

Modelling Material Effects on Flow-Accelerated Corrosion in Primary CANDU Coolant and Secondary Reactor Feed-Water

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Abstract

The effects of chromium content on flow-accelerated corrosion (FAC) of carbon steel have been predicted very well by including a passivating layer, which is a chromium-dependent diffusion barrier at the metal-oxide interface. By adjusting the properties of the chromium-dependent layer, described with a Passivation Parameter (PP), we can predict the FAC of carbon steel of different chromium contents in typical reactor feed-water environments (140°C and neutral or ammoniated chemistry). The model and an appropriate PP are also applied to the environment typical of carbon-steel feeders in the primary coolant of a CANDU reactor (310°C and lithiated chemistry). The model predicts FAC rate very well (with a deviation of 10% or less) in both situations.

1. Introduction

Flow-accelerated corrosion (FAC) is a persistent problem in power system coolants; it occurs in the secondary coolant of all types of nuclear reactor and in the primary coolant of CANDUs[®] [1], as well as in fossil plants. Low concentrations of common alloying elements such as chromium, copper and molybdenum reduce FAC rates of carbon steel and low-alloy steels [2, 3] and minimum levels of Cr are often specified to mitigate FAC in practical applications. A basic principle behind most postulated mechanisms of FAC is that there are two processes in series – the dissolution of the magnetite film and the transport of dissolved Fe and eroded oxide particles to the bulk coolant [4]. Additional parameters have been incorporated in the basic rate equation in order to predict the FAC rate of different types of steel in typical coolant systems [5].

2. Modelling the Effect of Cr

An additional barrier, the “passivating layer”, is postulated; it is very thin and could possibly consist of a combination of Cr-rich oxide and a layer of metal atoms depleted in Fe. The situation is shown schematically in Figure 1.

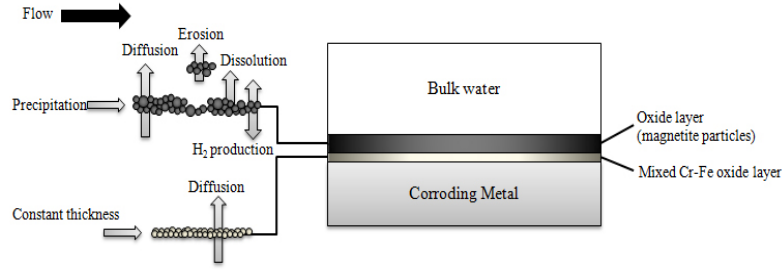


Figure 1 Schematic of Cr Effect on FAC

The equation for the FAC rate was derived and described in a previous publication [5]:

$$\frac{dm}{dt} = \frac{S(C_{M-P}^e - C_{P-O}^e) + \left(\frac{K_d F^* S C_{O-B}^e + h C_B}{k_d F^* + k} \right)}{PP + 0.467(1.101 + \phi_{OX}) \left(\frac{\delta_{OX} \zeta_{OX}}{\phi_{OX} D_{OX} \rho_{OX} (1 - \phi_{OX})} + \frac{1}{k_d F^* + k} \right)} \quad (1)$$

where PP is the “Passivation Parameter” which accounts for the Cr in the film and is characteristic of the material in its particular environment:

$$PP = \frac{\delta_P \zeta_P F_{Cr}}{\phi_P D_P} \left(\frac{1}{(1 - \phi_P) \rho_P} - \frac{M_{Fe}}{M_P \rho_{Fe}} \right) \quad (2)$$

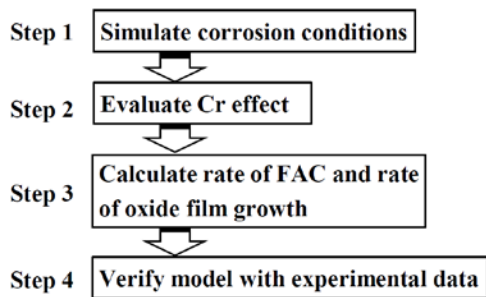
As corrosion proceeds, the oxide film growth rate is:

$$0.723 \frac{d\delta_{OX}}{dt} = 0.476 \frac{dm}{dt} (1 - \phi_{OX}) - k_d F^* (S C_{O-B}^e - C_B) \quad (3)$$

We now postulate that after a “spalling time” t_{sp} an oxide particle is eroded from the film (the diameter d of the particle is chosen at random from an assumed half-normal size distribution):

$$t_{sp} = \frac{0.016 \cdot d}{f'_s \cdot U^2 \cdot \rho_{H_2O} \cdot \phi_{OX} \cdot k_d F^* (S C_{O-B}^e - C_B)} \quad (4)$$

The computation proceeds step by step from the initial system simulation until the final convergence. The modelling steps and the system of modelling are shown in Figure 2 and the symbols used in the modelling are shown in Table 1.



Calculation targets	Cr effect	Corrosion conditions	Oxide film growth	Erosion
Input	Materials composition, pH, Temperature (T)	Flow velocity, T, pH, Oxide properties	Corrosion rate	Corrosion rate, Oxide thickness
Model	Inner layer model	Corrosion model	Thickness model	Spalling model
Output	PP	Corrosion rate	Oxide thickness	Corrosion rate, Oxide thickness
Verification	-	-	-	With experimental data

Figure 2 Calculation Steps (left) and System of Code (right) to Evaluate FAC Rate

Table 1 Symbols and Meanings

Symbol	Meaning	Symbol	Meaning	Symbol	Meaning	Symbol	Meaning
k_d	dissolution rate constant	k	mass transfer coefficient	$\frac{dm}{dt}$	corrosion rate	F^*	geometry factor
C_{M-O}^e	solubility at metal-oxide interface	C_{O-B}^e	solubility at oxide-bulk solution interface	C_{M-P}^e	solubility at metal/passivating-layer interface	C_{P-O}^e	solubility at passivating-layer/oxide interface
F_{Cr}	fraction of Cr in the metal	δ_p	passivating layer thickness	S	supersaturation factor	f_z'	friction factor
D_P	diffusivity of dissolved iron in passivating layer	D_{OX}	diffusivity of dissolved iron in oxide layer	ζ_P	tortuosity of passivating layer	ζ_{OX}	tortuosity of oxide layer
ϕ_{OX}	porosity of oxide layer	ϕ_P	porosity of passivating layer	ρ_P	density of passivating layer	ρ_{Fe}	density of iron
ρ_{OX}	density of oxide	ρ_{H_2O}	Density of water	U	linear velocity of coolant	d	oxide diameter
δ_P	passivating layer thickness	δ_{OX}	oxide thickness	D	probe diameter	$\frac{M_{Fe}}{M_P}$	mass fraction of iron in passivating layer

To illustrate the applicability of the model, three sets of FAC measurements using on-line probes of carbon steel with different chromium contents in a recirculating loop were simulated.

3. Results and Discussion

3.1 Modelling of FAC at Low and Moderate Chromium Content at 140°C

There were two steels used in FAC experiments at low temperature (140 °C) and neutral condition (pH 7): moderate-Cr (0.019% Cr - type A106B) and low-Cr (0.001% Cr - STPT480). The predicted oxide thicknesses and corresponding corrosion rates are shown in Figure 3. The predicted corrosion rate rapidly reduces as the oxide layer forms initially. The ultimate steady-state oxide thickness varies randomly around a mean value because of the random erosion events. The predictions indicate lower FAC rate due to higher Cr content.

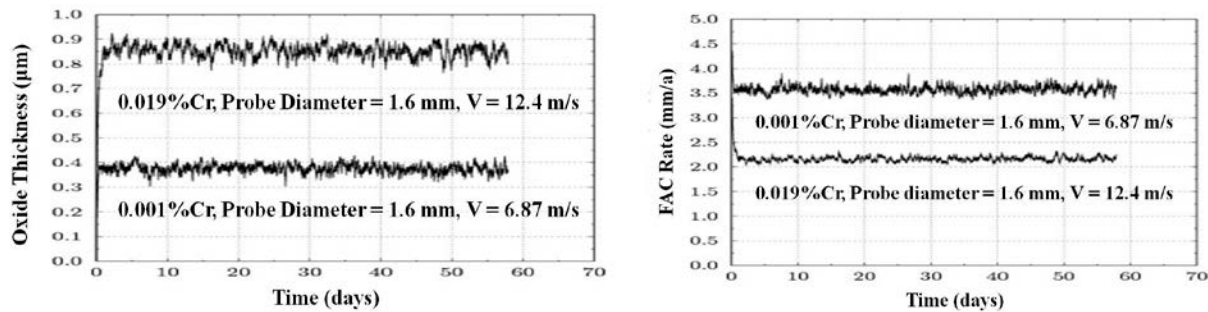


Figure 3 Predicted Oxide Thickness and FAC Rate of Low (0.001% Cr) and Moderate (0.019% Cr) Chromium Content

3.2 Modelling of FAC at Moderate Chromium Content at Low and High Temperature

Two sets of FAC measurements using probes of A106B steel were simulated. The first condition was 140°C and pH 7; the second condition was 310°C and pH 10.4 (LiOH) which represent the primary system of CANDU reactor conditions. Similar velocities from experiments at low and high temperature were chosen for comparison.

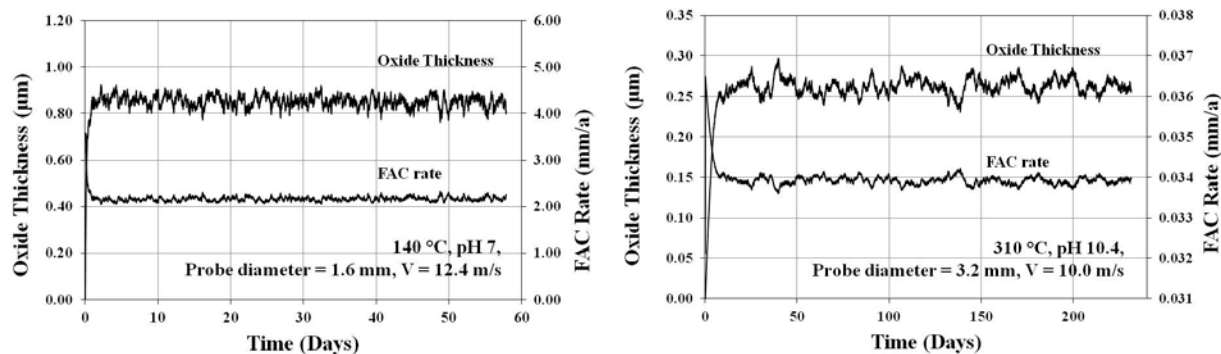


Figure 4 Predicted Oxide Thickness and FAC Rate at Low (140°C) and High (310°C) Temperature and Low (7) and High (10.4) pH

The predicted FAC rate at high temperature and high pH is much lower than that at low temperature and neutral pH, reflecting plant experience and as expected from the low magnetite solubility and dissolution rate at 310°C, pH 10.4. At high temperature and high pH, the predictions indicate a longer time (about 30 days) to achieve steady state than at low temperature and low pH (about two days).

3.3 Modelling Accuracy

The modelling predicts material and temperature effects of experimental results quite well. The deviation of the prediction from the measurement is generally lower than 10%, as indicated in Table 2.

Table 2 Experimental and Predicted Steady-State Average FAC Rates

Experimental condition	Velocity (m/s)	Steady state FAC rate (mm/a)	Predicted FAC rate (mm/a)	Deviation (%)
0.019% Cr, 140 °C, pH 7	12.4	2.14	2.17	1.4
0.001% Cr, 140 °C, pH 7	6.87	3.48	3.57	2.6
0.019% Cr, 310 °C, pH 10.4	10.0	0.030	0.033	10.0

4. Summary and Conclusions

A mechanistic model based on the principle that the corrosion-product film of magnetite is supplemented with a very thin, quasi-passivating layer rich in chromium has been developed to predict FAC of carbon steels of different chromium contents. The diffusional resistance of the layer is characterized by a “Passivation Parameter” that is proportional to the Cr content of the metal. Temperature and pH affect the dissolution rate whereas the increasing velocity improves the erosion in the corrosion process. The model predicts FAC rates very well and provides expected oxide film thicknesses pertinent to experimental results obtained at low (140°C) and high (310°C) temperature.

5. Acknowledgements

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6. References

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