

# A short report on the state of the Literature on the effect of KCl on the high temperature corrosion of metals at 400-500 °C

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## ABSTRACT

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## Introduction

Chemical looping combustion (CLC) has emerged as a promising technology in the quest for sustainable energy production and carbon management, specially now that the 2 °C threshold set by the Paris Agreement have been surpassed. By inherently separating CO<sub>2</sub> during the combustion process, CLC offers a highly efficient method for carbon capture with minimal energy penalties [1]. If waste/biomass is employed as a fuel in CLC systems, the process not only generates heat but also contributes to negative CO<sub>2</sub> emissions, due to the fact that the carbon in biomass is derived from atmospheric carbon, and its sequestration during CLC results in a net removal of CO<sub>2</sub> from it. Therefore, biomass fuel for the CLC presents a dual benefit of sustainable energy generation and carbon dioxide removal, positioning it as an attractive technology in addressing climate change and achieving carbon neutrality.

Alas, the introduction of biomass into the CLC environment causes severe corrosion (specially in super heaters) due to the chemically active (corrosive) species such as HCl(g), and/or alkali containing compounds such as NaCl, KCl, and K<sub>2</sub>CO<sub>3</sub>. The release of these species are unavoidable in the fuel reactor, where the biomass is burned. Unfortunately, there are evidence to the existence of these species in the air reactor as well, where it is not expected. This might pose a serious issue since the materials that are used to construct the air reactor, combined with the higher oxygen partial pressure can cause severe high temperature corrosion in the equipment. Therefore, to minimize this issue, operators need to lower the gas phase temperature of the whole system, which in turn reduce its efficiency. Hence, studying the effect of these species in laboratory setups comparable to the fuel and air reactors of CLC is valuable.

Two main mechanisms are proposed for the so-called "salt-induced high temperature corrosion". First, the "active oxidation", mechanism proposed by McNallan et al. [2] and developed by Grabke et al. [3], which propose that the accelerated corrosion of steels in the presence of HCl(g) and alkali salts are related to the formation of a subscale region containing metal chlorides, with a poorly protective, porous iron oxide surface film on it. Active oxidation is deemed to be a cyclic process, which initiated when at high pO<sub>2</sub> environment of gas/scale interface, Cl<sub>2</sub> molecules are released and then diffuse through the oxide scale where at the low pO<sub>2</sub> conditions of scale/metal interface, the formation of metal chlorides (*e.g.* FeCl<sub>2</sub>) becomes thermodynamically favorable. Consequently, due to the high vapor pressure of these metal chlorides, they diffuse through the metal oxide towards the surface (rate-controlling step) and decompose to form a porous metal oxide and Cl<sub>2</sub>, based on the following reaction:



Then, the newly formed chloride diffuse once again into the metal oxide, closing the "chloride cycle". While active oxidation is generally accepted in the literature, there are certain uncertainties associated with this mechanism. For instance, it cannot explain how the larger Cl<sub>2</sub> molecules can penetrate and diffuse through the oxide scale, but the smaller O<sub>2</sub> molecules are not able to do so. This issue creates profound complications for the usability of this mechanism, since having higher pO<sub>2</sub> at the scale/metal interface hinder the formation of volatile metal chlorides. Accordingly, the outward diffusion of much larger metal chlorides is also faced with the same difficulties. Additionally, active oxidation implicate that chlorides are concentrated in the scale/metal interface, however; chloride-rich areas have been reported in the literature [4].

Alternatively, [Folkesson et al. \[5\]](#) has suggested another mechanism, aiming to solve these issues. The so-called "electrochemical mechanism" propose that the adsorbed HCl on the surface will react with the present oxygen to form  $\text{H}_2\text{O}(\text{g})$  and  $\text{Cl}^-$ . In the case of adsorbed KCl, it reacts with  $\text{O}_2$  and  $\text{H}_2\text{O}$  forms KOH and  $\text{Cl}^-$ . Either way, the produced chloride ion then penetrates the oxide scale through the grain boundaries, reacting and producing metal chlorides throughout the scale (specially at grain boundaries) and the scale/metal interface. It is suggested that the higher corrosion rates in the presence of HCl and KCl has been related to the presence of  $\text{FeCl}_2$  in the grain boundaries that facilitate the diffusion of both metal and oxygen ions [5, 6].

In order to keep this essay focused on the possible corrosion of CLC, with a focus on the fuel reactor; only studies that are in the 400-500 °C range, and used KCl as the salt has been chosen to be considered. Although the literature is vast on the effect of KCl on the high temperature corrosion, the studies that fulfilled the aforementioned criteria is actually very numbered and are presented in a chronological order.

## Studies

The first studies on biomass boilers started with [Michelsen et al. \[7\]](#), where the high-temperature corrosion of a 10MW straw-fired boiler was investigated [7, 8]. They concluded that corrosion is negligible below 450 °C but becomes significant above 520 °C. Interestingly, they observed that at temperatures higher than 490 °C, selective leaching of chromium (and, to some extent, iron) occurs. Following this initial research, [Uusitalo et al. \[9\]](#) expanded the investigation to include the corrosion behavior of T22, austenitic steel (Fe-27Cr31Ni3.5Mo), and several other types of steel in a 500 vppm HCl, 20%  $\text{H}_2\text{O}$ , 3%  $\text{O}_2$  environment at 550 °C for 1000 hours. They observed that T22 developed a 100  $\mu\text{m}$  scale with severe spalling, and a weight gain of 160  $\text{mg.cm}^2$  was reported. The outer surface layer consisted mostly of iron oxides, while some chromium and molybdenum were present in the inner layers. On the other hand, the studied austenitic steel formed a distinct two-layer surface oxide film. A cracked and discontinuous chromium oxide inner scale, with a maximum thickness of 20  $\mu\text{m}$ , was observed. The porous outer layer, with a maximum thickness of 50  $\mu\text{m}$ , was also identified. The composition of this layer varied significantly; however, chlorine contents up to 5% were detected. The author of the present essay suggests that the presence of chlorine content in the outer film can be linked to the proposed "electrochemical mechanism," although it was not yet published at the time.

In 2006, [Cha and Spiegel \[10\]](#) used an atomizer to study the local reactions of KCl particles with the surfaces of iron, nickel, and chromium. Several aspects of this work should be mentioned in the context of the present report. First, the samples were initially impacted with KCl and then exposed to the corrosive environment. No simultaneous exposure to salt and the corrosive environment was conducted. Second, the exposure time was on the order of minutes, with a maximum of 40 minutes. They concluded that KCl reacts with iron at temperatures as low as 300 °C, while reactions between KCl and nickel and chromium occurred at 500 °C. In the same year, [Sroda and Tuurna \[11\]](#) exposed T22, Sanicro28, TP347H, Alloy 625, and some other types of steel to an 8%  $\text{O}_2$ , 15%  $\text{H}_2\text{O}$ ,  $\text{N}_2$  Bal. environment for 360 hours at 500-600 °C. The addition of 2000 vppm HCl and 200 vppm  $\text{SO}_2$  was also studied. For ferritic steels (T22) in the clean environment, they observed an outer hematite ( $\text{Fe}_2\text{O}_3$ ) layer, a middle magnetite layer ( $\text{Fe}_3\text{O}_4$ ), and an inner layer of iron-chromium spinel ( $(\text{Fe,Cr})_3\text{O}_4$ ). Sanicro28 and TP347H formed a double-layered surface film, with an inner (Cr, Ni, Mn)O film and an outer magnetite film. Alloy 625 was only partially corroded, and no cross-section analysis was performed on these samples. Additionally, when HCl was introduced to the environment, chlorine was found at the metal/scale interface as well as throughout the scale; which was related to the "active oxidation" mechanism.

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In 2011, T. Jonsson and N. Folkesson [12, 13] studied the impact of KCl on the high-temperature corrosion of T22 in two separate studies. In the first study, [Folkesson et al. \[13\]](#) studied the corrosion behavior of T22 in 5%  $\text{O}_2$ , 40%  $\text{H}_2\text{O}$ , at 400 and 500 °C, for durations ranging from one hour to one week. The authors reported an acceleration of corrosion in the initial stages of exposure, specifically at 500 °C. Interestingly, at 400 °C, the presence of KCl had a more noticeable effect than at 500 °C, as after 168 hours, the weight gains of samples with and without KCl were comparable. The "electrochemical mechanism" was also introduced in this paper. In the second study, [Jonsson et al. \[12\]](#) investigated the initial stages of KCl-induced high-temperature corrosion of T22 at 400 °C. They reported that the formation of KCl/ $\text{FeCl}_2$  melt rapidly spreads both species on the surface. Consequently,  $\text{FeCl}_2$  decomposes into iron oxide and HCl, while KCl reacts with  $\text{O}_2$  and  $\text{H}_2\text{O}$  at the gas/oxide interface and forms KOH,  $\text{KFeO}_2$ , and  $\text{Cl}^-$ . Hence, these two studies formed a strong foundation for future studies discussed in the following paragraphs.

In another interesting investigation, [Sui et al. \[14\]](#) investigated the effect of KCl, NaCl, and  $\text{K}_2\text{CO}_3$  on the corrosion behavior of Sanicro 28 at 450 and 535 °C. It is worthwhile to mention that in this paper, the samples are not exposed to a corrosive atmosphere; rather, the samples are in direct contact with the salt, and with the use of a counter/reference electrode, the corrosion current is measured. The measured current is very similar to the corrosion rate graphs found in the literature. They concluded that in the presence of cations, more chromate formation occurs, especially in the case of potassium ions. Anions, on

the other hand (specifically chloride and carbonate), accelerated the corrosion rates. The surface was later found to be more permeable to chloride ions than to carbonate ions.

By 2019, most of the literature focused on the initial stages of KCl-induced high-temperature corrosion. To address this issue, [Olivas-Ogaz et al. \[15\]](#) studied the effect of dilute amounts of KCl on pre-oxidized T22, which was exposed to an environment containing 5% O<sub>2</sub> and 20% H<sub>2</sub>O at 400 °C for 24, 48, and 168 hours. The authors reported that oxide thickness and microstructure significantly influence Cl<sup>-</sup>-induced corrosion, as the breakaway mechanism is diffusion-controlled. However, they found no correlation between incubation time to breakaway corrosion and scale microstructure. To further understand the shortcomings of the "chloride cycle," the permeation of chloride into the oxide layer (from either HCl or KCl) was mechanically modeled by [Cantatore et al. \[16\]](#). The authors divided the process into an outward-growing hematite layer and an inward-growing magnetite layer, proposing that chloride can use the oxygen vacancies produced at the metal/magnetite interface to form FeCl<sub>2</sub>. Unfortunately, this paper does not investigate the effect of Fe/Cr mixed spinels, which are commonly observed in other types of steel.

In 2020, [Persdotter et al. \[6\]](#) studied the crack formation mechanism on the surface of T22, at 400 °C when the samples were exposed to 20 % H<sub>2</sub>O, 5% O<sub>2</sub> for 24 hours. They reported that the existence of KCl on the surface increased the diffusion rate of species through the bulk/grain boundaries by lowering the required activation energy. Different layers of growth were observed and it was concluded that KCl also reduces the adhesion of the oxide scale. In another paper, [Larsson et al. \[17\]](#) found that in the presence of KCl, the corrosion process is accelerated by an electrochemical mechanism involving the formation of chemisorbed KOH at the surface and iron chloride (FeCl<sub>2</sub>) beneath the oxide scale. Adding HCl significantly increased the corrosion rate initially, but it slowed down afterward due to the insulating nature of the FeCl<sub>2</sub> layer, which disrupted the electrochemical process between the surface and the metal substrate.

## Conclusion

**Table 1.** Caption

Reference Num.	Year	Temperature °C	Materials	KCl Conc. $mg.cm^{-2}$	Exposure Duration Hours	O <sub>2</sub> Conc. (%)	H <sub>2</sub> O Conc. (%)	HCl Conc.	CO <sub>2</sub> Conc. (%)	Notes
[9]	2003	550	T22, One austenitic steel and several clad coated steels	—	100-400-1000	3	20	500 vppm	14	—
[10]	2006	300	Pure Fe, Cr, Ni	Atomizer was utilized	< 40	20	—	0,05 %	—	—
[11]	2006	500, 600	T22, San 28, Alloy 625, and others	—	< 360	—	—	—	—	—
[13]	2011	400, 500	T22	0,1	1, 24, 168	5	40	—	—	—
[14]	2016	450, 535	San 28	A salt pill was put on the sample	2	—	—	—	—	—
[12]	2011	400	T22	—	1	Very low	Very low	—	—	An ESEM study
[1]	2019	400	T22	0,1	24, 48, 168	5	20	—	—	Prexoidized
[16]	2019	400	T22	—	—	—	—	—	—	Modelling
[6]	2020	400	T22	0,1	24	5	20	—	—	—
[17]	2020	400	T22	0,1	24	5	20	—	—	—

## Acknowledgements

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