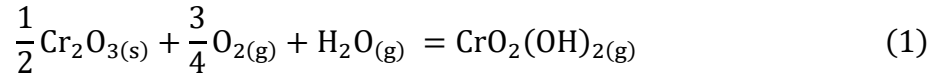


Cr volatilization calculation:

Among the various volatile compounds, $\text{CrO}_2(\text{OH})_2$ has been identified as the dominant species responsible for this degradation over a broad temperature range:



The rate of loss based on the mass transfer flux of $\text{CrO}_2(\text{OH})_2$ at the interface of gas-scale^{1,2} can be expressed as:

$$J_{\text{CrO}_2(\text{OH})_2} = \frac{k_m}{RT} p_{\text{CrO}_2(\text{OH})_2}^G \quad (2)$$

where k_m is a temperature dependant mass transfer coefficient and $p_{\text{CrO}_2(\text{OH})_2}^G$ the partial pressures of $\text{CrO}_2(\text{OH})_2$ at the gas-scale interface. The value of k_m was calculated for viscous gas flow conditions, using procedures outlined in reference². The partial pressure of $\text{CrO}_2(\text{OH})_2$ at equilibrium in reaction (1) can be calculated as:

$$p_{\text{CrO}_2(\text{OH})_2}^G = a_{\text{Cr}_2\text{O}_3}^{\frac{1}{2}} p_{\text{H}_2\text{O}} p_{\text{O}_2}^{\frac{3}{4}} \exp\left(-\frac{\Delta G^0}{RT}\right) \quad (3)$$

In this case, $a_{\text{Cr}_2\text{O}_3}$ represents the activity of Cr_2O_3 which is assumed to be 1 if the oxide is pure, p_i the indicated species partial pressures and ΔG^0 the standard Gibbs free energy change for reaction (S2), measured by Opila et al.³ as:

$$\Delta G^0 = 53500 + 45.5T \text{ (J/mol)} \quad (4)$$

If p_{O_2} is set at the maximum impurity level of 5.0×10^{-6} atm, the calculated partial pressure and volatilization fluxes of $\text{CrO}_2(\text{OH})_2$ are listed in Table S1.

Table S1- Calculated parameters and the flux density of $\text{CrO}_2(\text{OH})_2$ at 750 °C

Atmosphere	$p_{\text{CrO}_2(\text{OH})_2}^G$	$J_{\text{CrO}_2(\text{OH})_2}$
	atm	mol.cm ⁻² s ⁻¹
Ar-5H ₂ O	4.7×10^{-11}	4.9×10^{-15}
Ar-20H ₂ O	1.4×10^{-10}	1.7×10^{-14}

Based on the results in Table S1, the equivalent losses of Cr_2O_3 from the scale after 300 h reaction in Ar-5H₂O and Ar-20H₂O are $4.0 \times 10^{-4} \text{ mg/cm}^2$ and $1.4 \times 10^{-3} \text{ mg/cm}^2$, respectively. Actual measured weight gains of Fe-30Cr after 300 h were 0.15 mg/cm^2 for Ar-5H₂O and 0.22 mg/cm^2 (Fig. 1) for Ar-20H₂O. These measured weight gains are orders of magnitude greater than the expected consumption due to the volatilization of Cr_2O_3 , which renders the volatilization effect negligible. This conclusion is supported by a calculation of Cr_2O_3 scale thicknesses based on the measured weight gains:

$$d = \frac{\Delta W}{A} \frac{V_{\text{Cr}_2\text{O}_3}}{M_{\text{Cr}_2\text{O}_3}} \quad (5)$$

where $\frac{\Delta W}{A}$ is the weight gain, $V_{\text{Cr}_2\text{O}_3}$ ($29.1 \text{ cm}^3/\text{mol}$) and $M_{\text{Cr}_2\text{O}_3}$ (152 g/mol) denote the mole volume and mass of Cr_2O_3 , respectively. The calculated thicknesses for Fe-30Cr alloy after 300 h exposure are $0.3 \text{ }\mu\text{m}$ in Ar-5H₂O and $0.4 \text{ }\mu\text{m}$ in Ar-20H₂O. These values are in agreement with the measurements of Fe-30Cr scale thickness shown in Table 2, confirming the lack of any significant volatilisation.

References

- 1 Holcomb GR. Steam Oxidation and Chromia Evaporation in Ultra-Supercritical Steam Boilers and Turbines. *ECST*. **16**, 81 (2009).
- 2 Young DJ, Pint BA. Chromium Volatilization Rates from Cr_2O_3 Scales into Flowing Gases Containing Water Vapor. *Oxid. Met.* **66**, 137-153 (2006).
- 3 Opila EJ et al. Theoretical and experimental investigation of the thermochemistry of $\text{CrO}_2(\text{OH})_2(\text{g})$. *J. Phys. Chem. A*. **111**, 1971-1980 (2007).