Cr volatilization calculation:

Among the various volatile compounds, $CrO_2(OH)_2$ has been identified as the dominant species responsible for this degradation over a broad temperature range:

$$\frac{1}{2}Cr_2O_{3(s)} + \frac{3}{4}O_{2(g)} + H_2O_{(g)} = CrO_2(OH)_{2(g)} \quad (1)$$

The rate of loss based on the mass transfer flux of $CrO_2(OH)_2$ at the interface of gas-scale[1,2] can be expressed as:

$$J_{CrO_2(OH)_2} = \frac{k_m}{RT} p^G_{CrO_2(OH)_2} \quad (2)$$

where k_m is a temperature dependant mass transfer coefficient and $p^G_{CrO_2(OH)_2}$ the partial pressures of $CrO_2(OH)_2$ at the gas-scale interface. The value of k_m was calculated for viscous gas flow conditions, using procedures outlined in reference[2]. The partial pressure of $CrO_2(OH)_2$ at equilibrium in reaction (1) can be calculated as:

$$p^G_{CrO_2(OH)_2} = a^{\frac{1}{2}}_{Cr_2O_3} p_{H_2O} p^{\frac{3}{4}}_{O_2} exp\left(-\frac{\Delta G^o}{RT}\right) \quad (3)$$

In this case, $a_{Cr_2O_3}$ 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^o the standard Gibbs free energy change for reaction (S2), measured by Opila et al.[3] as:

$$\Delta G^o = 53500 + 45.5T\ (J/mol) \quad (4)$$

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 $CrO_2(OH)_2$ are listed in Table S1.

Table S1- Calculated parameters and the flux density of $CrO_2(OH)_2$ at 750 °C

Atmosphere	$p^G_{CrO_2(OH)_2}$	$J_{CrO_2(OH)_2}$
	atm	mol.cm^{-2}s^{-1}
Ar-5H_2O	4.7×10^{-11}	4.9×10^{-15}
Ar-20H_2O	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-5H_2O and Ar-20H_2O are 4.0×10^{-4} mg/cm^2 and 1.4×10^{-3} mg/cm^2, respectively. Actual measured weight gains of Fe-30Cr after 300 h were 0.15 mg/ cm^2 for Ar-5H_2O and 0.22 mg/ cm^2 (Fig. 1) for Ar-20H_2O. 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:

$$d = \frac{\Delta W}{A}\frac{V_{Cr_2O_3}}{M_{Cr_2O_3}} \quad (5)$$

where $\frac{\Delta W}{A}$ is the weight gain, $V_{Cr_2O_3}$ (29.1 cm^3/mol) and $M_{Cr_2O_3}$ (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 μm in Ar-5H_2O and 0.4 μm in Ar-20H_2O. 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 $CrO_2(OH)_2$(g). *J. Phys. Chem. A*. **111**, 1971-1980 (2007).