



The implications of chlorine-associated corrosion on the operation of biomass-fired boilers

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Received 9 February 1999; received in revised form 28 January 2000; accepted 28 January 2000

Abstract

The design of new biomass-fired power plants with increased steam temperature raises concerns of high-temperature corrosion. The high potassium and chlorine contents in many biomasses are potentially harmful elements with regard to corrosion. This paper condenses the current knowledge of chlorine-induced, high-temperature corrosion and describes the potential corrosion problems associated with burning biomass fuels either alone or in blends with coal, for electricity production.

Chlorine may cause accelerated corrosion resulting in increased oxidation, metal wastage, internal attack, void formations, and loose non-adherent scales. The partial pressure of HCl in a biomass-derived flue gas, is not high enough to cause severe gas-phase corrosion attacks, but may provide scale failure and increased sulfidation of water walls in areas where locally reducing conditions occur due to poor combustion and flame impingement. The most severe corrosion problems in biomass-fired systems are expected to occur due to Cl-rich deposits formed on superheater tubes.

The presence of alkali chloride salts in deposits may cause accelerated corrosion well below the melting point of the salt. The corrosion can be severe in air but may be further enhanced by SO₂ which may cause intra-deposit sulfation of the alkali chlorides liberating HCl or Cl₂ gas close to the metal surface. In case the metal surface temperature becomes high enough for molten phases to form in the deposit, the corrosion may be even further enhanced. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Corrosion; Ash deposition; Biomass; Waste; Superheaters; Chlorine

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1. Introduction

Global warming concerns have, in recent years, fostered interest in CO₂-neutral energy sources for power production. One-year biomass crops are largely CO₂-neutral, because of their short regeneration time, i.e. CO₂ produced during combustion is relatively quickly re-incorporated in plants. Only the relatively small amount of fossil energy used in cultivation and transportation of the biomass crops contribute to a net atmospheric CO₂-increase. The inorganic fraction of the fuel is known to cause severe deposition problems. Traditionally, biomass-fired boilers have not experienced great problems with high-temperature corrosion, mainly because the metal temperature of the superheater tubes has been kept low (in Denmark below 450°C). However, a desire to raise the temperature of the superheated steam in order to improve the electrical efficiency of biomass-fired plants has introduced potential high-temperature corrosion problems. The corrosion of superheater tubes is related to the tube material as well as the chemical composition of deposits formed on the tubes. In particular, the high content of potassium and chlorine in deposits formed during combustion of straws and grasses are potentially harmful elements with regard to corrosion of heat transfer surfaces. In Table 1, a list of common superheater materials is listed. For those materials that are used in biomass-fired boilers, the maximum steam temperature allowed for each specific material is also provided in Table 1.

Biomass includes a large variety of fuels with different chemical composition and combustion characteristics. Wood has a very little ash fraction and seldom causes trouble in boilers, whereas straw and grasses contain high concentrations of alkali metals and chlorine. Most biomass fuels have relatively low sulfur concentrations compared to coal. Baxter et al. (1996) [1] report values of potassium in biomass fuels between 0.033 and 1.66 wt% (dry fuel) and contents of chlorine between 0.025 and 2 wt% (dry fuel) for 11 different types of biomass examined. Sander [2] reports potassium contents of 0.2–1.9 wt% (dry basis), chlorine contents of 0.1–1 wt% (dry basis), and sulfur contents of 0.1–0.2 wt% (dry basis) in Danish straw. Each 0.1 wt% chlorine in biomass corresponds to approximately 100 ppmv chlorine in the gas phase.

In biomass, alkali metals are primarily organically asso-

ciated or present as simple salts. This means that they are readily released to the gas phase during combustion. The thermodynamic behavior of potassium during biomass combustion is primarily influenced by chlorine and sulfur. In general, chlorine increases the volatility of potassium, which is mainly found as KCl and KOH in the gas phase. At lower temperatures, potassium forms condensed sulfates, chlorides, and silicates. In case sufficient amounts of sulfur is present in the system, potassium sulfate will be the only stable solid phase. Aspects of the thermodynamics of alkali metals during combustion of straw is described elsewhere [3,4]. In Fig. 1, a principal sketch of the potassium, sulfur and chlorine chemistry in a biomass-fired boiler is shown. Notice, that the picture provided in Fig. 1, will be affected by several factors including variations in fuel composition and boiler operation.

Biomass deposits usually have a high content of potassium, silicon, and calcium, but may also be rich in sulfur and chlorine. Especially deposits from straw-fired plants have a high chlorine content [1,4–6]. Baxter et al. [1] report chlorine contents in the superheater deposits from two Danish straw-fired plants in the range of 23–26 wt%. Chlorine contents as high as 38 wt% were found in furnace deposits from a Danish straw-fired grate [6].

Chlorine can influence the corrosion of superheater tubes in many ways. Gases containing Cl₂, HCl, NaCl, and KCl may cause a direct corrosion by accelerating the oxidation of the metal alloys, a phenomenon often referred to as active oxidation. Such gases may also influence the corrosion caused by other mechanisms, such as molten alkali sulfate corrosion of superheater alloys and sulfidation of water walls. Chlorides may also deposit on superheater tubes and thereby influence the corrosion of these. Corrosion can be caused either directly by components in the gas phase, by deposits on the superheater tubes or by a combination of these.

The aim of this literature survey is to describe the knowledge of chlorine-associated, high-temperature corrosion and the potential corrosion problems associated with burning biomass fuels either alone or in blends with coal, for electricity production. Chlorine-based corrosion is affected by the temperature and concentrations of chlorine, sulfur, alkali metals, and oxygen. The corrosion-related effects of different fuels primarily derive from these factors. Therefore, the rest of this review focuses on the mechanisms of corrosion, citing literature from coal-, waste-, and biomass combustion to illustrate these mechanisms. The discussion is presented

Table 1

Composition of common superheater construction steels. The rest of the material, in addition to the elements listed in the table, is iron. *Notes:* (1) This material contains traces of N, (2) this material contains traces of B, (3) Super304H contains 3% (w/w) Cu in addition to Fe and the elements listed. FG: fine grained

Steel	Wt%										Maximum steam temperature when applied as superheater material in straw-fired boilers
	C	Cr	Ni	Mo	W	Mn	V	Nb	Ti		
15Mo3	0.15			0.30		0.60					< 450°C
13CrMo44	0.13	1.00		0.50							
10CrMo910	0.10	2.25		1.00		0.50					
HCM2S (1,2)	0.06	2.25		0.30	1.60		0.25	0.05			
P91 (1)	0.10	9.00		1.00			0.23	0.07			
NF616 (1,2)	0.10	9.00		0.50	1.80		0.20	0.06			
X20CrMoV121	0.20	12.00	0.50	1.00			0.30				< 470°C
HCM12	0.10	12.00		1.00	1.00		0.25	0.05			
Esshete 1250	0.10	15.00	10.00	1.00		6.00	0.30	1.00			
X3CrNiMoN1713 (1)	0.03	17.00	13.00	2.25							
TP347H FG	0.07	18.00	10.00					1.00			< 540°C
TP347H FG	0.07	18.00	10.00					1.00			< 585°C
Super304H (1,3)	0.10	18.00	9.00					0.40			
NF709	0.07	20.00	25.00	1.50				0.25	0.05		
HR3C (1)	0.06	25.00	20.00					0.40			
HR6W		23.00	43.00	1.00	6.00			0.20	0.10		

in the order of gas-phase, solid-phase, and molten-based mechanisms, followed by a summary of implications for biomass combustion.

2. Thermodynamic stability of metal oxides and chlorides

The stability of metal oxides and chlorides in terms of the prevailing chlorine and oxygen partial pressures at a specific temperature can be shown in Ellingham–Pourbaix stability diagrams. A stability diagram can provide information about

which corrosion products will be thermodynamically stable at the prevailing partial pressure of O_2 and Cl_2 . Fig. 2 describes the stability of the different corrosion products from corrosion of superheater alloys (composed primarily of iron, chromium, and nickel) at 727°C. At low partial pressures of Cl_2 and moderate pressures of oxygen, it can be seen that various oxides of the metals are stable, depending on the actual partial pressure. At high partial pressures of Cl_2 and low partial pressures of oxygen, the metal chlorides become stable.

Even though metal chlorides are typically solid at superheater temperatures, the metal chlorides are characterized

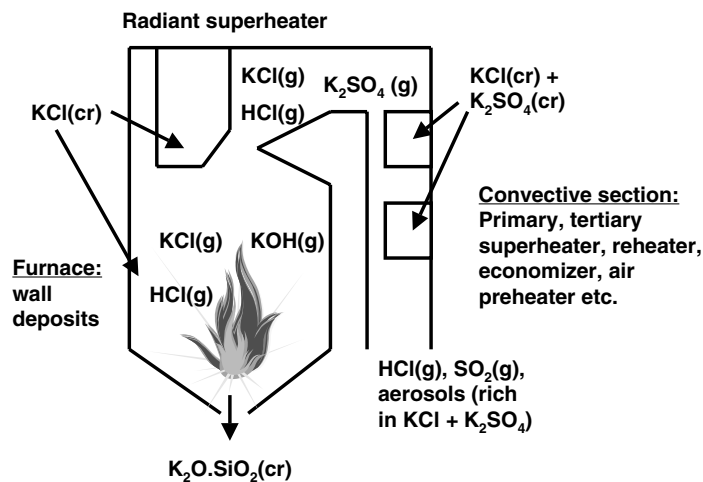


Fig. 1. Principal pathways of potassium, sulfur and chlorine in a biomass-fired boiler.

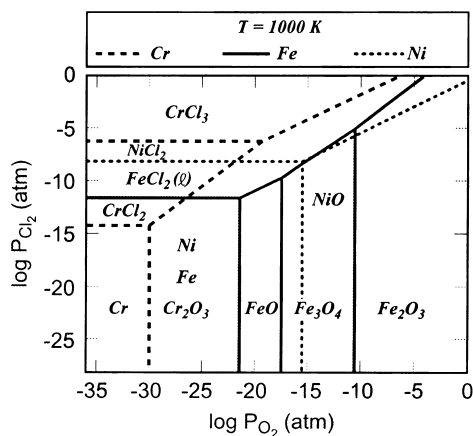


Fig. 2. Stability diagram of Cr/Fe/Ni–O–Cl at 727°C (adapted from Grabke [7]).

by having high vapor pressures even at low temperatures, which can lead to vaporization and rapid loss of metal from the surface. It has been suggested that volatilization can contribute to the corrosion mechanism when the vapor pressure of a species exceeds 10^{-6} atm [8]. Several authors agree that volatilization can be the dominant corrosion mechanism if the vapor pressure exceeds 10^{-4} atm [7,8]. The rates of mixed oxidation–chlorination may be substantially accelerated if liquid chlorides are formed which may cause fluxing of the oxide scale. The liquid metal chlorides will only be present in a narrow temperature range just above the melting point of the metal chloride. At higher temperatures the metal chlorides will evaporate. The effect of molten chlorides is discussed in detail in Section 5.

Table 2 lists the melting points and the temperatures at which metal chloride vapor pressures reach 10^{-4} atm for various species. Notice that the temperature in most systems will be higher than the melting point of ferrous chloride, FeCl_3 . Fig. 3 shows the vapor pressures of condensed chlorides as a function of temperature [7]. The behavior of elements in alloys is more complex than that of pure species, but these data qualitatively indicate vaporization and melting behaviors.

Table 2

Melting point (T_m) and temperatures (T_4) at which the chloride vapor pressure is equal to 10^{-4} atm [7]

Chloride	T_m (°C)	T_4 (°C)
FeCl_3	676	536
FeCl_2	303	167
NiCl_2	1030	607
CrCl_2	820	741
CrCl_3	1150	611

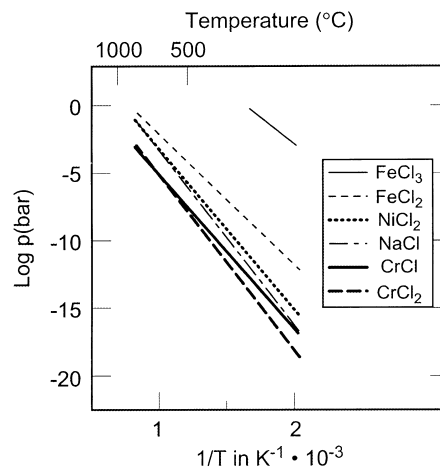


Fig. 3. Vapor pressures of condensed chlorides (adapted from Grabke [7]).

3. Corrosion associated with gaseous Cl-species

The presence of HCl or Cl_2 in the gas phase accelerates the corrosion rate of superheater alloys. In oxidizing environments this phenomenon is often referred to as active oxidation. Numerous investigations examine the influence of gaseous Cl_2 or HCl on high-temperature corrosion of different alloys [9–17]. There is a general acceptance that chlorides may cause breakdown of the normally protective surface oxide scales. The mechanisms proposed in the literature include corrosion caused by Cl_2 or HCl and corrosion caused by NaCl vapor. These are discussed separately.

3.1. Corrosion associated with Cl_2 and HCl

Gas-phase corrosion attack may be caused by several chlorine-containing species, the most common being HCl and Cl_2 . The former is the dominant Cl-species in the bulk gas, but Cl_2 may be present locally at higher temperatures and in the absence of moisture. Furthermore, Cl_2 may be formed in reducing environment by thermal decomposition of HCl [7].

3.1.1. Oxidizing conditions

When steel is exposed to an oxidizing environment at high temperatures, the metal will gradually oxidize to the thermodynamically stable oxides and form an oxide scale adjacent to the metal. This oxide layer is smooth and dense, and provides a barrier for further diffusion of oxygen and most other gaseous species to the metal. Thus, oxidation of metals is governed by a parabolic corrosion rate. However, chlorine has the ability to penetrate the protective oxide layer. Cl_2 diffuses through the oxide layer, presumably through pores and cracks, to the scale–metal interface where it reacts with the metal alloys to form metal chlorides. At the scale–metal interface, a very low oxygen potential

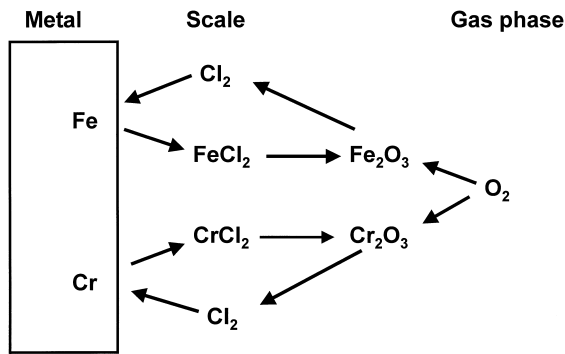
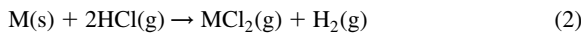


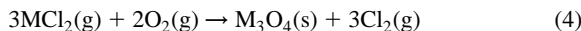
Fig. 4. Schematic drawing of corrosion caused by $\text{Cl}_2(\text{g})$.

exists (O_2 is consumed to produce metal oxides), at which volatile metal chlorides such as FeCl_2 and CrCl_2 are thermodynamically stable (Fig. 3). The HCl and/or Cl_2 may react with the metal according to reaction (1) to form metal chlorides. Metals can also react directly with HCl according to reaction (2). Metal chlorides have high vapor pressures at the metal–scale interface, and continuous evaporation may take place (reaction (3)).

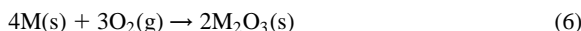


where $\text{M} \in \{\text{Fe}, \text{Cr}, \text{Ni}\}$.

These volatile metal chlorides may diffuse to the scale surface. The oxygen concentration increases with increasing distance from the metal, leading to oxidation, of the metal chlorides to solid metal oxides. The resulting oxides that precipitate from this gas-phase reaction form a very loose metal oxide layer, providing no protection against further attack. Thus, chlorine corrosion is often governed by a linear corrosion rate:



By reactions (4) and (5), chlorine is released and can diffuse to the bulk gas or back to the metal surface, and thus a cycle is formed. A graphical presentation of the corrosion mechanism is shown in Fig. 4. This cycle provides a continuous transport of metals away from the metal surface toward higher oxygen partial pressures with little net consumption of chlorides. The net reaction is thus:



Gas diffusion through the scale is believed to be the rate controlling step in the corrosion process. Grabke et al. [17] suggest that the rate is controlled by the outward diffusion of metal chlorides through the porous scale. They mention that

the penetration of chlorine species through the oxide scale is still not fully understood. The active oxidation starts with nearly no incubation time after introduction of a chlorine component, and the authors argue that neither solid state diffusion, grain boundary diffusion, nor molecular diffusion through cracks and pores of the scale are fast enough to explain the obtained results. It is concluded that somehow the chlorine itself must affect the creation of fast diffusion paths, possibly through grooves and fissures at grain boundaries [17].

Mayer and Manolescu [10] investigated how increasing concentrations of HCl changes the morphology of the protective oxide layer. With no HCl in the synthetic flue gas, a continuous nonporous scale was formed. At 0.1 vol% HCl , blisters in the Fe_2O_3 (hematite) layer occur, but the scale is still continuous. In the presence of 0.2 vol% HCl , the layer becomes porous and non-continuous. Increasing the concentration to 0.8 vol% makes the hematite layer (Fe_2O_3) completely disintegrated and the magnetite (Fe_3O_4) layer becomes irregular and porous. At 2 vol% HCl , the continuity of all the layers is destroyed and the corrosive gases have free access to the FeO layer and Fe .

Several authors report internal attack after exposure to a chlorine environment. The internal attack may be concentrated along the grain boundaries and is often associated with the formation of internal chromium carbides [8].

3.1.2. Reducing conditions

In reducing environments, where oxide phases will be absent or discontinuous, metal chlorides can form directly on the metal surface (reaction (7)):



The rate of corrosion is strongly temperature dependent because it is governed by the volatilization of the metal chloride. The rate law of corrosion of iron in HCl/N_2 is described by Chang and Wei [18]. The rate law is dependent on whether the growth of the chloride layer is fast enough to supply the amount required for volatilization. At temperatures below 500°C , the corrosion will be parabolic with time because a protective iron chloride layer is formed on the metal. At high temperatures, the weight first increases parabolically, followed by a linear decrease with time. The time for the shift, which is referred to as the critical thickness when the scale no longer grows, depends on the temperature, atmosphere, and the chloride characteristics. At higher temperature (approximately $>800^\circ\text{C}$), the growth of the chloride layer is not fast enough to supply the amount required for volatilization and the corrosion rate will show as a linear weight loss with time. Wright [19] reports that catastrophic corrosion in 100% HCl does not occur until the melting temperature of the metal chloride is reached.

Ihara et al. [20] found that adding oxygen to the HCl gas greatly accelerated the corrosion of iron due to the formation and sublimation of low melting ferric chloride (FeCl_3) by oxychlorination (reaction (8)). On the contrary, Hupa et al.

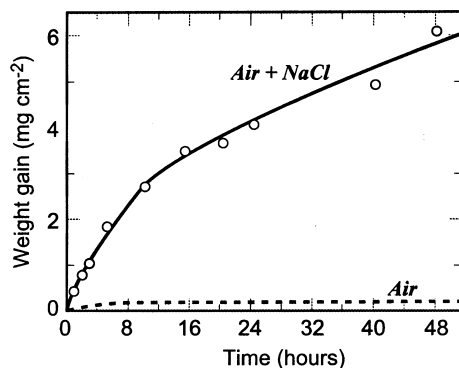


Fig. 5. Isothermal weight-gain vs. time for Ni–Ca–Al alloy at 850°C in air and in air–NaCl vapor (adapted from Hossein and Saunders [10]).

[12] have found that the corrosion rate of iron by HCl was higher under reducing conditions due to the absence of the protective oxide layer on the iron surface. They found that the reaction rate was increased by a factor of 2.5 when 2% CO was added, and then remained constant during further increase of the CO-content (up to 10% CO).

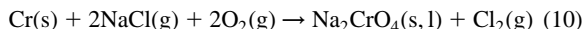
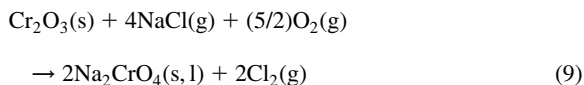


Under reducing conditions, HCl may act synergistically with both CO and H₂ to attack the oxide layer [21]. The presence of HCl may accelerate other types of gas phase corrosion, e.g. sulfidation by breaking down the protective oxides and allowing species such as H₂S to reach the metal surface. Haanappel et al. [15] exposed various steels to an atmosphere similar to coal gasification processes with and without 500 ppmv HCl. They found that the addition of 500 ppmv HCl to the oxidizing–sulfidizing environment increased the corrosion rate significantly and made the sulfide scales thick, porous, nonprotective, and nonadherent.

3.2. Corrosion associated with gaseous NaCl

Hossain and Saunders [22] studied the corrosion of Ni–Cr–Al (no Fe) alloys in the presence of 500 ppmv NaCl vapor, in air at 850°C. The authors found that NaCl in the vapor phase was able to cause a breakdown of protective oxide layers containing Cr₂O₃. NaCl vapor caused a marked increase in the oxidation rate compared to pure air, and the scale produced in the NaCl atmosphere spalled readily when the test elements were cooled to room temperature. The scale was richer in chromium when NaCl was present in the gas phase than without. The authors suggest a mechanism similar to the one described later for corrosion caused by chemically aggressive ash deposits in Section 4.2. In this mechanism, Na₂CrO₄ is formed. The chlorine gas released could then react with the alloy to form chromium or nickel chlorides. The increase in corrosion rate when adding

500 ppmv NaCl vapor to the system is shown in Fig. 5:



4. Solid phase reactions involving Cl-species in deposits

A number of experimental investigations are published on the corrosion potential of chlorides in deposits. Most of the literature concerns sodium or zinc and lead chlorides which are the most common chlorides found in deposits formed during coal respectively waste combustion. In biomass combustion, potassium chloride is the dominant chloride.

The literature consensus is that the presence of alkali chloride can cause very high corrosion rates well below the melting point of the pure salt [23–33]. The corrosion is severe, even when no components other than O₂ or air are present in the gas phase. Alexander [25] found that alkali chlorides significantly increase the rate of oxidation of both ferritic and austenitic steels at temperatures above 400°C. A number of 9/4Cr–1Mo steels were exposed to different salts in air, at 600°C, for as long as 1000 h. The results are shown in Fig. 6.

Hancock [28] described how deposition of NaCl may cause scale cracking if the salt particles are allowed to remain in contact with the surface scale at 700°C. Grabke et al. [17] conducted corrosion experiments with pure NaCl and fly ash from a waste incineration plant deposited on the scale of the steel. They found that adding NaCl on top of the steel caused active oxidation, and that the rate of oxidation was proportional to the area covered with NaCl at 500°C, which is well below the melting point of NaCl (801°C). The temperature had a great effect on the mass gain. At 450°C the oxidation rate was quite low, whereas it increased at higher temperatures. At 450°C, the corrosion rate was parabolic in time whereas at 650°C the corrosion rate was almost linear with time (Fig. 7). Caution should be taken when predicting corrosion rates from Fig. 7, because of the relatively short exposure time (100 h). Thus, the 650°C-curve could be regarded as the first part of a parabolic curve.

There are two basic ways proposed in the literature whereby the presence of chlorides in deposits may affect the corrosion:

1. High partial pressures of chlorinated species are generated in the deposit close to the metal surface, causing a corrosion mechanism similar to gas phase corrosion attack (Section 3). The generation of gaseous chlorine species could originate from sulfation of alkali chlorides or by reaction between the chlorides in the deposit and the metal scale.
2. The chlorides in the deposit may form low-temperature melting eutectics, which may flux the oxide layer.

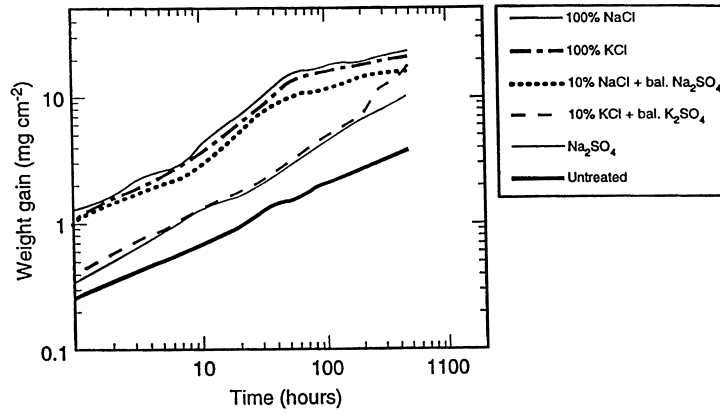
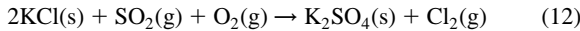
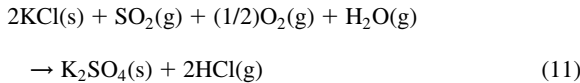


Fig. 6. Effect of different salt coatings on the oxidation of 9/4Cr-1Mo steel in air at 600°C (adapted from Alexander [25]).

4.1. In-deposit sulfation of alkali chlorides

Several authors suggest the sulfation of deposited alkali chlorides to be responsible for enhanced corrosion [26,33–40]. Deposited potassium chloride reacts with gaseous SO₂ and/or SO₃ forming condensed potassium sulfate which is consistent with thermodynamically driving forces. The sulfation reaction can be described by reactions (11) and (12), where HCl is preferably formed when water vapor is present:



The released HCl diffuses toward the metal surface to form volatile metal chloride (FeCl₂ or CrCl₂). Alternatively, HCl can be oxidized to Cl₂ according to reaction (13):

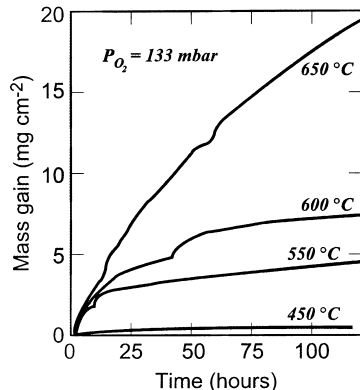
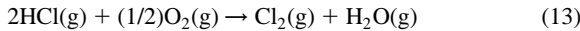
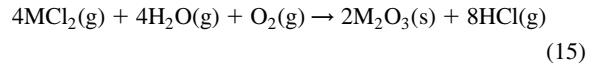
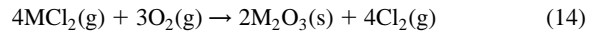


Fig. 7. Mass gain vs time after preoxidation of 9/4Cr-1Mo steel and addition of NaCl at different temperatures. Atmosphere: He + 13 vol.% O₂ (adapted from Grabke et al. [17]).

A portion of the MCl₂(g) product diffuses out through the deposit to areas with higher partial pressures of O₂ where MCl₂ may react with O₂, forming metal oxides by reactions (14) and (15):



where $M \in \{\text{Fe, Cr, (Ni)}\}$.

By these reactions, HCl or Cl₂ is released and can again diffuse towards the metal surface, reinforcing the process. Thus, the net reaction leads to a continuous transport of metal from the metal–scale interface toward the higher oxygen partial pressure in the bulk gas. After sulfation, the corrosion mechanism is similar to the one described in Section 3 for gas phase chlorine attack. By this mechanism, high partial pressures of chlorine may be formed close to the metal surface even though the concentration of chlorine in the bulk phase is low.

Grabke et al. [17] have argued that the sulfation of alkali chlorides mainly takes place near the outer surface of the deposit, and that most of the chlorine liberated by reaction (11) is lost to the atmosphere, but a small part diffuses inwards to the metal surface. The solid phase sulfation may either take place by means of SO₂ or SO₃ with the SO₃ pathway being significantly faster. Only minor concentrations of SO₃ are normally present in the bulk gas. However, SO₃ can be formed catalytically within the deposit, for example by Fe₂O₃ in the oxide layer. This would cause the most sulfation to take place in the inner part of the deposit, thus liberating gaseous Cl-species close to the metal surface.

Miller et al. [26] report laboratory experiments where carbon steels (A-106, A213-T11, Type 321) with alkali salts are exposed to a synthetic flue gas containing 250 ppmv SO₂ (80% Ar, 10% CO₂, 10% H₂O with 250 ppmv SO₂), at exposure times up to 50 h. They found that sodium chloride in the presence of flue gas was quite

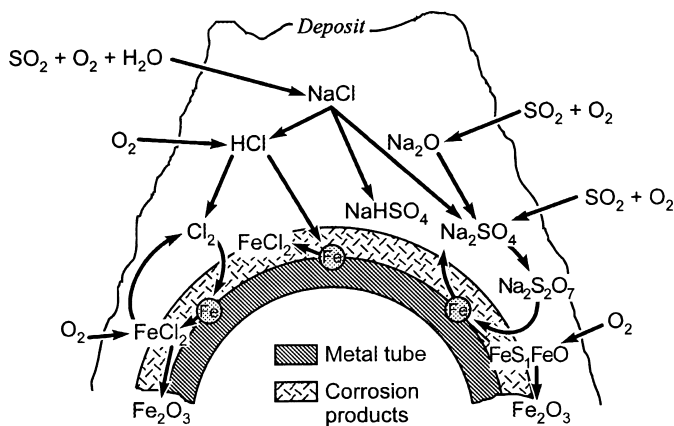


Fig. 8. Sequence of reactions occurring in incinerator deposits (adapted from Vaughan et al. [35]).

corrosive to carbon steels, and that the elimination of SO_2 from the flue gas decreased the corrosion remarkably for chloride and sulfate-chloride mixtures. Sulfide was detected in the corrosion product from the samples with NaCl deposit in flue gas indicating that a reaction involving the $\text{SO}_2(\text{g})$ was of importance since that was the only source of sulfur. They found synergia between NaCl and SO_2 on the corrosion i.e. the corrosion was more severe when the NaCl deposit and SO_2 were present simultaneously compared to the summed effect of NaCl deposit and $\text{SO}_2(\text{g})$, being present individually. Thus, the Cl-content in the deposit and SO_2 in the flue gas are important factors in the corrosion reaction, probably through a synergistic mechanism. The authors suggest the generation of HCl by a solid phase sulfation of NaCl (analogous to reaction (14)) in the deposit.

These findings are similar to the ones of Gotthjaelp et al. [33] who found that the presence of both aggressive gases (200 ppm HCl, 300 ppm SO_2 in oxidizing conditions) and ash deposit (mainly consisting of KCl and K_2SO_4) increase the corrosion rate synergistically. Gotthjaelp et al. [33] propose that the sulfation of KCl in the deposit by SO_2 and O_2 is the initiation reaction for the active oxidation mechanism, because the sulfation can only occur when both deposits and aggressive gases are present. They also found that the austenitic specimens embedded in ash deposits (from a straw-fired power plant) at 600°C corroded faster in a flue gas at 800°C than at 600°C . Sanicro 28 showed improved resistance to corrosion attack compared to Sandvik 8 LR30, probably due to the higher content of nickel and chromium. For Sanicro 28, the metal adjacent to the corrosion front was rich in nickel and depleted in iron and chromium.

Vaughan et al. [35] found that chlorine in refuse was responsible for the most serious corrosion in waste incinerators. Deposits collected on probes were high in chlorine content, ranging from 21 to 27 wt%. As the deposits aged, the amount of chlorine decreased because the chlorides were

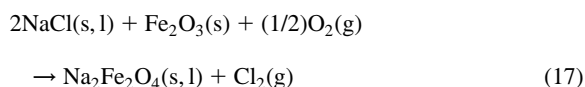
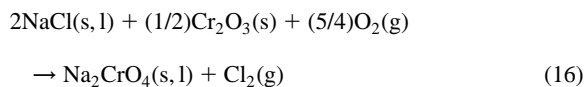
converted to sulfates. The authors suggest the in-deposit sulfation corrosion mechanism described above. The various complex corrosion mechanisms taking place under a deposit formed in a waste incineration plant were presented in Fig. 8. Potassium species should behave similar to the sodium species.

The finding of Vaughan et al. [35] agree with results reported by Salmenoja and co-workers [41] who found accelerated corrosion in the superheater section of a bubbling fluidized bed boiler burning a high-chlorine mixture of bark and biosludge. The corrosion was caused by high concentration of KCl, sulfating with time in the deposits.

The rate of the sulfation reaction is dependent on the gas-phase composition. In case sufficient sulfur is present, alkali chlorides will eventually react to form sulfates being the thermodynamically stable alkali species, at lower temperatures. However, the solid phase sulfation of alkali chlorides may be slow [4,42].

4.2. Reaction between Cl-species in the deposits and the metal scale

Instead of Cl_2 being generated by the sulfation of alkali chlorides, Grabke [7] and Spiegel and Grabke [43] suggest that the alkali chlorides react with the metal scale according to the following reactions:



Both of these reactions result in high partial pressures of Cl_2 and the corrosion mechanism can proceed as described in Section 4.1.

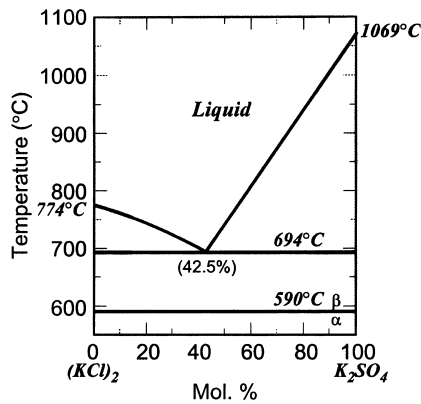
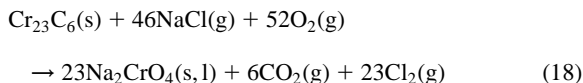


Fig. 9. Binary phase diagram of KCl–K₂SO₄ (adapted from Akopov and Korobka [46]).

4.3. Reaction between NaCl and chromium carbide

Fujikawa and Maruyama [30] studied the influence of NaCl deposit on superheater steels. It was found that the corrosion attack consisted of corrosion thickness loss and internal penetration depth. The total depth of corrosion in the alloys increased dramatically above 550°C. This was due to an increase in the internal penetration depth as well as in the general corrosion loss. The internal attack was assumed to be associated with carbides in the grain boundaries and the authors found that the internal penetration increased significantly with the carbon content in the steel. The chromium content in the steel was found to increase the corrosion at temperatures below the melting point of NaCl (801°C), but to decrease internal penetration attack. The authors [30] suggested that NaCl–vapor react with chromium carbide according to the following reaction:

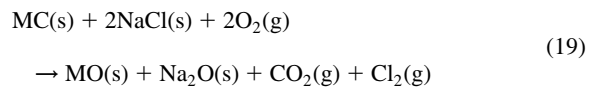


However, Fujikawa and Maruyama [30] found that chromium was a beneficial element in the steel above the melting point of NaCl.

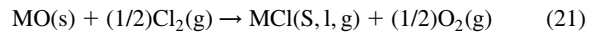
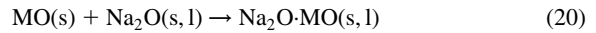
Hiramatsu et al. [31] studied the influence of NaCl coatings on stainless steel below the melting point of NaCl. The results agree well with the ones from Fujikawa and Maruyama [30]. Furthermore, Hiramatsu et al. [31] were able to detect Na₂CrO₄ as a corrosion product.

The interaction of NaCl with a number of metal carbides in oxygen was studied by Mobin and Malik [44] in the temperature interval 627–927°C using a microbalance (TGA). Iron and chromium carbide initially lost and then gained weight. The initial weight loss, it was postulated, resulted from reaction (19), where gaseous Cl₂ and CO₂ are liberated. The formation of Cl₂ and CO₂ was verified

by identification of Cl₂ and CO₂ by gas analyzers:



The Na₂O formed, may dissolve metal oxide to give sodium metal oxide, e.g. Na₂CrO₄, and Cl₂ evolved may react with metal oxide to form metal chloride according to reactions (20) and (21):



Some of the metal chlorides may evaporate resulting in a smaller weight gain.

5. Reactions involving molten Cl-species

Pure potassium chloride has a melting point of 774°C, but can form low-temperature eutectics together with several other substances. Molten phases increase the corrosion rate, and the presence of a liquid phase on the surface of a metal is usually necessary for high corrosion rates [45]. Kofstad [45] lists two principal reasons for this:

1. Chemical reactions may be faster in a liquid phase than as solid–solid reactions.
2. A liquid phase provides an electrolyte, or a pathway for ionic charge transfer, for the electrochemical attack.

Potassium forms low melting point eutectics with a variety of chemical species. For example the eutectic temperature between potassium chloride and potassium sulfate is 694°C (Fig. 9).

Potassium chloride also forms a low-temperature eutectic with iron and chromium. KCl forms low temperature eutectics with FeCl₂ and CrCl₂ at temperatures of 355 and 470°C, respectively. KCl forms very low-temperature eutectics with FeCl₃ as low as 202–220°C. A local liquid phase could be formed at the deposit–metal interface as potassium chloride in the deposit reacts with the scale or metal. The melting points of pure substances and eutectic points of binary systems of interest are summarized in Table 3. Fig. 10 shows the binary system FeCl₂ and KCl.

Paul and Daniel [32] studied chromia-scale and iron-oxide scale forming alloys in the laboratory using simulated ash deposits and flue gases at 316°C. They have found that rapid corrosion in molten chlorides was favored by oxidizing conditions and retarded by reducing conditions, with alternating flue gas compositions causing intermediate corrosion attack. However, this effect may be due to 1000 ppm SO₂ present in the oxidizing gas but absent in the reducing gas. Furthermore, both flue gases contained 1000 ppm HCl together with various concentrations of O₂, CO₂, CO, N₂, H₂, and H₂O. The authors explain their findings by the formation of molten

Table 3

Melting temperatures of eutectic temperatures for different pure species and binary mixtures. (1): Shinata [47]. All other data are from Jenz et al. [48]

System	Melting/eutectic temperature (°C)	Composition at eutectic point (mol% alkali)
NaCl	801	
KCl	772	
FeCl ₂	677	
FeCl ₃	300	
NaCl–FeCl ₂	370–374	~56
NaCl–FeCl ₃	151	45.3
KCl–FeCl ₂	340–393	45.8–91.8
KCl–FeCl ₃	202–202	24–47
CrCl ₂	845	
CrCl ₃	947	
NaCl–CrCl ₂	437	53.7
NaCl–CrCl ₃	544–593	68–95
KCl–CrCl ₂	462–475	36–70
KCl–CrCl ₃	700–795	54–89
Na ₂ CrO ₄	792	
K ₂ CrO ₄	980	
NaCl–Na ₂ CrO ₄	557	
KCl–K ₂ CrO ₄	650	68.4
Na ₂ Cr ₂ O ₇	356.7	
K ₂ Cr ₂ O ₇	398	
NaCl–Na ₂ Cr ₂ O ₇ (1)	592	30
KCl–K ₂ Cr ₂ O ₇	366–368	25–27.5

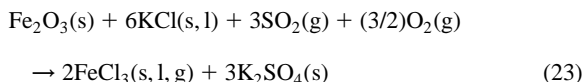
chloride salts (e.g. FeCl₂) which cause an anodic dissolution of metal in the molten salt [33]. The stainless steel was found to be quite resistant to the ZnCl₂ + KCl mixture whereas it corroded rapidly in the NaCl + FeCl₂ + KCl mixture, and the authors conclude that FeCl₂ changes the corrosive nature of the chloride melt and makes it aggressive towards stainless steel. Otsuka and Kudo [50] suggest that fluxing of Fe₂O₃ in molten chlorides is responsible for the corrosion in Japanese

waste incinerators (reaction (22)):

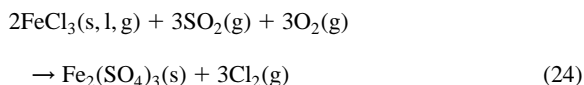


The corrosion (at 350°C) is expected to be self-sustaining for iron and chromium since these chlorides are highly volatile at these temperatures. By contrast NiO is expected to be protective since the product of the dissolution reaction is not volatile so that accelerated hot corrosion cannot be sustained.

Karissou et al. [51] have conducted laboratory experiments where mixtures of KCl with Fe, Fe₂O₃, Cr₂O₃, and a metal alloy, respectively, were heated in the presence of a 1:1 gas mixture of SO₂ and O₂. The mixture of Fe₂O₃ (or Fe) and KCl was observed to begin reacting with the gas at 310°C and the rate of reaction increased with temperature to approximately 500°C, above which the reaction decreased in the temperature range 500–650°C. When no SO₂ was present in the gas phase, no reaction was observed. X-ray diffractometry revealed the presence of K₃Fe(SO₄)₃ whereas FeCl₃ was not found in detectable amounts. Chlorine was produced in the reaction. The authors suggest that the corrosion is caused by the presence of liquid FeCl₃:



FeCl₃ can react with SO₂ and O₂ to form Fe₂(SO₄)₃(s) according to reaction (24), which could explain the absence of FeCl₃ in the corrosion product. FeCl₃ has a low melting temperature (310°C) and a high vapor pressure:



Reactions (23) and (24) combined gives reaction (25):

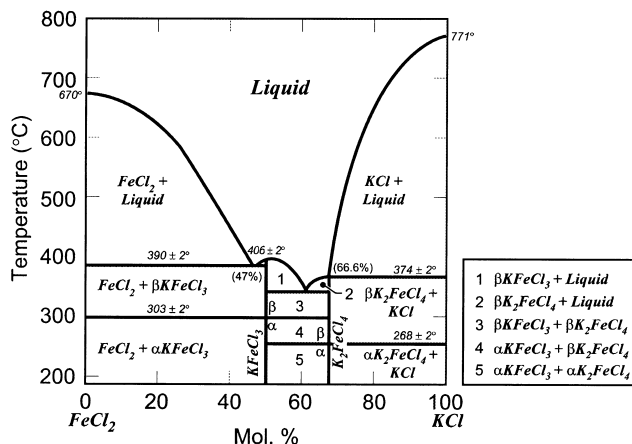
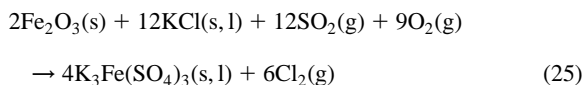


Fig. 10. Binary phase diagram of KCl–FeCl₂ (adapted from Pinch and Hirshon [49]).

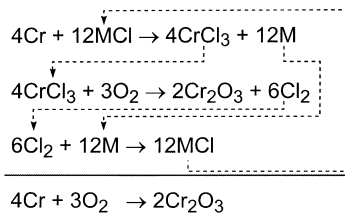
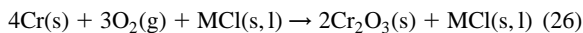


Fig. 11. Possible effect of metal chloride, MCl, on chromium, Cr–Ni alloys and stainless steels (adapted from Shinata and Nishi [52]).

A series of articles by Shinata and co-workers [29,47,52] describe the effect of NaCl on chromium, Cr–Ni alloys, and stainless steel. They have found that the presence of NaCl(s) in an oxidizing environment accelerates the oxidation of chromium and stainless steel.

Shinata and Nishi [52] investigated the oxidation and formation of liquid phases in the system NaCl–Cr using differential thermal analysis. They have found that during heating in oxygen an exothermic reaction occurs above 557°C on the DTA curve, associated with an abrupt increase in mass. No interaction between the metal and the salt occurred in argon. A distinct accelerated oxidation of chromium was observed in the presence of small amounts of NaCl, and hexavalent chromium was identified as Na_2CrO_4 in addition to Cr_2O_3 . The eutectic point in the system NaCl and Na_2CrO_4 is 557°C and it is suggested that Na_2CrO_4 is involved in the reaction mechanism by forming the eutectic with NaCl. The influence of chlorides other than NaCl on corrosion was also investigated [52]. The rate of oxidation varied with the cation, but in all cases corrosion accelerated. The authors have concluded that the Cl^- anion plays an important role in the process, while cations such as Na^+ , NH_4^+ , and Ni^{2+} only affect the magnitude of the acceleration rate. The authors conclude that NaCl appears to act as a catalyst for the accelerated oxidation, because accelerated oxidation can occur in the presence of a small amount of NaCl, and NaCl is not consumed significantly in the oxidation. The following mechanism is suggested:



The chloride takes part in various steps of this mechanism without being consumed. The reaction mechanism is not clearly understood with regard to the intermediate compounds, but the authors suggest that the mechanism could look like the mechanism depicted in Fig. 11. When applying the above corrosion mechanism to biomass-fired systems, it should be noted that the eutectic temperature in the KCl– K_2CrO_4 system is 650°C (Table 3).

The corrosion of different stainless steels in the presence of NaCl under flowing air, at constant temperature is described by Shinata et al. [29]. NaCl was found to accelerate the corrosion in the temperature range 650–900°C, where the acceleration was considerably higher above the melting temperature of NaCl. High-temperature corrosion

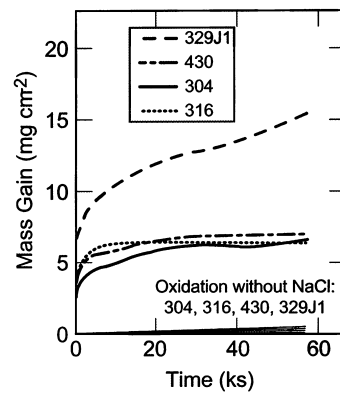


Fig. 12. Mass gain vs time for un- and NaCl-coated stainless steel oxidized at 750°C. NaCl coating: 20 mg/cm² (adapted from Shinata et al. [29]).

rates of the stainless steels investigated were found to increase about 30–120 times when coated with NaCl (Fig. 12). The chromium contained in the steels was oxidized selectively, forming a non-protective Cr_2O_3 scale. The authors found that chromium in alloys accelerates NaCl-associated high-temperature corrosion. Consequently, steels high in chromium were more severely corroded than lower chromium steels. Nickel reduces the corrosion below the melting point of NaCl, but above the melting point the restrictive action of nickel disappears.

Shinata [47] have studied the oxidation of chromium specimens coated with NaCl. He found that the oxidation mass gain curves generated could be divided into two types. Type I involved only accelerated oxidation during the initial stage, followed by the formation of a thin protective Cr_2O_3 -film. Type II, involved an accelerated corrosion continuing after the initial stage and a thick, non-protective Cr_2O_3 -film containing Na_2CrO_4 . The features of the two types of corrosion are summarized as follows:

- *Type I*: Occurred at low temperatures and with small amounts of NaCl-coatings. The initial oxidation is caused by the Cl^- -anion. Subsequently, a protective layer of Cr_2O_3 is formed and the corrosion rate decreases.
- *Type II*: Occurred at high temperatures and with large amounts of NaCl. After the initiation process, an eutectic melt is formed between NaCl and Na_2CrO_4 . Once the eutectic is formed, the oxidation reaction occurs in the melt. It is considered difficult to form a protective scale in such a melt. For the formation of the eutectic, a large amount of NaCl is necessary, because NaCl is consumed producing Na_2CrO_4 . Some of the NaCl is volatilized at high temperatures. Thus, accelerated oxidation did not continue when only a small amount of NaCl was present.

Nielsen et al. [53] report lab-scale corrosion experiments where metal test elements covered with KCl were exposed to a synthetic flue gas containing 60 ppmv SO_2 in an oxidizing simulated flue gas at 550°C. A distinguishable dense

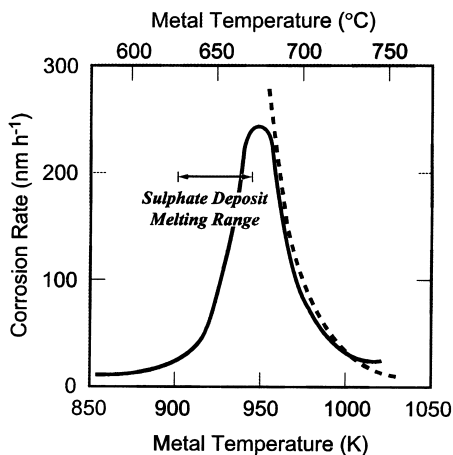
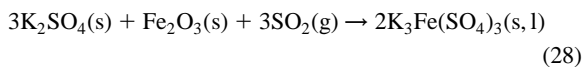
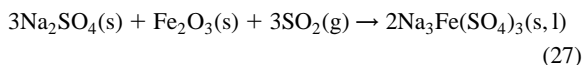


Fig. 13. Bell-shaped curve for the temperature dependence of corrosion on superheater tubes in coal-fired boilers. The dotted line is a theoretical prediction (adapted from Cutler and Raask [55]).

inner layer of K_2SO_4 with threads of iron oxide was formed on all the samples whereas the solid KCl-particles only showed little sulfation ($5\text{--}10\ \mu\text{m}$) in the rim of the particles. A corrosion mechanism is proposed where KCl forms a melt with components of sulfur and iron followed by a rapid sulfation occurring in the melt, and releasing gaseous Cl-species. The gaseous chlorine compounds may then cause chlorine corrosion, but as the dense inner layer of K_2SO_4 builds up it may cause a barrier for further corrosion by gaseous chlorine.

6. Molten sulfate corrosion

The most common form of accelerated corrosion of superheater tubes in coal-fired conventional boilers, is caused by the presence of molten alkali–metal–trisulfates. Fouling deposits on superheater tubes are often found to have an inner white layer rich in sodium sulfate, particularly when burning low-rank coals. The deposited alkali sulfate reacts with SO_2 and iron oxide to form liquid alkali–iron–trisulfate (reactions (27) and (28)):



The formation of alkali–iron–trisulfates requires a relatively high local concentration of SO_3 , which is generated by heterogeneous catalytic oxidation of SO_2 within the deposit, e.g. Fe_2O_3 catalyzes the oxidation of SO_2 to SO_3 . Corrosion caused by alkali–metal–trisulfates is well described in the literature [21,45,54–56]. This type of corrosion is generally described by what is called the basic fluxing model,

involving corrosive attack by forming a basic solute of the protective scale.

The temperature dependence of the rate of corrosion is described by the bell-shaped curve shown in Fig. 13 [55]. The bell-shaped curve can be explained by the behavior of the ash deposited on the surface of the tube and the effect of the temperature gradient in the deposit. At relatively low temperatures, below 550°C , the ash deposit is a porous layer which allows relatively free gas diffusion between the tube surface and the bulk flue gas. Corrosion proceeds at a modest rate, corresponding approximately to the temperature-dependent rate for gas-phase oxidation of the metal. The corrosion rate is dramatically increased at high metal temperatures, as the deposit forms a molten layer of alkali–metal–trisulfates next to the tube surface. The melting points of the sulfated deposit depends on both the partial pressure of SO_3 , the relative proportions of sodium and potassium, and the presence of calcium, which may have an inhibiting effect on the availability of alkalis for the formation of the alkali–iron–trisulfate [54,57].

The molten layer of alkali–metal–trisulfates modifies the oxidation potential at the outer surface of the oxide layer and allows the dissolution of the scale as metal sulfates. SO_3 is more soluble than O_2 in molten alkali sulfate. Furthermore, O_2 is consumed in the oxidation of the metals at the metal–scale interface. This increases the sulfur potential allowing sulfidation (reaction (29)) of the metal to occur. The scale formed is less protective than the one formed by normal oxidation:



The temperature gradient across the molten sulfate layer promotes continuous fluxing of the protective scale. At the scale–melt interface, metal ions are formed by a cathodic process, forming metal sulfates that diffuse outwards in the melt. Sulfates of iron and chromium have a high solubility at the scale–melt interface but, because of the temperature gradient, the solubility decreases outward in the sulfate melt, and eventually the metals are precipitated as metal oxides (Fig. 14) [21,56]. This promotes a continuous dissolution of the scale.

The right side of the bell-shaped corrosion curve (where the corrosion rate decreases with temperature) can be explained by the decreasing stability of the iron and chromium sulfates at higher temperatures [55].

The presence of chlorides can affect the molten sulfate corrosion in two ways:

1. Chlorides may cause the breakdown of the normally protective scale. Normally, SO_2 and SO_3 cannot diffuse through the scale. In case the scale ruptures, SO_x can penetrate the oxide layer through such ruptures in the scale. This may result in increased sulfate corrosion of superheater tubes.
2. The presence of chlorides in alkali sulfate decreases the melting temperature of the salt mixture, thus increasing

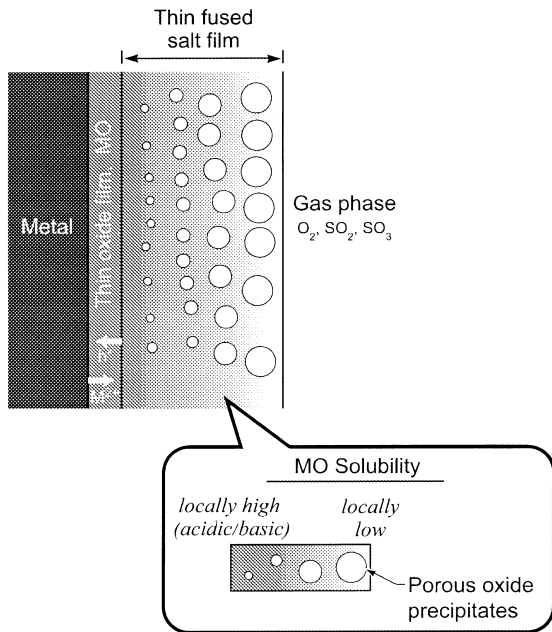


Fig. 14. Precipitation of MO to form a porous layer induced by the solubility gradient in a fused salt film (adapted from Rapp [56]).

the temperature range of corrosion, on the bell-shaped corrosion curve shown in Fig. 12.

Several authors [23–26] report significant increases in the corrosion rate when as little as 1 wt% NaCl was added to an alkali sulfate solution. The effect of small increases in chloride concentration is more marked for austenitic than for ferritic steels. The effect of different coatings of sodium salts on the oxidation of 18Cr–12Ni–1Nb steel at 650°C is shown in Fig. 15. The experiments carried out by Shirley [23], Lucas [24], and Alexander [25] were performed under isothermal conditions in air without the presence of sulfur

oxide gases. This may have an effect on the corrosion rate observed by molten sulfates, since the temperature difference across the melt plays a role in establishing continuous dissolution of the scale.

McKee et al. [58] report laboratory data concerning the role of NaCl in the mechanism of Na_2SO_4 -induced hot corrosion attack at 700–800°C. They found that when SO_2 is present together with small concentrations of NaCl in Na_2SO_4 in an oxidizing atmosphere, the alloys are rapidly attacked at around 750°C, whereas much less corrosion occurs when either SO_2 or NaCl is absent. As little as 100 ppm SO_2 with NaCl in the salt was found to be able to increase the rate of attack, compared to O_2 . The bulk of the deposit was not found to be molten, but it appeared that the salt grains in contact with the sample had formed a small amount of liquid phase. Caution has to be taken with these experiments as the short exposure time of 6 h may make them representative only of corrosion initiation.

Hancock [28] reports that the addition of sodium chloride to sodium sulfate eliminates the incubation period. Increasing the chromium content in the alloy usually has positive effects on corrosion resistance against alkali sulfates. However, the alkali metal chlorides destroy the protective chromium oxide layer and, above a threshold level of 0.1–1 wt% chlorine in the deposit, sulfur penetration occurs [25].

Cutler et al. [59] have found that addition of 500 ppm HCl to the combustion gas at combustion rig tests increased the rate of corrosion. The addition of HCl also extended the temperature range over which corrosion was observed. The authors have found that adding 1 mol% NaCl to the melt in laboratory experiments had a negligible effect on corrosion, which is contradictory to the observations of Alexander [25]. The effect of the HCl addition in the combustion rig tests may be due to an enhanced release of potassium from the coal and the subsequently deposition on the metal.

Generally, the presence of chlorine makes the bell-shaped curve in Fig. 12 wider and higher.

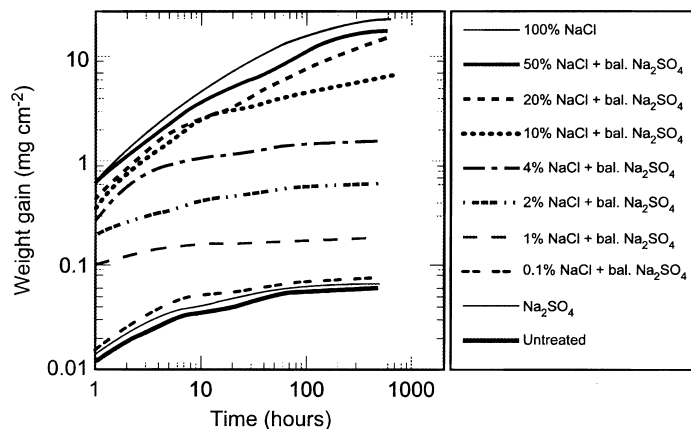


Fig. 15. Effect of coatings of sodium salts on the oxidation of 18Cr–12Ni–1Nb steel at 650°C (Lucas, 1963, adapted from Alexander [25]).

7. Potential corrosion problems in biomass-fired boilers

Biomass has a high content of alkali metals and chlorine, and most biomass fuels contain very little sulfur. The majority of potassium is released into the gas phase during combustion and is present in the gas phase mainly as potassium chloride and potassium hydroxide. When the flue gas passes through the convective pass of a boiler, it is cooled and some of the alkali metals condense on the heat exchanger tubes. Part of the alkali metals may condense on fly ash particles, which later may impact on the heat exchanger tubes. The alkali metals can either condense as chlorides or sulfates. The alkali metal of major concern in biomass is potassium.

Henriksen et al. [38] report selective chlorine corrosion when co-firing coal with straw in a circulating fluidized bed. The probes show selective corrosion, where mainly chromium and to some extent iron was removed from the metal grains and particularly from the grain boundaries, leaving these areas enriched in nickel. Chlorides were found in the degraded zone. The authors suggest that alkali chlorides are deposited on the tubes, sulfated by SO_2 thus releasing Cl_2 close to the metal surface. However, Henriksen et al. [38] did not find any signs of selective corrosion when the same proportions of straw were added to suspension-firing of coal. The authors suggest that in the suspension-firing system, the temperature in the combustion zone is high enough for the volatilized alkali metals to react with silicates and hereby be captured in a solid phase. This means that the alkali metals are no longer able to condense and thus being present on the heat exchanger tubes.

Skrifvars et al. [60] studied the corrosion mechanism in an fluidized bed burning Cl-containing fuels. In the case of biomass combustion, X-ray maps of deposits, revealed that potassium and chlorine often occur in combination. They suggest that potassium and chlorine condense from the gas phase together, probably as potassium chloride, and that the alkali chlorides decrease the melting point temperature of the fly ash, thus promoting molten phase corrosion. When burning a non-biomass, Cl-containing fuel, the potassium follows sodium and sulfur rather than chlorine and the corrosion proceeds through the chlorine containing grain boundaries. The authors suggest, based on thermodynamic considerations, that the corrosion is caused by $\text{Cl}_2(\text{g})$ or $\text{HCl}(\text{g})$, through the formation of volatile metal chlorides, as described in Section 3.

Larsen et al. [39] studied the effect of increased metal temperature on the corrosion of superheater tubes in future plants. The experiments were carried out on a 10.7 MW straw-fired grate. Only negligible corrosion of the existing superheater tubes, having a steam temperature of 450°C ($T_{\text{metal}} \approx 480^\circ\text{C}$), was observed, but corrosion probe measurements have showed that severe corrosion takes place at test probes with metal temperatures exceeding 500°C . The metal test elements were found to suffer from severe selective corrosion, where chloride attacks the

chromium and iron in the steel, leaving a skeleton rich in nickel behind.

Salmenoja and coworkers [40,41,61] report corrosion failure of superheater tubes in a bubbling fluidized bed boiler, after only six months of operation, burning a high-Cl bark-biosludge mixture. Maximum corrosion rates of up to 10 mm/year were measured for the ferritic X20 (X20CrMoV121) with a steam outlet temperature of 530°C (corresponding to a maximum metal temperature of $570\text{--}580^\circ\text{C}$). The corrosion was associated with a high content of KCl in the deposit on the downstream side of the tube and always occurred in the hottest section of the tertiary superheater where soot-blowing was effective. High chlorine concentrations were always found in the interface between the metal and scale and iron had diffused out from the metal to form an oxide layer outside the original outline of the metal. The internal corrosion was observed to take place through grain boundaries. The authors explain their findings by an observed sulfation of the KCl in the deposits which liberates HCl. The chlorine gas then acts as an activator and enhances the diffusion of iron and the formation of the iron oxide scale probably by the formation of volatile iron chlorides. The melting behavior of the deposit causing the corrosion was studied by TGA [41] and the first melting occurred around 430°C both for the down- and the upstream deposit. The next peak indicating melt formation occurred at 540°C for the downstream deposit. The melting behavior of the deposit indicated that liquid phase corrosion may be involved in the corrosion attack, even though the authors do not conclude this from their findings. Decreasing the steam temperature to 480°C had little effect on the corrosion rate and the failure occurred after eight months corresponding to a maximum rate of 5–6 mm/year. The corrosion problems were solved by changing the material to a high chromium and nickel austenitic steel (Werkstoff Nr. 1.4877) (26–28% Cr, 31–33% Ni) which showed about one-tenth of the corrosion rate of alloy X20 in corrosion probe measurements and have shown to behave well when installed in the boiler.

8. Conclusions

In summary, it is clear that chlorine under some conditions may cause accelerated corrosion resulting in increased oxidation, metal wastage, internal attack, void formations, and loose non-adherent scales. The corrosion caused by chlorine is closely connected to alkali metals, especially when present in the deposits.

When evaluating corrosion rates from different experiments, it is important to look not only at the weight change, but also at the depth of internal attack. Caution must be taken when extrapolating corrosion rates gained from short-time laboratory experiments to prediction of life times of superheater alloys.

The relatively high partial pressure of HCl in the bulk gas

in a biomass-fired boiler (up to 1000 ppmv) will probably not cause severe gas phase corrosion attacks. However, the high concentration of HCl may increase sulfidation of water-walls in areas where locally reducing conditions occur, due to poor combustion and flame impingement. This can both be of importance in biomass-fired boilers and in boilers co-combusted with coal and biomass. The high concentration of HCl and Cl₂ gas may influence the volatilization of alkali species from coal in co-fired systems resulting in higher concentrations of alkali on the superheater tubes.

Severe corrosion may occur when chlorine is present in the deposits which are in direct contact with the metal scale. The corrosion can be severe in air, but can be further enhanced by SO₂, which may cause intra-deposit sulfation of alkali chlorides releasing HCl(g) or Cl₂(g) close to the metal surface. Furthermore, alkali chlorides may react with the metal scale or with chromium carbide to form gaseous HCl or Cl₂ close to the metal. In case the metal temperature becomes high enough for the deposit to form molten phases, the corrosion may be further enhanced. Small concentrations of alkali chlorides may increase the corrosion rate caused by molten sulfates in the case of co-combustion of straw and coal.

All of the corrosion mechanisms which are reviewed here may take place in combustion systems. Which mechanism that is the dominant one will depend on the combustion environment, combustion temperature, metal temperature and the presence of other elements such as alkali metals, sulfur, silicon, and aluminum.

In biomass-fired boilers, the most severe corrosion problems is associated with deposits containing alkali chlorides mainly on the superheater tubes of the boiler. This literature review has shown that the presence of alkali chlorides in deposits may cause accelerated corrosion well below the melting point of KCl. The potential corrosion problems associated with power generation from high-alkali biomass fuels, such as straw and grasses, may be a serious issue to consider. Either the temperature of the steam must be kept low, new alloys must be found which are resistant towards chlorine corrosion, or ways to prevent potassium chloride to be present in the deposits must be found.

Acknowledgements

This project was carried out in collaboration between the CHEC research programme, Department of Chemical Engineering, Technical University of Denmark and The Combustion Research Facility, Sandia National Laboratories, Livermore, California. The CHEC research programme is financially supported by ELSAM, ELKRAFT, the Danish and the Nordic Energy Research Programmes, the Danish Technical Research Council, and the Technical University of Denmark. The Combustion Research Facility is financially supported by the US DOE

(Department of Energy), Office of Energy Efficiency and Renewable Energy's Biomass Power Program.

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