Materials and Corrosion

ARTICLE OPEN ACCESS

The Impact of Humidity on High Temperature Corrosion of Ferritic-Austenitic Model Alloys in the Presence of KCL

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Received: 26 July 2024 | Revised: 16 October 2024 | Accepted: 2 December 2024

Funding: The study was supported by the Helmholtz-Zentrum Berlin für Materialien und Energie (192-08532-ST and 202-09765-ST) and Deutsche Forschungsgemeinschaft (416318834).

Keywords: deposit induced corrosion | high temperature corrosion | humidity | Rietveld analysis

ABSTRACT

This study investigates the impact of humidity on the corrosion behavior of an Fe–18Cr–12Ni alloy in environments containing KCl, as a deposit, and either laboratory air or SO₂ at 560°C for exposure times up to 330 h. Corrosion characteristics were analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) with subsequent Rietveld analysis to quantify the obtained reaction products. Samples exposed to lab air and KCl showed half the weight gain in humid air than in dry atmospheres (0.80 $\frac{\text{mg}}{\text{cm}^2} \pm 0.06 \frac{\text{mg}}{\text{cm}^2}$ at 30.00% $\pm 0.07\%$ relative humidity (r.H.) vs. 1.63 $\frac{\text{mg}}{\text{cm}^2} \pm 0.01 \frac{\text{mg}}{\text{cm}^2}$ at 1.58% $\pm 0.09\%$ r.H.). The surface porosity, as determined by image analysis of SEM surface images, was lower for the samples exposed to humid air compared to dry air (5.5% $\pm 2.1\%$ vs. 11.0% $\pm 2.2\%$, respectively). In a SO₂ containing environment humidity decreased the scale thickness for deposit induced corrosion significantly by one order of magnitude, reflected by a low amount of oxide phases such as Cr₂O₃, Fe₂O₃, and Fe₃O₄. This study shows that humidity present in a hot gas containing other corrosive species, such as SO₂, can be beneficial for KCl deposit induced corrosion of stainless steels.

1 | Introduction

The importance of renewable energy has risen over the past years with increasing public awareness of climate change and a strive for energetic independence of fossil fuels [1–3]. One solution is the usage of biomass as a substitute for coal in power plants [4]. In the European Union, Bioenergy consumption has increased by 69% between 2005 and 2016, supplying $\approx 60\%$ of the renewable energy in 2016. By 2030, the renewable energy share is supposed to increase from 17% (2016) to 32% [1]. To further increase the renewable energy share, transitioning coal-powered to biomass-fired power plants is an option. Biomass has a much lower life cycle carbon footprint

(i. e., wheat straw at 22.73 $\frac{g}{MJ}$) than coal (117.01 $\frac{g}{MJ}$), mainly due to the CO₂ consumption during the plant's growth [5]. Therefore, the carbon emissions for power generation can be lowered to about $\frac{1}{5}$ by substituting coal with biomass.

The transition to biomass has the distinct advantage that only the feed apparatus of the coal power plant needs to be modified, keeping retrofitting expenses low, while providing benefits to the environment [3]. However, the addition of biomass also brings challenges since the chemistry of biomass is different from coal, thus the flue gas composition is different as well and care must be taken in regard to the biomass source [6]. Biomass, as opposed to coal, can contain significant amounts of K, Cl,

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and H_2O in addition to SO_2 [6]. KCl and H_2O are linked individually to accelerated corrosion rates [7–10].

Indeed, super heater tubes show a large corrosion attack when exposed to biomass firing due to the difference in chemistry. The steel needs to withstand this corrosive environment, either through alloying changes or careful selection of the biomass source. This poses several challenges that need to be understood and met. Super heater tubes need to withstand attacks from common combustion gases like SO_2 and H_2O as well as solid deposits like KCl.

Meißner et al. proposed the reactions:

$$8KCl + 2Cr_2O_3 + 3O_2 + 2H_2O \rightarrow 4K_2CrO_4 + HCl \quad (1)$$

$$8KCl + 2Cr_2O_3 + 5O_2 \rightarrow 4K_2CrO_4 + Cl_2$$

$$\tag{2}$$

These reactions show that the protective Cr_2O_3 can be attacked by KCl in both dry and humid atmospheres, with the main difference being the produced Cl species - HCl in humid and Cl_2 in dry atmospheres [11].

The behavior of 304L (a similar Fe–18Cr–10Ni steel) in a KCl + SO_2 + H_2O atmosphere has been previously studied by Karlsson et al. at 600°C [12]. Karlsson found that the corrosive properties of KCl relied on the destruction of the protective Cr_2O_3 by reacting to K_2CrO_4 . SO_2 functions as a corrosion inhibitor by allowing both the reaction of KCl to K_2SO_4 and rapidly (< 30min) converting K_2CrO_4 to K_2SO_4 [12]. These experiments show that in a humid atmosphere the protective K_2SO_4 layer can form, however the specific effect of water on corrosion behavior has not been established.

Therefore an understanding concerning the effect of humidity in combination with SO_2 and KCl needs to be established to minimize corrosion losses and enable better operating procedures for power plants.

In this work, the impact of humidity in the presence of KCl deposits on corrosion is examined using a Fe–18Cr–12Ni model alloy, through the use of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) with subsequent Rietveld analysis to quantify the reaction products after deposit and gas exposure. The aim of this study is to identify distinct reasons for accelerated or limited corrosion of a ferritic-austenitic alloy with respect to humidity content in a SO $_2$ containing hot gas.

2 | Materials and Methods

Studying the effects of corrosion on multi component systems, such as steel, is difficult. TP347H is a commonly used steel for super heater tubes with high amounts of Cr and Ni as well as other alloying elements like Mn, Si, C, P, S, and Nb [13, 14]. To reduce the chemical complexity and reduce the amount of variables in the experiments the model alloy Fe-18Cr-12Ni was chosen, reducing the amount of variables in the steel from 9 to 3.

Coupons with dimensions $20 \times 10 \times 3$ mm were cut from a model Fe–18Cr–12Ni alloy (vacuum melted, hot and cold rolled,

elemental purities: 99.95% Fe, 99.9% Cr, 99.9% Ni), then ground to grit size P1200 using SiC paper. The steel has been shown to have a ferritic-austenitic microstructure via etching and XRD measurements [7]. The composition was measured using electron probe micro analysis (EPMA) by averaging 31 individual measurement spots. The values are shown in Table 1.

Two distinct exposure experiments were conducted using this steel:

1. To identify the initial corrosion behavior in dry and wet air, short-term experiments were conducted at the synchrotron facility BESSY II [15].

For these experiments the steel was sprayed with a H₂O/KCl solution while being heated to > 100°C. This resulted in a thin (< 50 µm) KCl coating on the surface of the sample. The sample was then weighed, the dimensions measured and then exposed to pressurized dry (1.58% ± 0.09% relative humidity (r.H.)) or humid (30.00% ± 0.07% r.H.) lab air and heated to a surface temperature of ≈560°C using an Anton-Paar DHS 1100 furnace. The heating rate was set to 200 $\frac{K}{min}$ with a constant air stream of 100 $\frac{cm^3}{min}$. The high heating rate was chosen to minimize corrosion product formation before reaching the experimental temperature.

The sample was shielded from the surrounding air using a graphite dome during the experiment. After 5 h the furnace was switched off. The samples were weighed immediately after the experiment. Additional information of the experiment can be found in a previous paper [16].

2. Experiments conducted in SO₂ bearing atmospheres. Both the alumina crucible and KCl (99% purity) were dried for 1 day at 1000°C before the first experiment, then at 250°C for 1 day before the experiment according to DIN ISO 17224 [17]. The steel was partially embedded in KCl and exposed for 330 h in 0.5% SO₂/99.5% Ar (embedded in 4.5 g \pm 0.0 g KCl) or 0.5% SO₂/10%H₂O/89.5% Ar (embedded in 2.2 g \pm 0.0 g to 2.7 g \pm 0.0 g KCl) atmosphere at 560°C (heating rate: 5.5 $\frac{K}{\min}$) in a tubular furnace with a flowrate of 170 $\frac{mL}{\min}$ Ar and 0.9 $\frac{mL}{\min}$ SO₂ in dry and 638 $\frac{mL}{\min}$ Ar, 3.4 $\frac{mL}{\min}$ SO₂ and 3 $\frac{g}{h}$ H₂O in humid atmosphere at the second seco sphere. The reactive gases were introduced only once the experimental temperature was reached. The embedded area is shown in SEM and EDX images. A sketch of the experiment is depicted in a previously published paper [7]. After the exposure samples were carefully extracted from the crucible by separating the sample from the surrounding KCl keeping only sintered KCl particles stuck to the scale for further analysis.

A summary of the experiments is listed in Table 2.

TABLE 1 | Elemental composition of model alloys obtained byelectron probe micro analysis (EPMA) on a JEOL JXA 8200 Superprobeutilizing ZAF correction. Values given in wt.%.

Sample	Fe	Cr	Ni
Fe-18Cr-12Ni	Bal.	18.5 ± 0.5	11.8 ± 0.2

 TABLE 2
 |
 Summary of experimental conditions. Initial gas partial pressures were calculated with FactSage [18]. All experiments were conducted at 560°C.

Atmosphere	pO ₂ [Pa]	pH ₂ O [Pa]	pS ₂ [Pa]
Dry air	21.2×10^{3}	60.3	_
t = 5 h			
Humid air	21.0×10^{3}	1.1×10^{3}	—
t = 5 h			
SO ₂ /Ar	1.1×10^{-11}	N/a	4.3×10^{-6}
<i>t</i> = 330 h			
$SO_2/H_2O/Ar$	6.4×10^{-8}	23.4×10^{3}	8.3×10^{-14}
<i>t</i> = 330 h			

All samples were analyzed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) utilizing a Zeiss Sigma 300 VP at 20 kV. Cross-sections were prepared by embedding samples into an epoxy resin and polishing them to a P4000 finish. No water was used during grinding or polishing to preserve water soluble phases.

For post-exposure X-ray diffraction (XRD) analyses, sample scales were pulverized using a mortar. The powder was analyzed using Cu K-alpha radiation in a Pananalytical Empyrean diffractometer at 40 kV/40 mA. For Rietveld analysis the scale was removed using a diamond file until the silvery base metal was reached. The Rietveld refinement was done using the program GSAS II, by initially fitting a background and adding in the relevant phase data [19, 20]. Each phase's unit cell was then consecutively refined until a stable χ^2 was achieved. Then x,y,z, u, and u + w was refined. Finally microstrain, domain sizes, atom coordinates and phase fraction were refined.

3 | Results and Discussion

3.1 | Short-Term Experiments in Dry and Humid Air

Exposing KCl coated Fe–18Cr–12Ni to streaming lab air causes significant corrosion within the first 5 h at 560°C (Figures 1 and 2a,b). After 5 h exposure in dry air, Fe–18Cr–12Ni shows a surface normalized weight gain of 1.63 $\frac{\text{mg}}{\text{cm}^2} \pm 0.01 \frac{\text{mg}}{\text{cm}^2}$, while in humid air the measured weight gain is comparatively lower at 0.80 $\frac{\text{mg}}{\text{cm}^2} \pm 0.06 \frac{\text{mg}}{\text{cm}^2}$. The standard deviation is calculated from the surface area and weight measurements of the sample.

A continuous scale developed in both dry and humid air. The SEM backscatter electron (BSE) surface image of the dry sample (Figure 2a) shows more pores $(11.0\% \pm 2.2\%)$ of the surface area, calculated using gray scale tresholding of the SEM image) than the sample exposed to humid air $(5.5\% \pm 2.1\%)$ of the surface area, Figure 2b). The higher porosity allows for faster transport of gases to and from the surface of the alloy. The dry sample shows a higher weight gain than the humid one, as seen in Figure 1.

Figure 3 shows the cross-section of samples exposed to dry (a) and humid (b) lab air. Both samples show buckling of the scale with cracks in the base material due to internal attacks by



FIGURE 1 | Surface normalized weight change of samples in dry $(1.58\% \pm 0.09\% \text{ r.H.})$ and humid $(30.00 \pm 0.07\% \text{ r.H.})$ lab air. [Color figure can be viewed at wileyonlinelibrary.com]

corrosion. EDX was also performed and can be found in the supplementary materials. The sample exposed to dry air (Figure 3a) shows both Fe- and Cr-oxides, while the sample exposed to humid air (Figure 3b) shows Fe- and Cr-oxides as well as a K-bearing Cr-oxide, presumably $K_2Cr_2O_7$ based on EDX + XRD data. The presence of $K_2Cr_2O_7$ could indicate the oxidation of K_2CrO_4 or the presence of a liquid phase during the experiment, however, only the solid phase was identified [21, 22].

The increased weight gain is probably linked to multiple effects occuring during the exposure.

One contributing factor to the higher weight gain are the pores that form in the scale of dry sample, as seen in Figure 2a. The pores allow for a faster transport of the atmospheric gases, like oxygen or chlorine, to the metal surface. This leads to the formation of further metal oxides and metal chlorides at the cost of the bulk material. The prevalence of pores ($11.0\% \pm 2.2\%$ of the surface in Figure 2a) could inhibit the corrosion rate reduction that comes with diffusion controlled scale growth, leading to a poorer long-term performance [23]. The humid sample does not show as many pores ($5.5\% \pm 2.1\%$ of the surface area in Figure 2b), which leads to lower diffusion rates and therefore lower weight gain after 5 h.

Chlorine has been shown to be a driving force in corrosion involving KCl [7, 24, 25]. During the corrosion process, active



FIGURE 2 | Scanning electron microscopy (SEM) backscatter electron (BSE) surface images of Fe-18Cr-12Ni exposed to dry air (a, after Kingsbery et al. [16].) and humid air (b, 30% r.H.) for 5 h. Below the corresponding porosity map, pores colored in yellow. The porosity map was created using gray scale tresholding of the SEM BSE map. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 3 | Scanning electron microscopy (SEM) backscatter electron (BSE) cross-section images of Fe-18Cr-12Ni exposed to dry air (a, after Kingsbery et al. [16].) and humid air (b, 30% r.H.) for 5 h. [Color figure can be viewed at wileyonlinelibrary.com]

chlorine corrosion causes the steel to continuously form metal chlorides with high evaporation pressures [24]. This causes the metal chlorides to evaporate and diffuse towards the surface. Closer to the surface the oxygen partial pressure increases, allowing the metal chlorides to oxidize, forming metal oxides and chlorine.

The addition of H_2O allows for new phases to form. Using FactSage [18] to calculate the thermodynamic equilibrium of Cl-bearing phases with H_2O reveals HCl as a stable phase.

In a humid atmosphere, the oxidation of metal chlorides could take place via H_2O instead of O_2 , which allows for the

formation of HCl instead of Cl₂. This reaction is depicted in Equation (3) and results in a Gibbs free energy of $\Delta g = -1.2 \times 10^5$ J. Humidity also allows already formed Cl₂ to react according to Equation (4) with an Gibbs free energy of $\Delta g = -1.1 \times 10^4$ J, forming more HCl. Cr₂O₃ can act as a catalyst in the conversion of Cl₂ to HCl, known as the Deacon equilibrium. Cr₂O₃ therefore can reduce the time needed to reach equilibrium. Higher O₂ to H₂O ratios will shift the equilibrium towards Cl₂ [26]. Therefore, a humid atmosphere will contain more HCl than a dry one.

This could significantly lower the corrosion rate of the steel due to the different reaction rates of dry HCl and Cl_2 as shown by Brown on 18-8 steel [27].



FIGURE 4 | Corrosion rate of Cl₂ and HCl over temperature using Brown's [27] data for 18-8 steel. Least squares fit using $f(x) = ax^2 + bx + c$. [Color figure can be viewed at wileyonlinelibrary.com]

$$FeCl_3 + H_2O \rightarrow 1.9HCl + 0.1(FeCl_3)_2 + 0.1FeCl_3 + 0.3Fe_2O_3$$
(3)
$$\Delta G = -1.2 \times 10^5 \text{ J}$$

$$Cl_{2} + H_{2}O \rightarrow 0.9HCl + 0.6H_{2}O + 0.6Cl_{2} + 0.2O_{2} \qquad (4)$$
$$\Delta G = -1.1 \times 10^{5} \text{ J}$$

Brown documented reaction rates in the temperature range of $\approx 350^{\circ}$ C to 650° C for HCl and $\approx 300^{\circ}$ C to 450° C for Cl₂ [27]. Cl₂ exhibited consistently higher reaction rates than HCl.

To estimate the difference in corrosion rate at 560°C, Brown's data is plotted against the temperature in Figure 4 using the equation:

$$f(x) = ax^2 + bx + c \tag{5}$$

With a, b, c representing the polynomial fit parameters and x the temperature in °C.

This gives the formula:

$$f(x) = 8.73 \times 10^{-6} x^2 - 4.96 \times 10^{-3} x + 7.09 \times 10^{-1}$$
(6)

for Cl_2 and

$$f(x) = 3.70 \times 10^{-6} x^2 - 2.93 \times 10^{-3} x + 5.85 \times 10^{-1}$$
(7)

for HCl. This results in a corrosion rate at 560°C of $0.67 \frac{\text{cm}}{\text{month}} \pm 0.05 \frac{\text{cm}}{\text{month}}$ for Cl₂ and 0.10 $\frac{\text{cm}}{\text{month}} \pm 0.03 \frac{\text{cm}}{\text{month}}$ for HCl, using a 2 σ confidence interval.

The fit shows a significantly higher corrosion rate for Cl_2 at 560°C compared to HCl. This supports the weight change measurements, showing a higher weight gain for samples exposed to dry air when compared to samples exposed to humid air.

3.2 | Experiments in SO₂ Bearing Atmosphere

The behavior of the alloy exposed to 0.5% SO₂/Ar + KCl shows a strong dependence on humidity. The sample exposed to dry SO₂ shows extensive corrosion attacks, while in humid SO₂ only a thin corrosion layer is observed (see Figure 5).

In a dry environment a large scale ($408 \,\mu m \pm 25 \,\mu m$) formed and inner corrosion is observed, indicated by the material loss in the alloy (see Figure 5a). The scale shows buckling from the underlying metal. The large gray particles between the scale and metal are SiC introduced during the metallographic preparation.

The line scans shown in Figure 5c and d show the elemental composition change from the base alloy towards the surface. The EDX analysis reveals an abundance of Fe, Ni and O for the light gray phase (see Figure 5c), while the darker phase is a metal chloride (MCl, M = Fe, Cr, Ni) presumably an iron chloride (shown in Figure 5d). Furthermore, a significant Cr depletion is visible going from the bulk alloy towards the alloy/ scale interface. This indicates a large Cr consumption through oxidation or chlorination.

Figure 6 shows the elemental distribution of the scale in dry SO_2/Ar atmosphere, as indicated in Figure 5a. The scale shows both Cr_2O_3 and $CrCl_3$ close to the alloy/scale interface and Fe_2O_3/Fe_3O_4 towards the scale/gas interface.

Figure 5b shows Fe–18Cr–12Ni after exposure to a humid SO₂ bearing atmosphere. The addition of water decreased the amount of reaction products compared to the dry atmosphere (Figure 5a,b). The specimen shows a lower scale thickness $(11 \,\mu\text{m} \pm 4 \,\mu\text{m})$ and inner corrosion. The EDX images in Figure 7 show the elemental distribution and composition of the formed scale. It mainly consists of K₂SO₄ with a small Cr₂O₃ layer underneath, which seems to act as a protective layer and prevent large scale oxidation. The non-embedded, gas facing side of the partially embedded sample shows the same scale composition of Cr₂O₃ and K₂SO₄ (as seen in Figure 7) and can be found in the supplements.

The elemental segregation within the bulk alloy seen in Figure 7 are caused during the manufacturing process of the model alloy. In commercial alloys the segregation could be lower, depending on the exact thermomechanical processing utilized and their chemical composition. The commercial alloy TP347H also exhibits an austenitic microstructure as opposed to the ferritic-austenitic microstructure of the sample. This will impact the diffusion rates of elements throughout the steel, since ferrite allows for higher volume diffusion rates of Fe, Cr, and Ni compared to austenite [28–30]. This could cause, for example, Cr depletions in the commercial TP347H steel.

The phase composition of corrosion layers was studied by X-ray diffraction. Subsequently, the obtained diffractograms were then analyzed using the Rietveld method via the program GSAS 2 to obtain a quantitative phase composition [19, 20] (Figure 8).

The results are shown in Table 3. The dry sample shows a much higher amount of metal oxides (Σ = 72.3 wt.%) and only low



FIGURE 5 | Scanning electron microscopy (SEM) backscatter electron (BSE) cross-section of Fe-18Cr-12Ni exposed to 0.5% SO₂/Ar (a) (modified from Kingsbery et al. [7].) or 0.5% SO₂/10%H₂O/Ar (b). Below two line scans of the dry sample are shown, displaying the cumulative elemental concentration from the bulk alloy towards the surface. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 6 | Energy dispersive X-ray spectroscopy (EDX) images of Fe–18Cr–12Ni exposed to 0.5% SO ₂/99.5% Ar + KCl showing the elemental distribution. Modified from Kingsbery et al. [7]. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 7 | Energy dispersive X-ray spectroscopy (EDX) images of Fe–18Cr–12Ni exposed to 0.5% SO₂/10%H₂O/89.5% Ar + KCl showing the elemental distribution. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 8 | Rietveld refinement of X-ray diffraction (XRD) data using GSAS II. (a) Fe-18Cr-12Ni exposed to 0.5% SO₂/99.5% Ar + KCl. (b) Fe-18Cr-12Ni exposed to 0.5% SO₂/10% H₂O/89.5% Ar + KCl + KCl. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 | Weight fraction (in wt.%) of newly formed phases in scale with weighed profile residuals (R_{wp}) and squared goodness of fit (χ^2) value. Dry sample refers to 0.5% SO₂/99.5% Ar, humid sample to 0.5% SO₂/10%H₂O/89.5% Ar atmosphere. The phase data utilized can be found in the reference list [31–36].

Sample	K ₂ SO ₄	Cr ₂ O ₃	Fe_2O_3	Fe ₃ O ₄	$FeCl_2 * 2H_2O$	R _{wp} [%]	χ^2
Dry	6.4 ± 0.4	17.4 ± 0.2	15.8 ± 0.2	39.1 ± 0.2	1.6 ± 0.2	4.56	2.0
Humid	33.4 ± 0.4	2.2 ± 0.2	2.1 ± 0.2	1.5 ± 0.1	—	9.36	6.7

amounts of K₂SO₄ (6.4 wt.%). Hydrated FeCl₂ is also identified in the diffractogram, confirming the metal chlorides found in the EDX elemental maps (see Figure 5). The adsorption of H₂O probably occurred after the sample was removed from the furnace and subject to atmospheric air. Exposing the sample to a humid atmosphere increases the K₂SO₄ fraction significantly (33.4 wt.%) and the combined metal oxide fraction (i.e., Fe₃O₄ + Fe₂O₃ + Cr₂O₃) decreases significantly to 5.8 wt.%. These Fe- and Cr-oxides were also identified in the SEM-EDX cross sections in Figure 7. No metal chlorides were detected within this scale.

The Rietveld analysis shows the large impact of humidity on the resulting scale in these conditions. The H_2O allows a much larger proportion of K_2SO_4 to form in comparison to the dry sample. As seen in the EDX images in Figure 7, the K_2SO_4 forms a dense and continuous layer at the scale/atmosphere interface, inhibiting gas transport towards the metal. This can

TABLE 4 | Corrosion characteristics of ferritic-austenitic Fe–18Cr–12Ni, with deposited KCl, exposed to dry and humid lab air and SO₂ containing atmosphere at 560° C.

Atmosphere	Time	Reaction products	Characteristics
Dry lab air	5 h	Cr ₂ O ₃ , Fe ₃ O ₄ ,	Continuous scale, buckling,
(1.58% ± 0.09% r.H.)		Fe ₂ O ₃ ,	Surface porosity $-11.0\% \pm 2.2\%$
Humid lab air	5 h	Cr ₂ O ₃ , Fe ₃ O ₄ ,	Continuous scale, buckling,
(30.00% ± 0.07% r.H.)		Fe ₂ O ₃ , K ₂ Cr ₂ O ₇	Surface porosity $-5.5\% \pm 2.1\%$
0.5% SO ₂ /99.5% Ar	330 h	Cr_2O_3 , MCl (M = Fe, Cr),	Low amount of K_2SO_4 , large amount of oxides.
		Fe ₃ O ₄ , Fe ₂ O ₃ , K ₂ SO ₄	Thick scale (408 μ m \pm 25 μ m), inner corrosion, buckling.
0.5% SO ₂ /10% H ₂ O /89.5% Ar	330 h	Cr ₂ O ₃ , Fe ₃ O ₄ , Fe ₂ O ₃ , K ₂ SO ₄	Large amount of K_2SO_4 , low amount of oxides. Thin scale (11 µm ± 4 µm).

be seen in the scale composition (Table 3), which shows a much lower metal oxide fraction compared to the dry sample. Inhibiting the transport of gases will significantly reduce the growth of potential metal chlorides and oxides, resulting in lower corrosion.

4 | Conclusions

The impact of humidity on the KCl deposit induced high temperature corrosion of a ferritic-austenitic alloy (Fe–18Cr–12Ni) at 560°C was studied for atmospheres with and without 0.5% SO₂. The main characteristics of the observed material degradation are summarized in Table 4.

Without SO₂ humidity in the gas phase decreased the surface porosity and weight gain compared to dry air, but showed a similar corrosion attack in the BSE cross-section. The humid sample also showed the formation of $K_2Cr_2O_7$, which could be indicative of a liquid phase during the exposure or the possible oxidation of K_2CrO_4 . The reduced weight gain is linked to a combination of impacting factors. In the early stage of corrosion (5 h exposure), the presence of H_2O favors the formation of HCl in the presence of Cl_2 . As a result, the available Cl_2 for chlorination is reduced in favor of HCl. Since the amount of Cl_2 impacts the active corrosion by chlorine, a lower amount of Cl_2 also reduces the corrosion, since HCl has a lower reaction rate with steels than Cl_2 at 560°C.

With SO₂ in humid atmosphere $(0.5\% \text{ SO}_2/10\%\text{H}_2\text{O}/89.5\%$ Ar), K₂SO₄ was observed at the gas/scale interface, covering the KCl particles. The rapid reaction of K₂CrO₄ to K₂SO₄ could contribute to the reduced corrosion rate seen in humid atmospheres. Below this, a Cr₂O₃ layer is formed, as observed by XRD and SEM-EDX (see Figure 7). The Cr₂O₃ layer inhibits further oxygen transport towards the alloy interface and a much thinner scale is observed when compared to dry atmosphere (0.5% SO₂/99.5% Ar).

 H_2O therefore moderately decreases the corrosion attack in laboratory air and significantly lowers the corrosion attack in SO₂ bearing atmospheres in the presence of KCl.

Author Contributions

P. Kingsbery: conceptualization, investigation, analysis, writing original draft, visualization. **C. Stephan–Scherb:** conceptualization, analysis, writing–review and editing. **T. John:** analysis, writing-review and editing.

Acknowledgments

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—project number 416318834. HZB is gratefully acknowledged for the allocation of synchrotron radiation beamtime and financial support (192-08532-ST and 202-09765-ST). The authors gratefully acknowledge the help from A. Manzoni, P. Suarez Ocaño and D.M. Többens during the synchrotron experiments. G. Rüdiger is thanked for providing the Matlab code to calculate porosity.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The raw data required to reproduce these findings is available upon reasonable request.

References

1. N. Scarlat, J. Dallemand, N. Taylor, M. Banja, J. SanchezLopez, and M. Avraamides, *Brief on Biomass for Energy in the European Union* (Luxembourg: Office of the European Union, 2019).

2. U.S. Energy Information Administration. (2023).

3. DOE/EE-0288 U.S. "Department of Energy," Federal Technology Alert (2003).

4. A. Demirbaş, "Sustainable Cofiring of Biomass With Coal," *Energy Conversion and Management* 44, no. 9 (2003): 1465–1479.

5. Y. Zheng, C. Liu, J. Zhu, et al., "Carbon Footprint Analysis for Biomass-Fueled Combined Heat and Power Station: A Case Study," *Agriculture* 12, no. 8 (2022): 1146.

6. Y. Shao, J. Wang, F. Preto, J. Zhu, and C. Xu, "Ash Deposition in Biomass Combustion or Co-Firing for Power/Heat Generation," *Energies* 5, no. 12 (2012): 5171–5189.

7. P. Kingsbery and C. Stephan-Scherb, "Effect of KCL Deposits in High-Temperature Corrosion on Chromium-Rich Steels in SO_2 -

Containing Atmosphere," *Materials and Corrosion* 73, no. 5 (2022): 758–770.

8. N. Othman, N. Othman, J. Zhang, and D. Young, "Effects of Water Vapour on Isothermal Oxidation of Chromia-Forming Alloys in Ar/O₂ and Ar/H₂ Atmospheres," *Corrosion Science* 51, no. 12 (2009): 3039–3049.

9. T. Jonsson, B. Pujilaksono, A. Fuchs, and J.-E. Svensson, "The Influence of H₂O on Iron Oxidation at 600°C: A Microstructural Study," *Materials Science Forum* 595–598 (2008): 1005–1012.

10. J. Pettersson, N. Folkeson, L. G. Johansson, and J. E. Svensson, "The Effects of KCl, K_2SO_4 and K_2CO_3 on the High Temperature Corrosion of a 304-Type Austenitic Stainless Steel," *Oxidation of Metals* 76, no. 1 (2011): 93–109.

11. T. M. Meißner, B. Grégoire, X. Montero, E. Miller, J. Maier, and M. C. Galetz, "Long-Term Corrosion Behavior of Cr Diffusion Coatings on Ferritic-Martensitic Superheater Tube Material X20CrMoV12-1 Under Conditions Mimicking Biomass (Co-)Firing," *Energy & Fuels* 34, no. 9 (2020): 10989–11002.

12. S. Karlsson, T. Jonsson, J. Hall, J. E. Svensson, and J. Liske, "Mitigation of Fireside Corrosion of Stainless Steel in Power Plants: A Laboratory Study of the Influences of SO_2 and KCL on Initial Stages of Corrosion," *Energy & Fuels* 28, no. 5 (2014): 3102–3109.

13. K. Yoo, Y. He, S. Bae, and D. Kim, "Study on the Microstructural Degradation of the Boiler Tubes for Coal-Fired Power Plants," *KEPCO Journal on Electric Power and Energy* 4, no. 1 (2018): 25.

14. S. Liu, Z. Liu, Y. Wang, and J. Tang, "A Comparative Study on the High Temperature Corrosion of TP347H Stainless Steel, C22 Alloy and Laser-Cladding C22 Coating in Molten Chloride Salts," *Corrosion Science* 83 (2014): 396–408.

15. D. M. Többens and S. Zander, "KMC-2: An X-Ray Beamline With Dedicated Diffraction and Xas Endstations at Bessy Ii," *Journal of Large-Scale Research Facilities* 2 (2016): A49.

16. P. Kingsbery, A. M. Manzoni, P. S. Ocaño, D. M. Többens, and C. Stephan-Scherb, "High–Řtemperature KCL–Řinduced Corrosion of High Cr and Niăalloys Investigated by in Řsitu Diffraction," *Materials and Corrosion* 75, no. 10 (2024): 1272–1281.

17. ISO 17224:2015, Corrosion of Metals And Alloys - Test Method for High Temperature Corrosion Testing of Metallic Materials by Application of a Deposit of Salt, Ash, or Other Substances (Geneva, CH: International Organizationfor Standardization, 2015).

18. C. B. Bale, et al., "Factsage Thermochemical Software and Databases - 2010 - 2016," *Calphad* 54 (2016): 35–53.

19. H. Rietveld, "A Profile Refinement Method for Nuclear and Magnetic Structures," *Journal of Applied Crystallography* 2, no. 2 (1969): 65–71.

20. B. Toby and R. VonDreele, "Gsas-II: The Genesis of a Modern Open-Source All Purpose Crystallography Software Package," *Journal of Applied Crystallography* 46, no. 2 (2013): 544–549.

21. J. Lehmusto, D. Lindberg, P. Yrjas, B. J. Skrifvars, and M. Hupa, "Studies on the Partial Reactions Between Potassium Chloride and Metallic Chromium Concerning Corrosion at Elevated Temperatures," *Oxidation of Metals* 77, no. 3–4 (2011): 129–148.

22. J. Lehmusto, D. Lindberg, P. Yrjas, B. J. Skrifvars, and M. Hupa, "Thermogravimetric Studies of High Temperature Reactions Between Potassium Salts and Chromium," *Corrosion Science* 59 (2012): 55–62.

23. P. Kofstad, *High Temperature Corrosion* (Essex: Elsevier Applied Science Publishers, 1988).

24. H. Grabke, E. Reese, and M. Spiegel, "The Effects of Chlorides, Hydrogen Chloride, and Sulfur Dioxide in the Oxidation of Steels below Deposits," *Corrosion Science* 37, no. 7 (1995): 1023–1043.

25. D. J. Young, "Chapter 12 - Corrosion in Complex Environments." in *High Temperature Oxidation and Corrosion of Metals (Second Edition)*, eds. D. J. Young (Amsterdam: Elsevier, 2016), 603–645).

26. A. P. Amrute, C. Mondelli, and J. Pérez-Ramírez, "Kinetic Aspects and Deactivation Behaviour of Chromia-Based Catalysts in Hydrogen Chloride Oxidation," *Catalysis Science & Technology* 2, no. 10 (2012): 2057–2065.

27. M. Brown, W. DeLong, and J. Auld, "Corrosion by Chlorine and by Hydrogen Chloride at High Temperatures," *Industrial and Engineering Chemistry* 39, no. 7 (1947): 839–844.

28. A. W. Bowen and G. M. Leak, "Solute Diffusion in Alpha- and Gamma-Iron," *Metallurgical Transactions* 1, no. 1 (1970): 1695–1700.

29. F. S. Buffington, K. Hirano, and M. Cohen, "Self Diffusion in Iron," *ACTA Metallurgica* 9, no. 5 (1961): 434–439.

30. K. Hirano, M. Cohen, and B. L. Averbach, "Diffusion of Nickel into Iron," *ACTA Metallurgica* 1, no. 9 (1961): 440–445.

31. D. Walker, P. Verma, L. Cranswick, R. Jones, S. Clark, and S. Buhre, "Halite-Sylvite Thermoelasticity," *American Mineralogist* 89, no. 1 (2004): 204–210.

32. K. Ojima, Y. Nishihata, and A. Sawada, "Structure of Potassium Sulfate at Temperatures From 296 K Down to 15 K," *Acta Crystallographica Section B* 51, no. 3 (1995): 287–293.

33. R. Newnham and Y. M. Haan, de, "Refinement of the α Al₂O₃, Ti₂O₃, V₂O₃ and Cr₂O₃ Structures," *Zeitschrift für Kristallographie* 117, no. 2–3 (1962): 235–237.

34. R. Blake, R. Hessevick, T. Zoltai, and L. Finger, "Refinement of the Hematite Structure," *The American Mineralogist* 51 (1966): 123–129.

35. M. E. Fleet, "The Structure of Magnetite," Acta Crystallographica Section B 37, no. 4 (1981): 917–920.

36. B. Morosin and E. Graeber, "Crystal Structures of Manganese(II) and Iron(II) Chloride Dihydrate," *The Journal of Chemical Physics* 42, no. 3 (1965): 898–901.