FLOW EFFECTS ON CORROSION OF STEELS IN REACTOR PRIMARY COOLANT – EXPERIENCE AND UNDERSTANDING

by

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2008 October 20th
▲ CANDU reactors
1. Bruce A
   Bruce B
2. Pickering A
   Pickering B
3. Darlington

■ Uranium mines
1. Cluff Lake
2. McClean Lake
3. Midwest
4. Cigar Lake
5. McArthur River
6. Key Lake
7. Rabbit Lake

● Research reactors
1. U of Alberta
2. Saskatchewan Research Council
3. AECL Whiteshell Labs (decom.)
4. McMaster U
5. U of Toronto (decom.)
6. Royal Military College
7. AECL Chalk River Laboratories
8. MDS Nordion (decom.)
9. Ecole Polytechnique
10. Dalhousie U
FREDERICTON
UNB
**NUCLEAR POWER IN CANADA**

- In 2007, nuclear ≡ 14.6% of Canada’s electricity
- Installed nuclear gross capacity in 2008 (all CANDUs):

<table>
<thead>
<tr>
<th>Location</th>
<th>Reactor</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ontario</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pickering A</td>
<td>4 × 542 MW(e) (two in safe storage)</td>
<td></td>
</tr>
<tr>
<td>Pickering B</td>
<td>4 × 540 MW(e)</td>
<td></td>
</tr>
<tr>
<td>Darlington</td>
<td>4 × 934 MW(e)</td>
<td></td>
</tr>
<tr>
<td>Bruce A</td>
<td>4 × 805 MW(e) (two being refurbished)</td>
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<tr>
<td>Bruce B</td>
<td>1 × 845 MW(e)</td>
<td></td>
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<tr>
<td></td>
<td>3 × 872 MW(e)</td>
<td></td>
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<tr>
<td><strong>Québec</strong></td>
<td></td>
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<tr>
<td>Gentilly-2</td>
<td>1 × 675 MW(e) (to be refurbished 2011)</td>
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<tr>
<td><strong>New Brunswick</strong></td>
<td></td>
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<tr>
<td>Point Lepreau</td>
<td>1 × 680 MW(e) (being refurbished)</td>
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</table>
PROSPECTS FOR NEW BUILD IN CANADA

**Ontario**
To decide on technology for two new units in early 2009 (ACR-1000, Areva, Westinghouse)

**New Brunswick**
Negotiating for new unit – Point Lepreau II – ACR-1000 preferred

**Alberta and Saskatchewan**
Interested in new build
<table>
<thead>
<tr>
<th>Country</th>
<th>Reactors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Korea (Wolsong)</td>
<td>4 × CANDU-6</td>
</tr>
<tr>
<td>Argentina (Embalse)</td>
<td>1 × CANDU-6</td>
</tr>
<tr>
<td>Romania (Cernavoda)</td>
<td>2 × CANDU-6</td>
</tr>
<tr>
<td>China (Qinshan)</td>
<td>2 × CANDU-6</td>
</tr>
<tr>
<td>India</td>
<td>3 × prototype</td>
</tr>
<tr>
<td>Pakistan</td>
<td>1 × prototype</td>
</tr>
</tbody>
</table>
CANDU REACTOR CIRCUITS
CANDU PHTS CONDITIONS

- $D_2O$ with 3-10 cc/kg dissolved $D_2$ (H$_2$ gas added);
- Temperature 265-310°C;
- pH (apparent) 10.2-10.8 (lithium);
- Steam quality at core outlet $\rightarrow$ 6%;
- Dissolved O$_2$ < 5 ppb (unmeasurable – although coolant may be oxidising at core outlet).
MAIN PHTS MATERIALS

- Fuel sheaths – Zircaloy 4
- Pressure tubes – Zr-2½%Nb
- SG tubing (CANDU 6) – Alloy 800
- SG heads – carbon steel
- Feeders – carbon steel
- Headers – carbon steel
CANDU REACTOR FACE
In 1980s, some CANDUs experienced primary system fouling (reactor inlet temperature rise); e.g. Point Lepreau to May 1989
FEEDER THINNING

In 1996, ultrasonic measurements of wall thickness of carbon-steel outlet feeders at Point Lepreau indicated excessive corrosion: average rates inferred from estimates of initial thickness.
THINNING RELATED TO COOLANT FLOW – FAC (FLOW-ACCELERATED CORROSION)

\[ \text{FAC} \propto V^{1.5} \]

Plant Data

Model Prediction
In 1997, an outlet feeder at Point Lepreau developed a leak – removed and inspected.

Through-wall crack, now thought to be low-temperature creep, possibly exacerbated by hydrogen (deuterium) permeating through metal from FAC.

Several cracked feeders found since – one or two through-wall.

Only at Point Lepreau.
INSIDE SURFACE OF CRACKED FEEDER

- cracks intergranular
- medium-to-high-flow channels
- areas of high residual stress (many tight bends close to reactor face – “warm bent”)

END-FITTINGS AND FEEDERS
DETAILS OF REMOVED FEEDER INDICATE FAC

Scallops

Effects of Cr content of steel

Low-Cr steel a consequence of specifying low-Co material to control activity transport.
• All pre-Qinshan CANDUs display FAC: managed by stress analysis, dispositioning, removal and replacement if necessary;

• Darlington plant particularly susceptible (has thinner-wall feeders);

• Following a suggestion and early work at UNB Nuclear and later qualification studies, Darlington injected TiO₂ as possible inhibitor into one channel at Unit 3 in 2004 – observed a fall in FAC of > 25%: promising;

• Still too many uncertainties to proceed with Ti;

• Qinshan expected to have low FAC rates because 0.3% Cr steel specified.
FAC EXPERIMENTS AT UNB

Developed probe for on-line measurement of FAC in high-temperature water loop:

Increase in electrical resistance of thinning tube reflects FAC – “resistance probe”.
Probes made from Point Lepreau steel: SA106 Grade B (0.019%Cr)
Also developed wire probe – on-line measurement of resistance of thinning wire reflects FAC.

Experiments performed over range of conditions:

- flow rate;
- pH (LiOH);
- [Fe] saturation.
These results and plant data suggest shear stress important (flow dependence high).
TENTATIVE CORRELATION DERIVED:

CR = 7.65 \times (1 + 0.111 \tau^{0.75}) \times (1 + 1.51 \times 10^{-9} e^{1.87pH})

- Predicts reducing pH from 10.6 to 10.2 will decrease FAC rate by only \sim 12\%; differences among plants indicate no consistent trend;

- Predicts flow-rate dependence similar to plant.

N.B. Experiments with coolant nominally saturated in [Fe] still produced FAC – if at a lower rate
FAC processes at M-O produce H₂

Fe + 2H₂O → Fe(OH)₂ + 2H  ..............(1)

3Fe(OH)₂ → Fe₃O₄ + 2H₂O + H₂  ..........(2)

Molecular hydrogen from (2) diffuses to bulk coolant.

Atomic hydrogen from (1) effuses quantitatively through metal – measurement reflects FAC.
“HYDROGEN EFFUSION PROBE” - HePro®

Collection cup clamped to outside of pipe – evacuated periodically – increase in pressure monitored.

Diagram of HePro® mounted on pipe

Typical pressure increase
INDUSTRIAL APPLICATIONS

Feeder at Point Lepreau

Water wall at Coleson-Cove oil-fired plant
THERMALHYDRAULIC STUDY AT UNB

- High velocity dependence of FAC suggests shear stress distribution important;

- Full-scale mock-up of feeder and end-fitting constructed from transparent acrylic;

- Mounted in high-flow water circuit, two-phase (air-water) $\Delta P$ and phase distribution studied at $\sim 25^\circ\text{C}$;

- Computer simulations with cfd code FLUENT tested against observations.
Hydraulic loop for testing feeder
<table>
<thead>
<tr>
<th>Parameter</th>
<th>CANDU-6</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coolant</td>
<td>$D_2O$</td>
<td>$H_2O$</td>
</tr>
<tr>
<td>Temperature ($^\circ$ C)</td>
<td>310</td>
<td>25</td>
</tr>
<tr>
<td>Chemistry (pH $_{25^\circ}$ C)</td>
<td>10.2 (Li)</td>
<td>neutral</td>
</tr>
<tr>
<td>Voidage</td>
<td>0~0.3 (steam)</td>
<td>0~0.5 (air)</td>
</tr>
<tr>
<td>$Re_{\text{liq}}$</td>
<td>$\sim 4.3\times10^6$</td>
<td>$5\times10^5$</td>
</tr>
</tbody>
</table>
PREDICTABLE FLOW PATTERN IN BEND

0.05 voidage, $Re_{liq} \sim 4.5 \times 10^5$
UNPREDICTABLE FLOW PATTERN IN BEND

0.2 voidage, $Re_{liq} \sim 4.2 \times 10^5$
FLUENT FAILS TO PREDICT PHASE DISTRIBUTION IN BEND

Test section mid-plane

Recirculating flows influenced by upstream end-fitting

0.2 voidage, $Re_{liq} \sim 4.2 \times 10^5$
SCALLOPING

- Effect of surface sculpting as “scallops” still unknown;

- Research at UNB Nuclear indicates scallops cannot be treated as conventional “sand-grain roughness” (i.e., influencing $\Delta P$ via Moody relations);

- Scallop shapes create different $\Delta P$ in forward and reverse flow;

- Experiments under feedwater conditions (FAC at 140° C in neutral water) indicate constant “scallop Reynolds number”.
PROCESSES TO BE MODELLED

1 - Corrosion
2 - Precipitation
3 - Diffusion
4 - Dissolution
5 - H₂ Production
6 - Erosion
MODEL REFLECTS SYNERGY BETWEEN FILM DISSOLUTION AND SPALLING

• Electrochemical processes affected by potential – ECP computed in parallel;
• Diffusing Fe\textsuperscript{2+} predicted to be unchanged Fe(OH)\textsubscript{2} – straightforward Fick’s Law applied;
• Rate constant for magnetite dissolution from literature (one reference) SHOULD CONTROL (<<m.t.c.);
• Same rate constant assumed for precipitation (no reference);
• Erosion treated stochastically – random-number generator used to decide size of particle to spall from size distribution;
• Time for particle to be loosened and removed;

\[ \theta \propto \frac{d}{\tau \cdot Q_i k_d \Delta C} \]

• When particle disappears, film thins instantaneously by d and corrosion rate jumps.
MODEL PREDICTS (using CFD code to calculate local shear stress)

- corrosion rates at different positions in feeders;
- ECP ~ -700 to -900 mV (vs. SHE);
- oxide film thicknesses (0.7 μm to 3 μm);
- growth of oxide to steady-state;
- corrosion and oxide film thickness of inlet feeders (saturated in dissolved iron, lower temperature).
PREDICTED OXIDE FILM THICKNESSES IN OUTLET FEEDERS
PREDICTED CORROSION RATE AND OXIDE FILM THICKNESS FOR INLET FEEDER:
MODEL FITS PLANT DATA WELL
ACKNOWLEDGEMENT

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