

Chloride corrosion in biomass-fired boilers – Fe-O-Cl system thermodynamic analysis

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Abstract. The most common and easiest alternative technologies for conventional fossil fuel combustion are biomass combustion and co-combustion. However, high-chlorine fuels ($Cl^{ar} > 0,2\%$) like: biomass, waste and high chlorine coals generate the risk of intensified corrosion process and a limited steel mechanical strength is observed.

The paper presents a thermodynamic analysis of chloride-induced corrosion in the Fe-O-Cl system. The ranges of the metallic, oxide and chloride phase stability are determined within the temperature range $T = 750-1000$ K. Based on the parametric equations the equilibrium concentration of gaseous phase determined by Deacon reaction are presented. The effect of H_2O concentration in the gaseous phase on high-temperature corrosion process and gaseous NaCl influence on $NaFeO_2$ formation in the passive oxide scale layer ($FeO/Fe_3O_4/Fe_2O_3$) are discussed as well. The results are correlated with available in the literature laboratory experimental data and industrial corrosion process observations. Presented thermodynamic analysis is compared with assumptions of "active oxidation" model. The results may be used for experimental research prediction and a corrosion prevention in the industry.

1 Introduction

In the last update of LCP BREF document, a significant change in emission limits, especially for fossil fuel combusting units was introduced [1]. Therefore, modernization of flue gas treatment systems in existing power plants will be necessary and the energy production costs will increase. The Polish 2020 renewables target assumes 15% share of renewable energy in gross final energy consumption. [2] Biomass combustion and co-combustion are one of the most developed RES technologies in Poland. A major problem associated with biomass combustion is a limited material strength and corrosion resistance of boiler heat exchanging surfaces at higher temperatures. To reduce negative effects, the steam temperature in biomass fired boilers is decreased to 725-825 K. [3] However, it also reduces the efficiency of the unit and as a consequence increases the energy production cost. The highest risk of the intensified corrosion process is observed during combustion of fuels with chlorine content greater than 0,2% - $Cl^{ar} > 0,2\%$ (high-chlorine coal, biomass, waste). [4] Chlorine compounds in flue gas, fly ash and eutectic mixtures agglomerated on the heat exchanging surfaces has been reported as the main sources of high-temperature chloride-induced corrosion [3, 5]. The

kinetics of the corrosion process is determined by: flue gas and fly ash deposits composition (especially the chlorine content), corrosive species concentration in a tube boundary layer and temperature gradient defined by a combustion process parameters [5]. An average gas composition for selected fuels is presented in Tab. 1.

Table 1. Approximate flue gas composition in coal, biomass and waste firing units [3]

GAS \ FUEL	COAL	BIOMASS	WASTES
O ₂ [%]	~4-5	~5-10	~5-11
CO ₂ [%]	~12	~8-15	~8-14
H ₂ O [%]	~4-16	~10-20	~10-20
SO ₂ [ppm]	~400-1200	~0-70	~0-150
HCl [ppm]	~10-50	~25-1000	~250-1300
KCl + NaCl [ppm]	-	~5-50	<120

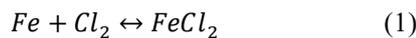
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2 Chloride-induced corrosion process of steel - an “active oxidation” model interpretation

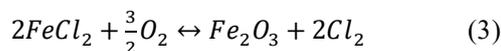
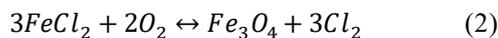
Laboratory experiments and field measurements indicate an acceleration of steel degradation process by gaseous HCl in flue gas. The analysis of gaseous chlorine compounds shows that chlorine (Cl₂) is a much more corrosive agent than hydrochloric acid (HCl). Although, chlorine in biomass and waste is released mainly as HCl and (K,Na)Cl (Tab. 1).

Chloride-induced corrosion rate of iron and selected steel grades in Ar/He-O₂-HCl atmosphere was examined in [6, 7, 8, 9, 10]. The oxidation of iron exposed to alkali and heavy metal chlorides and sulfates mixtures was discussed in [11]. The corrosion process in a solid-liquid phase with a presence of low-melting eutectic mixtures in the deposits was also investigated in [12, 13, 14, 15]. Some fundamental conclusions come from experimental results. A passive oxide scale composed of iron oxides is formed during boiler operation. The rate of oxide scale formation in Fe-O system is rather slow and it depends on steel grade. The oxygen concentration in a gas phase does not affect the kinetics of the process [7, 16]. Direct reaction of iron (Fe) and hydrochloric acid (HCl) occurs only in elevated temperatures, in reducing atmosphere with high HCl concentration [17]. However, experimental results shows that high temperature corrosion proceeds already in 5% O₂/500-3000 ppm HCl atmosphere and FeCl₂ is formed according to an active oxidation model mechanism presented in Fig. 1. [6-11] Fundamental assumptions of an active oxidation model [18, 19] include:

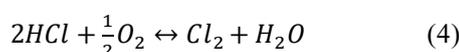
1. Diffusion of gaseous Cl₂/HCl through pores and cracks of a metal oxide scale to the scale/metal interface where iron chloride is formed:



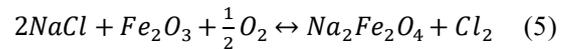
2. Volatility of FeCl₂(s)→ FeCl₂(g) in the metal wall boundary layer and further iron chloride diffusion through porous and loose oxide scale layer back to flue gas, where chloride vapors oxidation takes place:



The diffusion of Cl₂ through the Fe₃O₄/Fe₂O₃ oxide scale, formation of FeCl₂(g), which penetrates the scale backward to flue gas and final oxidation (reactions (2), (3)) form a closed cycle of reactions. Such repeatability causes a severe oxide scale destruction and steel protective properties against chloride corrosion are lost. Exothermic Deacon oxidation reaction of hydrochloric acid catalyzed by metal oxides (Weldon process) is a one of the main sources of chlorine in gas phase:



During combustion process of biomass gaseous alkali metal chlorides are released. The chlorides in gas phase can react with oxide scale and cause its further destruction and additional chlorine is formed:



A reaction cycle according to proposed model is presented below.

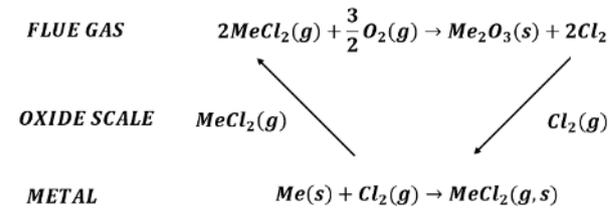


Figure 1. Cl-induced corrosion cycle described in [3, 18]

A steel oxidation process accelerated by chlorine presence in flue gas called an active oxidation model is widely described in literature. However, it determines the chloride-induced corrosion process only to Fe-Cl-O system and limits the diffusion through oxide scale layer to Cl₂ and FeCl₂(g) only. Selectivity of oxide scale layer Fe₃O₄/Fe₂O₃ in diffusion process of gas phase components between flue gas and metal surface and neglect of other gas phase components (e.g. H₂O) influence on corrosion process arouses some controversy among scientists.

3 Chloride-induced corrosion process of iron - a thermodynamic analysis

A characteristic of Cl-induced corrosion process of iron determined by [O₂-Cl₂-H₂O-NaCl] gas phase was accomplished based on thermodynamic fundamental principles, thermodynamic properties of pure substances taking part in the reaction and properties of solutions formed in a gas phase. For a random chemical reaction, the Gibbs free energy change ΔG⁰_T was determined according to relation below:

$$\Delta G_T^0 = \sum_{i=1}^{m_1} k_{B_i} \cdot \mu_{B_i}^0 - \sum_{i=1}^{m_2} k_{A_i} \cdot \mu_{A_i}^0 \quad (6)$$

Where: A_i, i = 1, ... m₁ and B_i, i = 1, ... m₂ are reactants and products respectively, k_{A_i} and k_{B_i} are stoichiometric coefficients for reactants and products in the reaction, μ⁰_{A_i} and μ⁰_{B_i} represents standard chemical potential of pure substances for reactants and products. In the calculations was suggested a relation: ΔG⁰_T = A + BT + CTln(T). The function shape comes from thermodynamic properties of pure components (C_p). The relation between Gibbs free energy change and thermodynamic equilibrium constant K was used as well:

$$\Delta G_T^0 = -RT \ln K \quad (7)$$

where: K represents a limit the process is tending to and is determined by reagents activities a_i.

$$K = \frac{\prod_{i=1}^s a_{B_i}^{k_{B_i}}}{\prod_{i=1}^s a_{A_i}^{k_{A_i}}} \quad (8)$$

Activity of components in solid or liquid phase, in a pure state is equal to unity. Although for gases, the activities of chemical reaction components might be determined by partial pressures expressed as the components mole fractions $P_i = x_i P_{tot}$ (P_{tot} – total pressure). In isothermal-isobaric conditions, the reaction gas phase composition changes linearly and a conversion from initial to final (equilibrium) state can be described by a vector parallel to the linear function [20, 21, 22, 23]:

$$x_i = x_i^0 + \tau \frac{k_i - x_i^0 \sum_{i=1}^s k_i}{\sqrt{\sum_{i=1}^s (k_i - x_i^0 \sum_{i=1}^s k_i)^2}} \quad (9)$$

where: x_i , x_i^0 – equilibrium and initial molar fraction of „i” component, $\tau \in \mathbb{R}$ – straight line parameter,

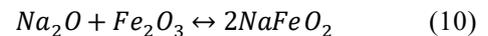
k_i – „i” reagent stoichiometric coefficient. Positive stoichiometric coefficients (k_i) are defined for products, negative for reactants and zero for reagents doesn't taking part in the reaction. The direction cosines are time independent and they are functions of initial composition and stoichiometric coefficients only. In reaction ($\sum_{i=1}^s k_i \neq 0$) the phase composition change proceed along straight lines intersecting at a so-called “characteristic point” (\bar{x}_i). In case of reaction ($\sum_{i=1}^s k_i = 0$) the direction cosine depends on stoichiometric coefficients only. Initial composition does not affect the direction cosine and a change of reagents concentration proceed along straight lines parallel to each other. The presented computational process analysis was carried out based on thermodynamic data [24, 25] and a numerical computing environment - MATLAB.

Table 2. Equilibrium composition of gaseous phase in Deacon reaction (4) defined by parametric equations.

$\sum_{i=1}^5 k_i$	i	k_i	$\bar{x}_i = \frac{k_i}{\sum_{i=1}^5 k_i}$	$x_i = x_i^0 + (\bar{x}_i - x_i^0)\tau$	T=800 K			
					x_i^0	x_i	x_i^0	x_i
-0.5	HCl	-2	4	$x_{HCl} = x_{HCl}^0 + (4 - x_{HCl}^0)\tau$	$3 \cdot 10^{-3}$	$1.311 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$2.979 \cdot 10^{-3}$
	O ₂	-0.5	1	$x_{O_2} = x_{O_2}^0 + (1 - x_{O_2}^0)\tau$	$5 \cdot 10^{-2}$	$4.960 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$4.999 \cdot 10^{-2}$
	Cl ₂	1	-2	$x_{Cl_2} = x_{Cl_2}^0 + (-2 - x_{Cl_2}^0)\tau$	0	$8.449 \cdot 10^{-4}$	0	$1.056 \cdot 10^{-5}$
	H ₂ O	1	-2	$x_{H_2O} = x_{H_2O}^0 + (-2 - x_{H_2O}^0)\tau$	0	$8.449 \cdot 10^{-4}$	0.35	0.35
	N ₂	0	0	$x_{N_2} = x_{N_2}^0 - x_{N_2}^0 \tau$	0.947	0.9474	0.597	0.597

In a temperature range T=750-1000 K the phase stability areas of iron compounds in [Fe-O-Cl] system were determined based on the thermodynamic equilibrium condition of chemical reactions. At given temperature, phase stabilities of oxides (FeO, Fe₃O₄, Fe₂O₃), chlorides (FeCl₂) and pure iron (Fe) depends on Cl₂ and O₂ concentration in gas phase. A phase stability diagram for [Fe-O-Cl] system at T=800K is presented in Fig. 2. Protection of iron against chloride and oxide corrosion at T= 800K is possible in low partial pressures of chlorine and oxygen $P_{Cl_2} = 10^{-16}$ [atm.], $P_{O_2} = 10^{-27}$ [atm.]. At partial pressure of oxygen $P_{O_2} = 10^{-8}$ [atm.] and chlorine $P_{Cl_2} = 10^{-3}$ [atm.], formation of chloride phase in contact with pure hematite (FeCl₂/Fe₂O₃) might be observed. In a full-scale biomass fired units and in laboratory experiments carried out in conditions similar to biomass combustion, the oxygen content in flue gas is around 5% and HCl is 500-3000 ppm. It is not enough to form an iron chloride phase and an iron(III) oxide - Fe₂O₃ is the stable phase in these conditions. The oxide corrosion is a main process in these conditions. Oxygen (O₂) and chlorine (Cl₂) are the main reagents in the gas phase. Introduction of gaseous NaCl with oxygen to the environment creates a new [Fe-O-Cl-NaCl] system. When oxygen is present in the atmosphere, Fe₂O₃ reacts with NaCl and 2NaFeO₂ with Cl₂(g) are formed according to reaction (5). Assuming

activity of solid phase components equal to unity ($a_{2NaFeO_2} = a_{Fe_2O_3} = 1$), the change of gas phase composition for $P_{NaCl} = 100$ ppm in an oxide corrosion area is shown in Fig. 2. Sodium oxide (Na₂O), a product of NaCl oxidation is an active component of 2NaFeO₂ formation. At T=800K, calculated activity of sodium oxide in the reaction with hematite:



equals to $a_{Na_2O} = 10^{-10}$ and corresponds to the results in [26]. When NaCl is present in the atmosphere, 2NaFeO₂ is formed on a hematite surface. Such reaction can be destructive for passive oxide layer (Fe₂O₃). During biomass or waste combustion, low-melting eutectic mixtures are formed. They may deposit on a surface of iron oxide layer and 2NaFeO₂ can dissolve in the liquid phase of the deposits. It led to an activity decrease ($a_{2NaFeO_2} < 1$) and as a consequence an iron oxide corrosion process is intensified. Proposed mechanism of high-temperature corrosion of iron in [O-Cl] atmosphere seems to be correct, however it includes gaseous NaCl reactions on boundary layer of [NaCl-O] – [Fe₂O₃/2NaFeO₂] within oxide corrosion range only. In analyzed temperature range and gas phase composition (O₂ - 5%, HCl <1300 ppm), presented above mechanism of chloride corrosion has no thermodynamic basis. According to reaction (4) HCl

introduced with oxygen atmosphere determines formation of water vapor in the system. The actual composition of the gas phase was defined by a set of parametric equations. [20-23]. The calculation results presented in Tab. 2 were obtained for initial concentrations of oxygen, chlorine and nitrogen expressed in terms of molar fractions ($x_{O_2}^0 = 5 \cdot 10^{-2}$, $x_{HCl}^0 = 3 \cdot 10^{-3}$, $x_{N_2}^0 = 0.947$). Total pressure of the system was assumed to be 1 atm. ($P_{tot}=1$ atm). The initial parameters correspond to conditions of the experiment described in [8]. Calculations for the Deacon reaction (4) show a formation of steam and chlorine in equilibrium concentrations $x_{H_2O} = x_{Cl_2} = 8.5 \cdot 10^{-4}$. At constant steam concentration $P_{H_2O}=\text{const.}$, equilibrium concentrations $Cl_2=f(O_2)$ tend to gaseous chloride corrosion with a decrease of moisture in the flue gas. According to an active oxidation model, it may cause an activation of a corrosive agent – Cl_2 . This conclusion coming from the thermodynamic calculations was confirmed by results of laboratory experiments [12].

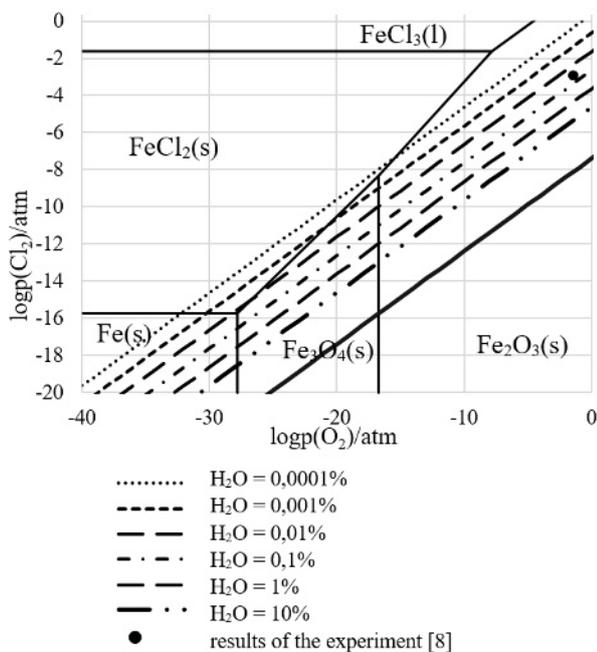
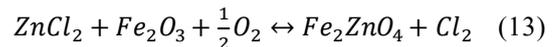
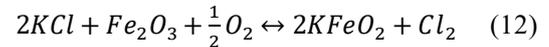


Figure 2. Phase stability diagram for Fe-O-Cl at T = 800K; HCl=1300ppm

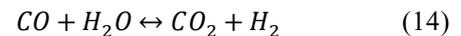
For pure iron, nickel and low-chromium alloys (16Mo3) it is confirmed experimentally that corrosion rate decrease with steam concentration increase in flue gas. However, when additional deposits rich in chlorides (39PbCl₂–50KCl–11ZnCl₂ wt.%, T=673K) are introduced to the system, anticorrosive properties of iron and chromium alloys decrease. The mechanism of the process is changed and the influence of water vapor on chloride-induced corrosion is rather insignificant. In this case steam accelerates the oxide corrosion rate. According to reactions (4) and (5), an increase of steam content in flue gas and dissolution of 2NaFeO₂ in low-melting ash components cause a decrease of hematite activity:

$$a_{Fe_2O_3} = \frac{K_4}{K_5} \left(\frac{P_{HCl}}{P_{NaCl}} \right)^2 \frac{a_{2NaFeO_2}}{P_{H_2O}} \quad (11)$$

At T=800 K, for a gas atmosphere 1000 ppm-HCl, 100 ppm-NaCl, 10 %-H₂O just above an oxide phase Fe₂O₃/2NaFeO₂ an activity decrease $a_{Fe_2O_3} < 1$ in molten ash deposits appears already at $a_{2NaFeO_2} > 10^{-3}$. Steam concentration in flue gas $P_{H_2O}=45$ atm. will prevent a dissolution of 2NaFeO₂ in the deposits. Similar to the behavior of NaCl(g), components of molten eutectic mixture KCl – ZnCl₂ may react with hematite according to relations:



In this case, the corrosion rate of iron increases ($a_{Fe_2O_3} < 1$) when in deposit molten phase activities are equal to $a_{Fe_2ZnO_4} > 10^{-7}$; $a_{2KFeO_2} > 10^{-27}$ at the gas phase saturation point (1000 ppm HCl, 10 % H₂O). It seems that the corrosion process of iron in atmosphere rich in chlorine compounds and steam has a two-way mechanism. The increase of the water vapor concentration and the presence of the low-melting components in the deposits accelerate the corrosion rate in the oxide area. Although, a decrease of steam partial pressure in gas phase activates chlorine toward gaseous chloride corrosion area. Moisture content in the flue gas depends on oxidizing/reducing combustion conditions according to reaction:



And is inversely proportional to CO concentration in the gas phase:

$$P_{H_2O} = \frac{P_{CO_2} P_{H_2}}{P_{CO} K_{13}} \quad (15)$$

In reducing conditions ($O_2 < 1\%$, $CO > 2\%$) steam concentration is decreasing. Low steam concentration promotes gaseous chloride corrosion of iron. Equilibrium concentrations for reaction (14) determined based on parametric equations method are presented in Fig. 3.

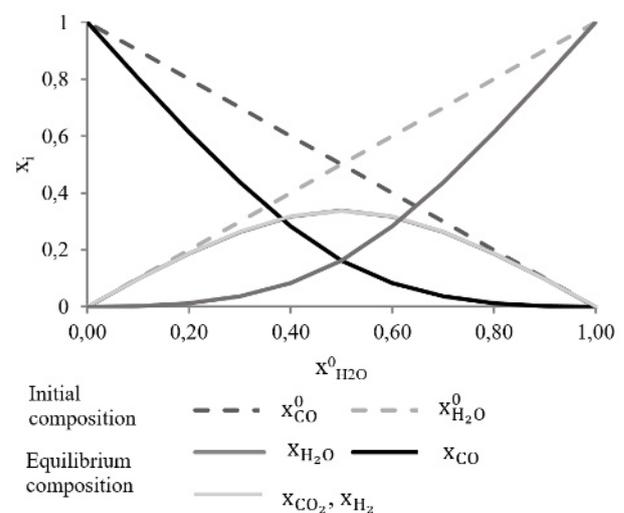


Figure 3. Equilibrium concentrations x_i gaseous phase components of the reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$; T=800K, according to parametric equations model.

4 Conclusions

Several conclusions come from the presented analysis of high-temperature corrosion of iron in gas atmosphere rich in chlorine compounds. In the temperature range $T=750-1000\text{K}$ and gas phase ($\text{O}_2 - 5\%$, $\text{Cl}_2 < 1300 \text{ ppm}$), chloride corrosion process mechanism doesn't have any thermodynamic basis. Introducing of HCl with oxygen to the system determines steam formation. At constant water vapor concentration $P_{\text{H}_2\text{O}}=\text{const.}$, equilibrium concentrations $\text{Cl}_2=f(\text{O}_2)$ tend to gaseous chloride corrosion with a decrease of moisture in the gas phase. According to an active oxidation model it may cause activation of the corrosive agent – Cl_2 . However, when deposits rich in chlorides (PbCl_2 , KCl , ZnCl_2) are introduced to the system, the influence of steam on chloride corrosion process is small. In this case steam accelerates the rate of oxide corrosion. It seems that the corrosion process of iron in atmosphere rich in chlorine compounds and steam has a two-way mechanism. The increase of the water vapor content and the presence of a low-melting ash components in the system accelerates the corrosion rate in the oxide area. Although, a decrease of H_2O partial pressure in the flue gas activates Cl_2 towards gaseous chloride corrosion area. In reducing conditions steam concentration in the system is decreasing. Low steam concentrations promotes gaseous chloride corrosion. Presented conclusions can be used for combustion processes optimization as well as in interpretation of steel chloride-induced corrosion experiments.

Acknowledgments

The present work was supported by the Polish Ministry of Science (Grant AGH No. 11.11.210.312).

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