\textsubscript{2} will form. If in such cases, the exchange with the flue gas was fully suppressed, the corrosion rate should decrease.\textsuperscript{[24,35]} However, a certain exchange between the plant atmosphere and the “micro” atmosphere beneath the deposit will always occur, as the deposit in the plant is a “living system” that constantly changes over time.

ACKNOWLEDGMENTS

The authors would like to thank the Federal Ministry of Education and Research Germany (BMBF) for financing this study (Vokos, FKZ: 03X3589) and all project partners especially Ragnar Warnecke from GKS Schweinfurt for providing the field‐returned superheater tube.

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How to cite this article: Krumm L, Galetz MC. Corrosion of 15Mo3 carbon steel superheater tubes in waste incineration plants: A comparison between a field‐returned tube and laboratory tests. Materials and Corrosion. 2020;71:166–177. https://doi.org/10.1002/maco.201911091