Corrosion of Reactor Components

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# Cost of Corrosion in NPPs

Table 15. Summary of total cost of corrosion to the electrical utilities industry.

<table>
<thead>
<tr>
<th>FACILITY</th>
<th>REASON FOR CORROSION COST</th>
<th>CORROSION COST PER YEAR ($ x billion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear</td>
<td>O&amp;M</td>
<td>2.013</td>
</tr>
<tr>
<td></td>
<td>Depreciation</td>
<td>1.546</td>
</tr>
<tr>
<td></td>
<td>Forced Outage</td>
<td>0.670</td>
</tr>
<tr>
<td></td>
<td><strong>SUBTOTAL</strong></td>
<td><strong>$4.229</strong></td>
</tr>
<tr>
<td>Fossil Fuel</td>
<td>O&amp;M</td>
<td>0.698</td>
</tr>
<tr>
<td></td>
<td>Depreciation</td>
<td>1.214</td>
</tr>
<tr>
<td></td>
<td>Forced Outage</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td><strong>SUBTOTAL</strong></td>
<td><strong>$1.912</strong></td>
</tr>
<tr>
<td>Hydraulic &amp; Other Products</td>
<td>O&amp;M</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>Depreciation</td>
<td>0.066</td>
</tr>
<tr>
<td></td>
<td>Forced Outage</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td><strong>SUBTOTAL</strong></td>
<td><strong>$0.141</strong></td>
</tr>
<tr>
<td>Transmission &amp; Distribution</td>
<td>O&amp;M</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Depreciation</td>
<td>0.607</td>
</tr>
<tr>
<td></td>
<td>Forced Outage</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td><strong>SUBTOTAL</strong></td>
<td><strong>$0.607</strong></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td><strong>$6.889 billion</strong></td>
</tr>
</tbody>
</table>

$17.27$ billion  
EPRI estimate  

G. Koch, CC Technologies
Outline

• Forms of corrosion
• Corrosion basics
• Materials in reactor components
• Environments for reactor components
• Operational experience with corrosion of reactor components
• Summary
Forms of Corrosion
Types of Corrosion Damage

- General Corrosion
- Galvanic Corrosion
  - Dissimilar “Metals” and an Electrolyte
- Environmentally Induced Cracking (SCC, Corrosion Fatigue)
  - Combination of Tensile Stress, Specific Environment, Material
- Hydrogen Damage
- Dealloying
- Localized Corrosion
  - Pitting
  - Crevice Corrosion
  - Intergranular Corrosion
- Flow Assisted Corrosion
  - Combination of Flow Velocity and Corrosion
- Erosion-Corrosion
  - Combination of Erosive Environment, Flow and Corrosion
- Microbial Induced Corrosion
Corrosion in LWRs

• General Corrosion, cation release & fouling

• Flow Assisted (Accelerated) Corrosion

• Erosion-corrosion (Steam cutting)

• Localized corrosion (Pitting, crevice and microbial corrosion)

• Stress corrosion cracking and hydrogen embrittlement

• Corrosion fatigue
Corrosion Basics
Electrochemical Nature of Corrosion

- In water, most solutes are dissociated into anions and cations
- Due to the dipolar character of the water molecule, positive cations are bound to a sheath of water molecules called the solvation layer
  - Formation of a complex solvated cation $Mz^+(H_2O)_n$ with $n=6$ in many cases
  - Metallic cations are at the center of octahedra that are the base element of hydroxides or oxides formed by hydrolysis

Courtesy Pierre Combrade
When a metal is immersed in an aqueous solution, electrical charges accumulate at the interface, both in the metal and in the solution, creating a so-called “electrical double layer” that can be represented as a series of capacitors. A potential difference appears between the metal and the aqueous solution.

- Metal/solution potential (electrode potential)

\[ E = \Phi_m = \Phi_s \]
A Closer Look at the Metal-Solution Interface
The Metal

• Uniform corrosion isn’t really “uniform”: Terrace-Ledge-Kink (TLK).
• Active sites present (preferred anodes)-grain boundaries, dislocations, precipitates/other phases, etc.
• Film formation
• Film instability
• Occluded regions (crevices, pits, etc.)
• Crystallographic effects
• Plastic deformation-dislocations exiting surface
The Water

• Dissolved metal ions
• Other species in solution, O$_2$, H$^+$, OH$^-$
• Water
  – Water will play a role, polar molecule
  – Hydration sheath
• Concentration gradients (Concentration polarization)
• Potential gradients
Metal/Water Interface

- Multiple Reactions
  - Oxidation-Metal Dissolution
- Dissolution process has an “activation” barrier.
  - Reduction (hydrogen, oxygen)
- Hydrogen (or oxygen) reduction not so simple-multi step process
- Double Layer formation
  - Net negative charge on metal balances by net positive charge from the aqueous solution
- Film formation-”passivation”
  - Chemisorbed
  - Adsorbed
Electrochemical Corrosion

Zinc goes into solution (Oxidation-Anode)

\[ Zn \rightarrow Zn^{++} + 2e^- \]

Hydrogen gas is released (Reduction-Cathode)

\[ 2H^+ + 2e^- \rightarrow H_2(gas) \]

Drop a piece of Zn Metal into 1M HCl

Note: Electrons are released by oxidation of Zn and consumed by hydrogen
Reduction-Charge cannot be stored.

\[ \sum_A = \sum_C \]

Courtesy Ron Ballinger
Electrochemical Reactions

Reactions occur that involve charge transfer between the metal and solution.

- **Anodic (Oxidation)**
  - General: \( M \rightarrow M^{n+} + ne^- \)
  - \( Fe \rightarrow Fe^{2+} + 2e^- \)
  - \( Fe^{2+} \rightarrow Fe^{3+} + e^- \)
  - \( Ni \rightarrow Ni^{2+} + 2e^- \)
  - \( Al \rightarrow Al^{3+} + 3e^- \)

- **Cathodic (Reduction) Reactions**
  - \( 2H^+ + 2e^- \rightarrow H_2(g) \), Hydrogen Reduction
  - \( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \), Oxygen Reduction-Neutral of Basic Solutions
  - \( O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \), Oxygen Reduction-Acid Solutions
  - \( 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \)
  - \( M^{n+} + ne^- \rightarrow M \), Metal Deposition

*Courtesy Pierre Combrade*
Electrochemical Reactions Produce an Electrical Current

- Charge transfer gives rise to:
  - an electrical current in the metal
  - an ionic current in the solution

- Faraday’s law gives the reaction rate in terms for a current intensity through the metal/solution interface

\[ w = kI t \]

- Electron flow in external circuit from anode to cathode
- BUT: Current in a circuit by definition flows from positive to negative
  - Anode is thus negative
  - Cathode is thus positive

- Electrical neutrality of each phase requires that no net charge accumulates, therefore:

\[ \Sigma i_{\text{Anodic}} = \Sigma i_{\text{cathodic}} \quad \text{or} \quad \Sigma i_{\text{Oxidation}} = \Sigma i_{\text{Reduction}} \]
How do we know whether a reaction will occur?

(1) \( Cu + H_2O(l) + \frac{1}{2}O_2(g) \Rightarrow Cu(OH)_2(s) \) \( \Delta G^0 = -1.19 \times 10^5 \text{ J/Mole} \)

(2) \( Mg + H_2O(l) + \frac{1}{2}O_2(g) \Rightarrow Mg(OH)_2(s) \) \( \Delta G^0 = -5.96 \times 10^5 \text{ J/Mole} \)

(3) \( Au + \frac{3}{2}H_2O(l) + \frac{3}{4}O_2(g) \Rightarrow Au(OH)_3(s) \) \( \Delta G^0 = 6.5 \times 10^4 \text{ J/Mole} \)

Reactions (1) and (2) have a negative \( \Delta G \) and therefore will occur spontaneously. Reaction (3) has a positive \( \Delta G \) and is therefore will not occur.
Relationship between Free Energy and Potential

Relationship Between $\Delta G$ and Potential ($E$)

$$\Delta G = -nFE$$

- $F =$ Faraday’s Constant (96,500 Coulomb/Equivalent)
- $n =$ Number of electrons involved in the reaction

Consider the general reaction:

$$lL + mM + \ldots \Rightarrow qQ + rR + \ldots$$

$l, m, q, r =$ # moles of a substance

The change in free energy, $\Delta G$, for the reaction is:

$$\Delta G = \left( qG_o + rG_R + \ldots \right) \left( lG_L + mG_m + \ldots \right)$$
Nernst Equation

The Nernst equation gives the EMF of a cell.

\[ E = E^0 - \frac{RT}{nF} \ln \frac{a^q a^r}{a^l a^m} \ldots \]

\( E^0 \) is the Standard potential defined at room temperature and atmospheric pressure.
### Reduction potentials

<table>
<thead>
<tr>
<th>Reduction Reaction</th>
<th>$E^0$ (V)</th>
<th>Oxidation Reaction</th>
<th>$E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li}^+ + e^- \rightarrow \text{Li}$</td>
<td>-3.04</td>
<td>$\text{Li} \rightarrow \text{Li}^+ + e^-$</td>
<td>3.04</td>
</tr>
<tr>
<td>$\text{K}^+ + e^- \rightarrow \text{K}$</td>
<td>-2.92</td>
<td>$\text{K} \rightarrow \text{K}^+ + e^-$</td>
<td>2.92</td>
</tr>
<tr>
<td>$\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$</td>
<td>-2.90</td>
<td>$\text{Ba} \rightarrow \text{Ba}^{2+} + 2e^-$</td>
<td>2.90</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$</td>
<td>-2.87</td>
<td>$\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$</td>
<td>2.87</td>
</tr>
<tr>
<td>$\text{Na}^+ + e^- \rightarrow \text{Na}$</td>
<td>-2.71</td>
<td>$\text{Na} \rightarrow \text{Na}^+ + e^-$</td>
<td>2.71</td>
</tr>
<tr>
<td>$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$</td>
<td>-2.37</td>
<td>$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$</td>
<td>2.37</td>
</tr>
<tr>
<td>$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$</td>
<td>-1.66</td>
<td>$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$</td>
<td>1.66</td>
</tr>
<tr>
<td>$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$</td>
<td>-1.18</td>
<td>$\text{Mn} \rightarrow \text{Mn}^{2+} + 2e^-$</td>
<td>1.18</td>
</tr>
<tr>
<td>$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2 \text{OH}^-$</td>
<td>-0.83</td>
<td>$\text{H}_2 + 2 \text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2e^-$</td>
<td>0.83</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$</td>
<td>-0.76</td>
<td>$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$</td>
<td>0.76</td>
</tr>
<tr>
<td>$\text{Cr}^{2+} + 2e^- \rightarrow \text{Cr}$</td>
<td>-0.74</td>
<td>$\text{Cr} \rightarrow \text{Cr}^{2+} + 2e^-$</td>
<td>0.74</td>
</tr>
<tr>
<td>$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$</td>
<td>-0.44</td>
<td>$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$</td>
<td>0.44</td>
</tr>
<tr>
<td>$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$</td>
<td>-0.41</td>
<td>$\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-$</td>
<td>0.41</td>
</tr>
<tr>
<td>$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$</td>
<td>-0.40</td>
<td>$\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$</td>
<td>0.40</td>
</tr>
<tr>
<td>$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$</td>
<td>-0.28</td>
<td>$\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$</td>
<td>0.28</td>
</tr>
<tr>
<td>$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$</td>
<td>-0.25</td>
<td>$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$</td>
<td>0.25</td>
</tr>
<tr>
<td>$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$</td>
<td>-0.14</td>
<td>$\text{Sn} \rightarrow \text{Sn}^{2+} + 2e^-$</td>
<td>0.14</td>
</tr>
<tr>
<td>$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$</td>
<td>-0.13</td>
<td>$\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$</td>
<td>0.13</td>
</tr>
<tr>
<td>$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$</td>
<td>-0.04</td>
<td>$\text{Fe} \rightarrow \text{Fe}^{3+} + 3e^-$</td>
<td>0.04</td>
</tr>
</tbody>
</table>

### Oxidation potentials

<table>
<thead>
<tr>
<th>Reduction Reaction</th>
<th>$E^0$ (V)</th>
<th>Oxidation Reaction</th>
<th>$E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2 + 2e^- \rightarrow 2\text{H}^+$</td>
<td>0.00</td>
<td>$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$</td>
<td>0.00</td>
</tr>
</tbody>
</table>
### Arbitrary Neutral: H₂

<table>
<thead>
<tr>
<th>Reduction Reaction</th>
<th>E⁰ (V)</th>
<th>Oxidation Reaction</th>
<th>E⁰ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H⁺ + 2e⁻ → H₂</td>
<td>0.00</td>
<td>H₂ → 2H⁺ + 2e⁻</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Cathodic** - exhibits greater tendency to gain electrons

<table>
<thead>
<tr>
<th>Reduction Reaction</th>
<th>E⁰ (V)</th>
<th>Oxidation Reaction</th>
<th>E⁰ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S + 2H⁺ + 2e⁻ → H₂S</td>
<td>0.14</td>
<td>H₂S → S + 2H⁺ + 2e⁻</td>
<td>-0.14</td>
</tr>
<tr>
<td>Sn^{4+} + 2e⁻ → Sn^{2+}</td>
<td>0.15</td>
<td>Sn^{2+} → Sn^{4+} + 2e⁻</td>
<td>-0.15</td>
</tr>
<tr>
<td>Cu^{2+} + e⁻ → Cu⁺</td>
<td>0.16</td>
<td>Cu⁺ → Cu^{2+} + e⁻</td>
<td>-0.16</td>
</tr>
<tr>
<td>SO₄^{2-} + 4H⁺ + 2e⁻ → SO₂ + 2H₂O</td>
<td>0.17</td>
<td>SO₂ + 2H₂O → SO₄^{2-} + 4H⁺ + 2e⁻</td>
<td>-0.17</td>
</tr>
<tr>
<td>AgCl + e⁻ → Ag + Cl⁻</td>
<td>0.22</td>
<td>Ag + Cl⁻ → AgCl + e⁻</td>
<td>-0.22</td>
</tr>
<tr>
<td>Cu^{2+} + 2e⁻ → Cu</td>
<td>0.34</td>
<td>Cu → Cu^{2+} + 2e⁻</td>
<td>-0.34</td>
</tr>
<tr>
<td>ClO₃⁻ + H₂O + 2e⁻ → ClO₂⁻ + 2OH⁻</td>
<td>0.35</td>
<td>ClO₂⁻ + 2OH⁻ → ClO₃⁻ + H₂O + 2e⁻</td>
<td>-0.35</td>
</tr>
<tr>
<td>2H₂O + O₂ + 4e⁻ → 4OH⁻</td>
<td>0.40</td>
<td>4OH⁻ → 2H₂O + O₂ + 4e⁻</td>
<td>-0.40</td>
</tr>
<tr>
<td>Cu⁺ + e⁻ → Cu</td>
<td>0.52</td>
<td>Cu → Cu⁺ + e⁻</td>
<td>-0.52</td>
</tr>
<tr>
<td>I₂ + 2e⁻ → 2I⁻</td>
<td>0.54</td>
<td>2I⁻ → I₂ + 2e⁻</td>
<td>-0.54</td>
</tr>
<tr>
<td>O₂ + 2H⁺ + 2e⁻ → H₂O₂</td>
<td>0.68</td>
<td>H₂O₂ → O₂ + 2H⁺ + 2e⁻</td>
<td>-0.68</td>
</tr>
<tr>
<td>Fe³⁺ + e⁻ → Fe²⁺</td>
<td>0.77</td>
<td>Fe²⁺ → Fe³⁺ + e⁻</td>
<td>-0.77</td>
</tr>
<tr>
<td>NO₃⁻ + 2H⁺ + e⁻ → NO₂ + H₂O</td>
<td>0.78</td>
<td>NO₂ + H₂O → NO₃⁻ + 2H⁺ + e⁻</td>
<td>-0.78</td>
</tr>
<tr>
<td>Hg²⁺ + 2e⁻ → Hg</td>
<td>0.78</td>
<td>Hg → Hg²⁺ + 2e⁻</td>
<td>-0.78</td>
</tr>
<tr>
<td>Ag⁺ + e⁻ → Ag</td>
<td>0.80</td>
<td>Ag → Ag⁺ + e⁻</td>
<td>-0.80</td>
</tr>
<tr>
<td>NO₃⁻ + 4H⁺ + 3e⁻ → NO + 2H₂O</td>
<td>0.96</td>
<td>NO + 2H₂O → NO₃⁻ + 4H⁺ + 3e⁻</td>
<td>-0.96</td>
</tr>
<tr>
<td>Br₂ + 2e⁻ → 2Br⁻</td>
<td>1.06</td>
<td>2Br⁻ → Br₂ + 2e⁻</td>
<td>-1.06</td>
</tr>
<tr>
<td>O₂ + 4H⁺ + 4e⁻ → 2H₂O</td>
<td>1.23</td>
<td>2H₂O → O₂ + 4H⁺ + 4e⁻</td>
<td>-1.23</td>
</tr>
<tr>
<td>MnO₂ + 4H⁺ + 2e⁻ → Mn²⁺ + 2H₂O</td>
<td>1.28</td>
<td>Mn²⁺ + 2H₂O → MnO₂ + 4H⁺ + 2e⁻</td>
<td>-1.28</td>
</tr>
<tr>
<td>Cr₂O₇²⁻ + 14H⁺ + 6e⁻ → 2Cr³⁺ + 7H₂O</td>
<td>1.33</td>
<td>2Cr³⁺ + 7H₂O → Cr₂O₇²⁻ + 14H⁺ + 6e⁻</td>
<td>-1.33</td>
</tr>
</tbody>
</table>
Pourbaix (Stability) Diagrams

- Electrode Potential/Ph Diagram-A graphical presentation of the thermodynamic equilibrium states of a metal-electrolyte system
- Lines dividing zones are calculated using Nernst

\[
E = E^0 - \frac{RT}{nF} \ln \frac{a_Q^{aq} a_R^{ar}}{a_L^{il} a_M^{im}} \quad E = E^0 - 2.303 \frac{RT}{nF} \log \frac{\text{[Products]}}{\text{[Reactants]}}
\]

- Dividing lines for dissolved species defined for an activity of $10^{-6}$
- Horizontal Lines: REDOX (Reduction/Oxidation) reactions. Charge transfer, **no pH dependence.** (Includes OH⁻, H⁺)
- Vertical Lines: No REDOX, No charge transfer, **pH Dependence.**
- Diagonal Lines: BOTH REDOX, and pH dependence
- NOTE: H₂O, H⁺, OH⁻ always present
Limitations

- Diagrams represent EQUILIBRIUM behavior.
- Diagrams provide no information regarding kinetics.
- Most diagrams are for pure metals @ standard conditions in aqueous solutions.
  - High temperature diagrams are available (and can be calculated) as are those for alloys.
- Do not (necessarily) take into account non-ideal behavior.
Example of a Pourbaix Diagram

Courtesy Ron Ballinger
Fe-H$_2$O system at 25°C

Courtesy Ron Ballinger
Reactions represented in a Pourbaix diagram

- Reduction of aqueous cations (horizontal line)
  \[ M^{n+} + n\text{e}^- = M \]

- Reduction of metal hydroxide or oxide (sloped line)
  \[ M(\text{OH})_n + n\text{H}^+ + n\text{e}^- = M + n\text{H}_2\text{O} \]

- Reduction of a soluble aqueous anion (sloped line)
  \[ \text{MO}_m^{n-2m} + 2m\text{H}^+ + n\text{e}^- = M + m\text{H}_2\text{O} \]

- Change in chemistry with no change in oxidation state (vertical line)
  \[ 2M^{3+} + 3\text{H}_2\text{O} = M_2\text{O}_3 + 3\text{H}_2 \]
What can Pourbaix diagrams reveal and not reveal about corrosion?

Pourbaix diagrams indicate:
- Regions where corrosion is likely
- Regions where protection may be possible
- Regions where no significant corrosion is possible - immunity

However, Pourbaix diagrams do not reliably indicate regions of protection by surface oxides
- The existence of a stable oxide does not mean that it will form or that it will be protective
- The nature of the protective passive film is often different from that of bulk oxide phases

Pourbaix diagrams are equilibrium diagrams - they do not give indications of corrosion rates
KINETICS

When the potential of a metal/solution interface differs from the equilibrium potential, a current will flow. The departure from equilibrium potential is called the overpotential, $\eta$.

$$\eta = E - E^0$$

The relationship between potential and current is given by the Tafel equations.

$$\eta_c = \beta_c \log \frac{i}{i_0}$$

$$\eta_A = \beta_A \log \frac{i}{i_0}$$

$i_0$ is the exchange current density and $b$ are Tafel “slopes”
Polarization diagram

\[ \eta_c = \beta_c \log \frac{i}{i_0} \]

\[ \eta_A = \beta_A \log \frac{i}{i_0} \]
Establishment of a “mixed” potential

\[ \eta_c = \beta_c \log \frac{i}{i_0} \]

\[ \eta_A = \beta_A \log \frac{i}{i_0} \]
Back to Zinc in Acid solution

Zinc goes into solution (Oxidation-Anode)

\[ Zn \Rightarrow Zn^{++} + 2e^- \]

Hydrogen gas is released (Reduction-Cathode)

\[ 2H^+ + 2e^- \Rightarrow H_2(gas) \]

Drop a piece of Zn Metal into 1M HCl

Note: Electrons are released by oxidation of Zn and consumed by hydrogen
Reduction-Charge cannot be stored.

\[ \Sigma_A = \Sigma_C \]
Polarization diagram for zinc in acid solution

Courtesy Pierre Combrade
Passivation

- A metal is passive if it substantially resists corrosion in a given environment resulting from marked polarization
  - Cr, Ni, Mo, Ti, Zr, Stainless Steels
- A metal is passive if it substantially resists corrosion in a given environment despite a marked thermodynamic tendency to react.
  - Pb/H₂SO₄, Mg/H₂O
Passivation

Graph showing the relationship between potential (E) and current density (i) with regions labeled Passive, Transpassive, and Active.
Elements of the environment relevant to nuclear reactor systems

- Temperature
- Stress/Pressure
- Corrosive medium
- Radiation
Elements of the environment relevant to nuclear reactor systems

- Corrosion
- Radiation + stress
- Radiation + radiation + stress
- Stress + stress
- High temperature

- Corrosion + radiation
- Corrosion + stress
- Corrosion + radiation + stress
- Radiation + stress
- High temperature
Materials in Reactor Components
Principles of Materials Selection for LWRs

Requirements
Ability to manufacture large size components, 
- Hardenability and metallurgical homogeneity, 
- Weldability, 
- Avoid any significant fabrication defect (cast, welds, underclad...) 
- Control (NDT).

Long life (40-60 years) in specific environment: 
- Neutron irradiation: 
  • Embrittlement 
  • Activation of species 
- Temperature ~300°C: Thermal Ageing 
- Environment: Primary Water, Secondary: Corrosion

Consequences
- Use commercial grades well known by the manufacturers: mainly steels 
- Optimize these grades to get: 
  • Good resistance to fast fracture (level of impurities: S, P, Cu…, Toughness, RTNDT< -20°C…) 
  • Corrosion resistance to reduce release of activated corrosion products

Courtesy J. P. Massoud
Material Property requirements for PWR components

<table>
<thead>
<tr>
<th>Material Property</th>
<th>RPV</th>
<th>Internals</th>
<th>Pressurizer</th>
<th>Primary Piping</th>
<th>Pump casing</th>
<th>SG Tubes</th>
<th>Secondary Piping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toughness</td>
<td>x</td>
<td>(x)</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Hardenability</td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Material Homogeneity</td>
<td>x</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Weldability</td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Corrosion Resistance</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Irradiation Resistance</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Courtesy J. P. Massoud
## Summary of Major Materials in PWR

<table>
<thead>
<tr>
<th></th>
<th>Carbon Steels</th>
<th>Low-Alloy Steel</th>
<th>Stainless Steel</th>
<th>Ni-Alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cristal structure</strong></td>
<td>BCC</td>
<td>BCC</td>
<td>FCC</td>
<td>FCC</td>
</tr>
<tr>
<td><strong>Microstructure</strong></td>
<td>Ferritic, Bainitic</td>
<td>Ferritic, Bainitic</td>
<td>Austenitic</td>
<td>Austenitic</td>
</tr>
<tr>
<td><strong>Main alloying elements</strong></td>
<td>0.5-1.5%Mn, Si... Total (out of Ni) &lt; 1%</td>
<td>Mn, Ni, Mo, Cr... Total &lt; 5%</td>
<td>~18% Cr, ~10% Ni</td>
<td>~15% Cr, ~10% Fe</td>
</tr>
<tr>
<td><strong>Price</strong></td>
<td>low</td>
<td>low</td>
<td>high</td>
<td>Very high (Ni base)</td>
</tr>
<tr>
<td><strong>Grades</strong></td>
<td>TU, A-48 ; TU, A-42, 20MN5M, A106, A333, A515...</td>
<td>16MND5 , A533 Cl.1, A508 Cl.2/3, ...</td>
<td>304 (L), 316 (L) Welds : 308L, 309L CF3M, CF8M,...</td>
<td>Alloy 600/182/82 Alloy 690/152/52 X750,...</td>
</tr>
<tr>
<td><strong>Fabrication</strong></td>
<td>Forged, Rolled or cast (valves...)</td>
<td>Forged or rolled and cladded</td>
<td>Forged, Rolled or cast</td>
<td>Forged, Rolled</td>
</tr>
<tr>
<td><strong>Heat Treatment</strong></td>
<td>Austenitizing + air cooling</td>
<td>Quenched + tempered + post-weld HT</td>
<td>Solution Annealed (SA) (+ cold work)</td>
<td>Mill annealed Thermally Treated</td>
</tr>
<tr>
<td><strong>Yield Strength</strong></td>
<td>250-450 MPa</td>
<td>250-450 MPa</td>
<td>~200 MPa (SA) if CW, YS increases</td>
<td>~300 MPa (SA) if CW, YS increase</td>
</tr>
<tr>
<td><strong>Toughness/ductility</strong></td>
<td>High, DBTT</td>
<td>High DBTT</td>
<td>Very high No DBTT</td>
<td>Very high No DBTT</td>
</tr>
<tr>
<td><strong>Irradiation resistance</strong></td>
<td>N/A</td>
<td>Moder. (%Cu, P low)</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td><strong>Corrosion resistance</strong></td>
<td>Risk for FAC</td>
<td>moderate</td>
<td>high</td>
<td>high</td>
</tr>
</tbody>
</table>

*Courtesy J. P. Massoud*

*Vessel, Primary Piping, SG Tubing, Divider*
PWR Components & Materials

- Low alloyed steels: 1900t
- Stainless Steels: 900t
- Base Nickel Alloys: 280t

- Zirconium Alloys
- Nuclear Alloys (Ag-In-Cd)
- Ceramics (UO2-PuO2)
- Cu, Ti...

Control Rods
 alloys Ag-In-Cd

Vessel
155 bars

Internals Structures
Austenitic Stainless Steels

Pressurizer
Low Alloys Steel

Duplex Stainless Steels

Primary Circuit

Steam Generator

Secondary Circuit

turbine

Nickel base Alloy

Low alloyed steel

Pressure vessel wall

Austenitic Stainless Steel

Zirconium Alloy

Fuel (UO2) ceramics

Fuel tube

Courtesy J. P. Massoud

Michigan Engineering

Center for Materials Science of Nuclear Fuel
Low Alloy Steels: Reasons for selecting and risks

- Fine-grained structural steels with bainitic microstructure and high toughness.

  - **Hardenability and materials homogeneity:**
    Balance Mn, Ni, Mo, Cr...

  - **Toughness:** $S < 0.010\%$, $S$, toughness

- Risk of ageing: shift of DBTT (fracture toughness decrease)
  - Irradiation embrittlement: low Cu ($Cu < 0.05\%$) and low P content
  - Thermal ageing: low P content

*Courtesy J. P. Massoud*
Austenitic Stainless Steels: Reasons for selecting and risks

- Effect of alloying elements:
  - Cr% for general corrosion resistance
  - Ni% for austenite phase stability
  - C and N% for strength and austenite stability

- Nonmagnetic, good weldability (%B low), easy forming (forging, cast)...

- Risk of Intergranular Corrosion (due to chromium depletion at carbides)
  - Low carbon SS (304L)
  - Ti or Nb stabilized grade (321 or 347)

- SS weld materials designed to have 5-10% d-ferrite to avoid hot cracking

- Cast stainless steels CF3M and CF8M also 5-20% d-ferrite,
  Risk of thermal ageing: ferrite as low as possible
Nickel Base Alloys: Reasons for selecting and risks

- Good general corrosion resistance (low corrosion products release rates)
- Resistance to chloride cracking (secondary side)
- Similar thermal expansion coefficients with LAS
- PWSCC of Alloy 600 → Alloy 690

Courtesy J. P. Massoud
Welds and Claddings

- Welds and Heat Affected Zones are critical components locations (defects, residual stresses, NDT),

- Homogeneous welds: SS to SS (ferrite content), LAS to LAS

- Dissimilar welds: LAS to SS or LAS to A600 (A690)
  - Different chemical compositions: Dilutions
  - Different thermal expansion coefficients: Thermal stresses

- Heat Affected Zones (HAZ):

- Weld Defects: Hot cracking, lack of fusion, weld roots defects, relaxation cracking, excessive dilution (low ferrite content or martensite in SS welds)

Courtesy J. P. Massoud
Zirconium Alloys

• Very low neutron absorption cross section

• Very poor corrosion resistance as a pure metal, but can be alloyed to produce good corrosion resistance

• Susceptible to I-induced SCC (I is a fission product)

• Zr has an hcp structure, so it is highly anisotropic
  - susceptible to radiation induced hardening
  - radiation induced growth
  - radiation induced creep

Courtesy J. P. Massoud
Environments of Reactor Components
PWR Water Chemistries

**Primary Water Chemistry**

<table>
<thead>
<tr>
<th>Role</th>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burnable poison</td>
<td>H$_3$BO$_3$</td>
<td>1500 ppm to zero</td>
</tr>
<tr>
<td>pH adjust</td>
<td>LiOH</td>
<td>Adjust to meet 7.1-7.4 pH$_T$</td>
</tr>
<tr>
<td>Minimize radioolytic oxygen</td>
<td>H$_2$</td>
<td>25-50 STP cc/kg</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O$_2$</td>
<td>&lt; 5 ppb</td>
</tr>
<tr>
<td>Corrosion product</td>
<td>Fe, Ni, Co</td>
<td>No spec.</td>
</tr>
<tr>
<td>Contaminant</td>
<td>Cl, SO$_4$, F</td>
<td>Each &lt; 0.15 ppb</td>
</tr>
</tbody>
</table>

**Secondary Water Chemistry**

<table>
<thead>
<tr>
<th>Role</th>
<th>Species</th>
<th>Conc., ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH control</td>
<td>NH$_3$</td>
<td>~ X</td>
</tr>
<tr>
<td>O$_2$ decrease</td>
<td>N$_2$H$_4$</td>
<td>≤ 8xO$_2$</td>
</tr>
<tr>
<td>Leaks</td>
<td>O$_2$</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Boil off remnant</td>
<td>H$_2$</td>
<td>~ 1</td>
</tr>
<tr>
<td>Corrosion product</td>
<td>Cu</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Contaminant</td>
<td>Cl$_2$</td>
<td>&lt; 10</td>
</tr>
<tr>
<td></td>
<td>SO$_4$</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>

**Bulk PWR Environments:**

Primary Circuit:
- Residual stresses:
  - Welds, at yield stresses
  - Cold bends, at yield stresses
- Irradiation:
  - Maximum 1x10$^{14}$ n/cm$^2$-sec
- Internal environment in fuel: I$_2$, Cs, Ar, Kr, Xe
- Temperature: 293°C
- Pressure: 2250 psi
- Steam temperature: 345°C, 2250 psi
- Saturated steam: <0.05% moisture

Secondary Circuit:
- High-velocity fluids produce FAC
- Oxygen and impurity entry through leaks at seals and perforated tubes
- Condenser
- Power Transformer
- Cooling Water
- Oxygen and impurity entry through leaks at seals and perforated tubes
- Pressure: 227°C, 1000 psi
- Temperature: 50°C
Primary water chemistry

- avoid water radiolysis via low corrosion potential
- minimize oxidation of zirconium clad
- minimize activity of circuit
- minimize crud deposition on fuel

Source: P. Combrade
Water chemistry in PWR primary circuit

**Pressure**
- high enough to avoid boiling
- local boiling may occur and cause formation of deposits that lead to axial offset anomaly (AOA)

**Boric acid**
- controls nuclear reaction
- decreases throughout fuel cycle

**Lithium hydroxide**
- to control pH - product of nuclear reaction with B
- conc. from 2.1 -> 3.5 ppm to reduce activity in circuit

**Oxygen**
- specification is <0.1 ppm
- much lower in service

Source: P. Combrade
**Water chemistry in PWR secondary circuit**

- Minimize corrosion problems (SG tubes, C-steel, Cu alloys in condenser tubing)
- Minimize formation of deposits (fouling of tube in free span, blockage of TSPs)
- Minimize costs and waste release

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>5.4 – 7.2</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>284 - 305</td>
</tr>
<tr>
<td>Oxygen (ppm)</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Conductivity (µS.cm⁻¹)</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>NH₃, morpholine or ethanolamine</td>
<td>As required for pHₜ</td>
</tr>
</tbody>
</table>
| Hydrazine (ppb)            | Initially [O₂]+ 5  
                            | Now 50 to 100  
                            | Or > 20 and > 8X[O₂] (EPRI) |
| Sodium (ppm)               | <0.005  |
| Chloride (ppm)             | <0.03   |
| SiO₂ (ppm)                 | <1      |
| pH₂₅                       | 8.9 - 10 |

*Source: P. Combrade*
Operational Experience with Corrosion of Reactor Components
Material degradation in PWRs

Deposits on fuel raise surface temperature and accelerate corrosion of fuel cladding.

Axial offset anomaly. Boron incorporated in deposits and reduces local power.

Sulfide carry over caused by $N_2H_4$ reduction of sulfate: deposit on turbine surfaces.

$SO_4^{2-} + N_2H_4 \rightarrow S^{2-}$

Superheated crevices concentrate even very dilute chemicals to saturation; these solutions are generally corrosive and unpredictable owing to the complexity of their chemistries.

Expansion of corrosion products in tight geometries produces high local stresses.

Even thin deposits can produce corrosive conditions at the TTS.
Corrosion of SG Broached Tube Support Plates

TSP broached area and typical blockage deposit (after Corredera et al., 2008)

Too low a secondary side pH seems to be the main aggravating factor

Courtesy Peter Scott
Pitting Corrosion

Type 304 stainless steel pitted in a rinsing solution containing chloride ions and unidentified sulphur species

Type 304 stainless steel in a bromide solution: note the role of scratches on pit initiation

After Désestret

After During

Courtesy Peter Scott
Crevice Corrosion

Corrosion under a Type 316 stainless steel seal in brackish water (after During)

Corrosion under deposits of a Type 316 L ship tank washed with sea water and inefficiently rinsed (After A. Désestret)

Courtesy Peter Scott
Flow Assisted (Accelerated) Corrosion

Scalloped surface of C-steel in 200 °C water (condensate)

Monel back-pressure control valve of a pump for cooling margarine: 80% Water (pH 4, 8% NaCl), 20% fat, 45 °C (After During)

Courtesy Peter Scott
Effect of Flow Rate, Temperature and Chromium Content on FAC Carbon Steel

* Effect of flow rate and T

* Effect of Cr

* Minor effect of N$_2$H$_4$

Courtesy Peter Scott
Mihama 3 FAC Incident, 2004

Courtesy Peter Scott
Erosion Corrosion

- Erosion Corrosion = metal loss due to abrasive particles in the environment

Type 914L Pump rotor in phosphoric acid containing solid salt particles: After a few months of service (After Audouard)

Duplex Stainless Steel in natural gas containing particles of sand and clay (After During)

Courtesy Peter Scott
Cavitation-corrosion

- Cavitation-corrosion = mechano-chemical damage due to cavitation (caused by implosion of vapour bubbles) in high turbulent flow
  - Compared to FAC, cavitation corrosion creates ragged surfaces with some surface cold work due to the mechanical effect of cavitation

Type 316 SS pump impeller in skimmed milk at 70 °C (after During)

Courtesy Peter Scott
Boric Acid Corrosion of Low Alloy Steel Bolting

- General corrosion by boric acid and steam cutting due to primary water leaks can lead to a severe reduction in shank diameter

Czajkowski, 1983

Courtesy Peter Scott
Davis Besse
RPV Head Degradation- Nozzle 3
Davis-Besse is not a unique incident

Source: R. Staehle
BAC in US PWR Primary Systems

Pressurizer Manway Closure Studs
- St. Lucie
- Calvert Cliffs

Pressurizer Spray Valve Studs
- Connecticut Yankee
- Arkansas Nuclear One Unit 1
- H.B. Robinson Unit 2

Reactor Vessel Closure Studs
- Palisades
- Turkey Point 4
- Calvert Cliffs 1

CRDM Housing Nut Rings
- Arkansas Nuclear One Unit 1

Reactor Coolant Pump Studs
- Fort Calhoun
- Calvert Cliffs
- Indian Point 2
- Oconee Units 1, 2, & 3
- Indian Point 2

Reactor Vessel Head
- Turkey Point 4
- Salem 2

Reactor Coolant Pump Suction Piping
- Calvert Cliffs

Steam Generator Manway Closure Studs
- St. Lucie
- Arkansas Nuclear One Unit 2
- Calvert Cliffs
- Arkansas Nuclear One Unit 1
- Maine Yankee

Pressurizer Bottom Head
- Arkansas Nuclear One 2

Courtesy Peter Scott
Frequency of BAC as a Function of Location in PWR Systems

Courtesy Peter Scott
Microbial Corrosion

- Aerobic and anaerobic microorganisms

Duplex weld SS possibly corroded by SRB

Pit induced by ennoblement due to Manganese Oxidising MicroOrganisms (MOMOs) in low chloride water (after Linhardt)

Courtesy Peter Scott
Example of MIC in a FFW-line

(After Maussner, 2006)

- Perforation after approx. 2 years of operation
- Material: 1.4541 (equivalent to Type 321)
- Medium: Deep well water, drinking water, stagnant
- Temperature: Ambient

Courtesy Peter Scott
MIC in NPPs

- Significant number of events:
  - mainly in auxiliary circuits;
  - some of them involving very large numbers of weldments

Courtesy Peter Scott
Stress Corrosion Cracking

- Cu alloys in presence of ammonia

Coffee pot left during one night in the vicinity of « polluted » baby nappies (After A. Désestret)

Al brass (Cu 2Al Mn) condenser bolt in the presence of traces of ammonia in condensate (after During)

Courtesy Peter Scott
Stress Corrosion Cracking

- Ex: Type 316 SS under insulation (after During)
  - Penetration by rinsing water with 60 ppm Cl\(^-\)
  - Temperature 50-60 °C
  - SCC in a few months

Longitudinal cracks due to residual stresses

Courtesy Peter Scott
Stages of crack initiation and propagation

- **Precursor**: Defines necessary condition for initiation to occur, but not part of SCC.
- **Incubation**: First SCC segment but not generally visible penetration.
- **Slow Growth**: About 1/100th to 1/10th rate of propagation; part of SCC and visible in optical microscopy. Transition from initiation to propagation: 50-500μm

> 10 years!

Courtesy Roger Staehle
Alloys 600, X-750, 82&182 in PWR Primary Circuit

Courtesy Peter Scott
SCC of Ni-base Alloys in BWRs

- SCC of Ni-base alloys has been found in several BWRs
  - Cracking of the heat affected zone of Alloy 600 shroud head bolts
  - Cracking of Alloy 182 weld metal in shroud supports and CRD stub tubes.
    - *SCC of shroud support welds is a recent concern for BWRs*
      - Inspection/mitigation necessary - poor accessibility at the bottom of the RPV for repairs.

(after Fujimori 2008)
Brief History of Nickel Base Alloys in PWRs

• Cracking in service of Alloy 600 from the 1970s onwards
  – 1980s: Steam generator tubes and Pressurizer sleeves
  – 1990s: Upper Head CRDM nozzles
  – From 2000: Alloy 182 welds and steam generator divider plates
• Remedies
  – Mid 1970s – Thermal treatment of Alloy 600 for steam generators tubes at ~700°C → Alloy 600 TT - Generally good operating experience
  – Mid 1980s – decision to use Alloy 690 → excellent operating experience - no in-service corrosion induced cracking to date
• From the 1980s to date – management of Alloy 600 in service
  – Development of NDE techniques
  – Empirical models for predicting in-service cracking
• From the early 1990s to date – reliability of Alloy 690TT examined

 Courtesy Peter Scott
Primary side cracking of Alloy 600 SG tubes

Source: P. Combrade
Secondary side cracking of Alloy 600 SG tubes

- ICA-SCC under deposits formed inside Tube to Tube Support Plate (TSP) gaps or on top of tubesheet.
25 mode-location cases of corrosion with Alloy 600 tubes and drilled hole tube supports

From Staehle and Gorman, 2004
Sub-modes of SCC for Alloy 600 in HT water

Source: R. Staehle
Effect of temperature on crack initiation

Source: P. Combrade
Effect of cold work (scratches)

Source: P. Combrade
Metallurgical variables

Source: P. Scott
Alloy X750 Guide Tube Pin Cracking

After Benhamou, 2004

Courtesy Peter Scott
PWSCC in upper head CRDM penetrations

Source: P. Combrade
SCC in one component can lead to other forms of corrosion.
SCC has been observed in outlet nozzle weldments

VC-Sumner, 2000

Source: R. Staehle
Steam Generator Channel Head

- SG divider plates
  - 12 SG affected out of 87 inspected
  - Cracks on the hot-leg side of the stub runner
  - Mainly located in two lines parallel to the weld axis
  - No cracks in the divider plate itself
  - Superficial cracks - depth < 2 mm in most cases
  - No propagation after successive inspections

 Courtesy Peter Scott
Operating times to Alloy 182 Weld Cracking (for different types of welds)

![Graph showing cumulative number of cracked welds vs. operating time (hours) for butt welds and J-welds.](image)

Courtesy Peter Scott
Incidence of Stress Corrosion Cracking in Nickel-Base Alloys in PWRs

- Only cold worked and/or as-welded Alloy 600/182/82 components have been affected so far
- Components subjected to heat treatment due to stress relief of adjacent low alloy steel components (typically 610°C for 10 hours) have not cracked to date:
  - Mockup studies show that the surface residual stress is very significantly reduced even though the stress relief temperature is not optimized for nickel base alloys
  - Microscopic examination shows that stress relief occurs due to recrystallization during heat treatment of heavily cold worked surface layers from grinding

Courtesy Peter Scott
Field Experience of SCC in Austenitic Stainless Steels in PWRs

- Austenitic stainless steels Type 304 or 316 have generally performed very well in PWR primary water service with relatively few service failures associated with the following
  - Very high levels of cold work
  - Presence of solution impurities in dead legs, e.g. Cl\(^{-}\), SO\(_4\)\(^{-}\) and O\(_2\)
  - High neutron doses
- Failures for SA 453 Grade 660 (A 286) bolting due to stress corrosion cracking in primary water have been reported due to excess preload or bad design (shank to head radius)

Courtesy Peter Scott
BWR SS Piping --> Core Components

Stress Corrosion Cracking History:
1969 1st detected in sensitized SS
1970s Stainless steel welded piping
1980s BWR internals
1990s Low stress BWR internals, CW & crevices
2000s Internals, CW

Alloy 182/600
Type 304, 304L or 347 SS

(From Andresen, 2008)
There is a clear association between the incidence of cracking and hardness $>300$ HV but plant age is not a risk factor. Thermal sensitization is only important in occluded zones. The phenomenon in “normal RCS water” is often (unfortunately) labeled “PWSCC.”
Degradation of fatigue strength of low carbon & LAS steels at high potential is caused by dissolution of MnS inclusions.

Degradation of fatigue strength of low stainless steel at low potential could be due to their higher corrosion rate compared to high potential or due to hydrogen.

Courtesy Peter Scott
### IASCC service experience

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Reactor Type</th>
<th>Possible Sources of Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Cladding</td>
<td>304 SS</td>
<td>BWR</td>
<td>Fuel Swelling</td>
</tr>
<tr>
<td>Fuel Cladding</td>
<td>304 SS</td>
<td>PWR</td>
<td>Fuel Swelling</td>
</tr>
<tr>
<td>Fuel Cladding *</td>
<td>20%Cr/25%Ni/Nb</td>
<td>AGR</td>
<td>Fuel Swelling</td>
</tr>
<tr>
<td>Fuel Cladding Ferrules</td>
<td>20%Cr/25%Ni/Nb</td>
<td>SGHWR</td>
<td>Fabrication</td>
</tr>
<tr>
<td>Neutron Source Holders</td>
<td>304 SS</td>
<td>BWR</td>
<td>Welding &amp; Be Swelling</td>
</tr>
<tr>
<td>Instrument Dry Tubes</td>
<td>304 SS</td>
<td>BWR</td>
<td>Fabrication</td>
</tr>
<tr>
<td>Control Rod Absorber Tubes</td>
<td>304/304L/316L SS</td>
<td>BWR</td>
<td>B₃C swelling</td>
</tr>
<tr>
<td>Fuel Bundle Cap Screws</td>
<td>304 SS</td>
<td>BWR</td>
<td>Fabrication</td>
</tr>
<tr>
<td>Control Rod Follower Rivets</td>
<td>304 SS</td>
<td>BWR</td>
<td>Fabrication</td>
</tr>
<tr>
<td>Control Blade Handle</td>
<td>304 SS</td>
<td>BWR</td>
<td>Low stress</td>
</tr>
<tr>
<td>Control Blade Sheath</td>
<td>304 SS</td>
<td>BWR</td>
<td>Low stress</td>
</tr>
<tr>
<td>Control Blades</td>
<td>304 SS</td>
<td>PWR</td>
<td>Low stress</td>
</tr>
<tr>
<td>Plate Type Control Blade</td>
<td>304 SS</td>
<td>BWR</td>
<td>Low stress</td>
</tr>
<tr>
<td>Various Bolts **</td>
<td>A-286</td>
<td>PWR &amp; BWR</td>
<td>Service</td>
</tr>
<tr>
<td>Steam Separator Dryer Bolts **</td>
<td>A-286</td>
<td>BWR</td>
<td>Service</td>
</tr>
<tr>
<td>Shroud Head Bolts **</td>
<td>600</td>
<td>BWR</td>
<td>Service</td>
</tr>
<tr>
<td>Various Bolts</td>
<td>X-750</td>
<td>BWR &amp; PWR</td>
<td>Service</td>
</tr>
<tr>
<td>Guide Tube Support Pins</td>
<td>X-750</td>
<td>PWR</td>
<td>Service</td>
</tr>
<tr>
<td>Jet Pump Beams</td>
<td>X-750</td>
<td>BWR</td>
<td>Service</td>
</tr>
<tr>
<td>Various Springs</td>
<td>X-750</td>
<td>BWR &amp; PWR</td>
<td>Service</td>
</tr>
<tr>
<td>Various Springs</td>
<td>718</td>
<td>PWR</td>
<td>Service</td>
</tr>
<tr>
<td>Baffle Former Bolts</td>
<td>316 SS Cold Work</td>
<td>PWR</td>
<td>Torque, differential swelling</td>
</tr>
<tr>
<td>Core Shroud</td>
<td>304/316/347 /L SS</td>
<td>BWR</td>
<td>Weld residual stress</td>
</tr>
<tr>
<td>Top Guide</td>
<td>304 SS</td>
<td>BWR</td>
<td>Low stress (bending)</td>
</tr>
</tbody>
</table>
IASCC has been realized both in-plant and in laboratory experiments.

**Plant**

- BWR Creviced Control Blade Sheath
- Threshold Fluence for IGSCC
  \[ \approx 5 \times 10^{20} \text{ n/cm}^2 \]

**Laboratory**

- Neutron Fluence (n/m², E>1 MeV)
- %IGSCC

Data from:
- Kodama et al. 1993
- Clark and Jacobs 1983
- Jacobs et al. 1993
- Kodama et al. 1992

- 304 SS
- 316 SS

Approximate Threshold: \[ \approx 5 \times 10^{20} \text{ n/cm}^2 \]
Pressure Vessel and Core Components of a PWR-Baffle-Formaer Bolt Cracking
Baffle bolts experience some of the highest fluences and temperatures in a PWR core.
Many different irradiation processes influence material performance as well as susceptibility to cracking.
Failure as a percent of irradiated yield strength vs. dose

- Failures (Freyer)
- Non-Failures (Freyer)
- Stress threshold (Freyer)
- Failures (Takakura)
- Chooz A 30 dpa (Toivonen)
- Failures (Nishioka)
- Chooz A 23 dpa Failures
- Chooz A 23 dpa Non-Failures
- Barseback 11 dpa Failures
- Barseback 11 dpa Non-Failures

% of Irradiated Yield Strength vs. dpa

0 20 40 60 80

100 120 140

0 20 40 60 80 100 120 140

CIR final report, 2010
Effect of irradiation on crack growth in stainless steels in high temperature water

Sensitized 304 Stainless Steel
30 MPa m, 288°C Water
0.06-0.4 µS/cm, 0-25 ppb SO₄

SKI Round Robin Data
filled triangle = constant load
open squares = "gentle" cyclic

316L (A14128, square)
304L (Grand Gulf, circle)
non-sensitized SS
50%RA 140°C (black)
10%RA 140°C (grey)

GE PLEDGE Predictions
30 MPa m
Sens SS

GE PLEDGE Predictions for Unsens. SS (upper curve for 20% CW)

Means from analysis of 120 lit. sens SS data
0.06 µS/cm

Summary of IASCC in BWRs

- SCC of 316L(NG)/304L core shrouds and has been found in many BWRs
  - Elimination of surface cold work is important during fabrication
  - Neutron and gamma-ray irradiation may assist cracking
- IASCC of 316L has been found in handles and sheaths in many control rods
  - Crevices should be avoided in the core region

Neutron fluence dependence of control rod sheath cracking

After Fujimori 2008
General corrosion is the dominant form of degradation of fuel cladding.

- In primary environment (water or steam), Zr alloy cladding undergoes corrosion according to following chemical reaction:

\[
\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2(1 - w)\text{H}_2(\text{coolant}) + 4w\text{H} (\text{metal})
\]

- \( w \): fraction of reaction produced hydrogen absorbed by the metal
- Progressive formation of a \( \text{ZrO}_2 \) layer
- Hydriding of the cladding metal bulk

Source: B. Cheng
General corrosion is the dominant form of degradation of fuel cladding

- In a primary environment, Zr alloys undergo corrosion

\[ \text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2 \]

- Progressive growth of a ZrO\(_2\) layer
- Hydrogen uptake results in hydriding of the cladding
Hydrogen content correlates with oxide thickness

Source: B. Cheng
There are distinct variations in corrosion between zirconium alloys

- Uniform corrosion resistance is strongly dependent upon the chemical composition and the microstructure of the Zr alloy.
- M5 (Binary alloy with fully recrystallized microstructure) appears the most corrosion resistant while CWSR Zircaloy is the less resistant.

Source: B. Cheng
Hydrogen pickup leads to hydriding and hydride cracking

Fracture proceeds by Delayed Hydride Cracking (DHC) mechanism

- Phenomenon might be activated under decreasing temperature, for instance during Dry Storage
- The pre-existence of a crack is required (For instance, initiation in hydride rim under reactor operation)
- Propagation of the crack is assisted by hydrogen diffusion and hydride precipitation at the crack tip

Source: B. Cheng
Secondary-degradation can lead to “sun-burst” hydrides

- Secondary degradation results from water ingress in the fuel rod after primary failure (PCI, fretting, CILC)
- Water causes oxidation of the inner surface of the cladding as well as of the fuel pellet
- Significant amount of hydrogen is produced which is picked up by the cladding at some distance away from the primary defect
- Hydride Sun Burst can be formed leading to the perforation of the cladding
Irradiation-enhanced oxidation in zirconium alloys
PCI in Zircaloy Fuel Cladding
Effects of thermal expansion and fuel swelling

Source: B. Cheng
Additional sources of stress in PCI
SCC on OD of stainless steel cladding caused by pellet-clad interaction (PCI)
SCC on the ID of Zircaloy cladding caused by pellet-clad Interaction (PCI)
Managing Corrosion in Reactors

• Materials selection
  - select materials that are appropriate for the environment
  - control microstructure through processing/heat treatment

• Environment control
  - maintain a low corrosion potential
  - minimize impurities
  - keep conductivity low

• Engineering design
  - minimize residual stresses
  - avoid dissimilar metal welds
  - avoid crevices
  - surface finish
Managing Corrosion in Reactors

Increasing tensile stress decreases time for crack initiation and increases the propagation rate of pre-existing cracks.

Sources of tensile stress:
- Applied
- Residual
- Thermal
- Welding
- “Oxide Wedging”

Susceptible BWR Materials:
- Alloy 600
- Alloy 182
- Alloy X750
- SS 304
- SS 304L and 316L
- SS 347, 321, 348

Environmental Considerations:
- Water quality (impurities)
- Radiolysis/oxidant concentrations
- Temperature
- Surface treatments
- Flow rate
- Irradiation

Source: K. Fruzzetti
Managing Corrosion in Reactors

Even the PUREST water will NOT provide IGSCC immunity in the BWR - good water quality delays initiation, but IGSCC still occurs.

Source: K. Fruzzetti
Managing Corrosion in Reactors

• **PWRs**
  - pH control to control corrosion
  - hydrogen addition to suppress corrosion potential on the primary side
  - minimize impurities on secondary side

• **BWRs**
  - hydrogen water chemistry to suppress corrosion potential
  - noble metal addition
  - TiO$_2$ technology

*Examples of BWR water chemistry strategy evolution*
BWR IGSCC Mitigation using HWC

Source: K. Fruzzetti
Beyond HWC alone

Lower Vessel ECP, V(SHE)

Feedingwater Hydrogen Concentration (ppm)

How to make stainless steel react as if it was Pt?
Answer: Incorporate Pt onto the surfaces.

Source: K. Fruzzetti
HWC and noble metal additions

- HWC effective for IGSCC Mitigation (all U.S. BWRs applying)
- Adding noble metals results in catalytic surfaces and reduces amount of hydrogen needed by factor of ~4 or more
- Noble metals can be added 3 ways:
  - During plant shutdown (hold process) (NMCA)
  - During normal full power operation (OLNC)
  - To piping surfaces (after a decontamination) (LTNC)
- Majority of U.S. BWRs now apply noble metal (29 of 35 to date)

...but hydrogen is not always being injected at BWRs

Source: K. Fruzzetti
TiO$_2$ technology for IGSCC Mitigation

- Toshiba/TEPCO technology
- Cathodic reaction by photo excitation reaction
- Expected to mitigate SCC of components exposed to UV
- ECP decrease to $<-230\text{mV}$
- No hydrogen addition is required for reactor internals mitigation
- Expected advantages:
  - No main steam radiation increase
  - Effective for almost all reactor internals
  - No crack flanking for reactor internals
  - Compatible with HWC and/or Noble metals
- Application at 2-F-1 plant in June 2010, evaluation of plant response is ongoing

Source: K. Fruzzetti
Summary

• Aqueous corrosion is an electrochemical process in which the metal *and* the solution play equally important roles

• Corrosion takes many forms; general, galvanic, localized, SCC, CF, hydrogen, FAC, Erosion, MIC….

• Material selection must include the response the environment

• Environments are often dictated by one component, but can affect others

• Corrosion in LWRs covers the full space of corrosion modes, and differs between plant types, conditions, components, etc.
Summary

• Management of corrosion includes accounting for:
  - material
  - environment
  - external factors; stress, irradiation, etc

• Management of corrosion is not an insurmountable task, but it needs to be done as a preventative measure - when the systems are planned - not after they’re built!
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