Radiochemistry Webinars

Nuclear Fuel Cycle Series

Chemistry and Radiochemistry of the Reactor Coolant System

In Cooperation with our University Partners
Meet the Presenter...

Robert Litman, Ph.D., has been a researcher and practitioner of nuclear and radiochemical analysis for the past 42 years. He is well respected in the nuclear power industry as a specialist in radiochemistry, radiochemical instrumentation and plant systems corrosion. He has co-authored two chapters of MARLAP, and is currently one of a team of EMS consultants developing radiological laboratory guidance on radionuclide sample analyses in various matrices, radioactive sample screening, method validation, core radioanalytical laboratory operations, contamination, and rapid radioanalytical methods. He authored the Primary Water Chemistry Guidelines on Radionuclides section of the EPRI PWR, and has been a significant contributor to the EPRI Primary-to-Secondary Leak Detection Guidelines. Dr. Litman has worked with the NRC in support of resolving GSI-191 issues (chemical effects following a loss of coolant accident) at current nuclear power plants and reviewed designs for addressing that safety issue for new nuclear power plants. His areas of technical expertise are gamma spectroscopy and radiochemical separations. Dr. Litman has been teaching courses in Radiochemistry and related special areas for the past 28 years.

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Chemistry and Radiochemistry of the Reactor Coolant System

Robert Litman, PhD
Objectives

- Review the basic operation of a PWR and why chemistry control is important
- Describe the chemistry control regime in a PWR
- Describe the effects of chemistry control on radionuclide activity in the RCS
- Identify the principal radionuclides in the RCS and how they are formed
- Identify changes to RCS radiochemistry as a function of fuel condition and plant operation
Typical Reactor Coolant System of a PWR

Diagram from http://www.nrc.gov/reactors/power.html
Typical U-Tube Steam Generator

Purified steam

U-bend region

Tube bundle with support plates

Hot leg inlet to SG tubes

Diagram from http://westinghousenuclear.com/Operating-Plants/PWR/Products-and-Services/cid/54/Steam-Generators
A PWR Fuel Assembly

Courtesy of Westinghouse at http://integoogle.westinghousenuclear.com/search?q=fuel+assembly&site=default_collection&client=westinghouse_frontend&proxystylesheet=westinghouse_frontend&output=xml_no_dtd
What is the Job of the Plant Chemist at a PWR?

Minimize Corrosion
Why Minimize Corrosion?

- Minimizes activation to radioactive species
- Maximizes plant efficiency and power output
- Minimizes the probability of fuel defects occurring
- Minimizes the release of radionuclides to the environment and dose to the public
- Minimizes contamination in the plant
- Minimizes dose to plant staff
RCS Principal Metallurgy
(% Surface Area Exposed to RCS)

- **Stainless Steel (~5%)**
  - Piping
  - Pumps
  - Vessel, SG bowl and pressurizer internal cladding

- **Inconel 600, 690, X-750 or 718 (60-70%)**
  - SG tubes
  - Upper and lower internals

- **Zircalloy or Zirlo (20-30%)**
  - Fuel clad
  - Grid straps
RCS Components

- Stainless Steel
  - Accounts for ~5% of surface area in RCS
  - Contains ~18% chromium, ~8% nickel, ~74% iron
  - Has the highest general corrosion rate of all internal RCS surface materials (10^{-3} to 10^{-5} mil/yr)
  - Forms two different layers of corrosion during initial power cycle
RCS Components

• Inconel
  – Accounts for 60-70% of surface area
  – Composition
    • ~74-77% nickel, 14-17% chromium, 6-10% iron
    • Minor constituents (0.01-1%): Al, Cu, Ti, Si, Mn, C, Co, and S
RCS Components

• Zirconium alloys
  – Zirc-4 (98% Zr, ~1.4% Sn, 0.2% Fe, ~0.1% Cr)
  – Zirlo (99%Zr, ~1%Nb, ~0.1% Sn, lower Fe and Cr than Zirc-4)
  – Principally as the fuel cladding
  – Accounts for about 20% of the surface area
  – Also used as the grid straps on the fuel assemblies
What are the Contaminants of Concern in the RCS?

• **Major:**
  – Chloride
  – Fluoride
  – Oxygen
  – Sulfate
  – Zeolite formers (Al, Ca, Mg, Na, Si)

• **Minor**
  – Nitrates
  – Ammonia
  – Organics
Contaminants

- **Oxygen** (<5 ppb)
- **Anionic**
  - Cl (<150 ppb)
  - F (<150 ppb)
  - $\text{SO}_4^{2-}$ (<150 ppb)
- **Scale formers**
  - Ca (<40 ppb)
  - Mg (<40 ppb)
  - Al (<80 ppb)
  - Si (<100 ppb)
Principal Corrosion Mechanisms in the RCS

- **General corrosion**: all metals

- **Intergranular attack**
  - Primary water stress corrosion cracking (PWSCC): stainless, Inconel
  - Hydriding: zirlo, zircalloy

- **Crevice corrosion**: stainless
RCS General Corrosion (stainless steel)

RCS Fluid Flow

Several Hundred microns
RCS Corrosion Film Characteristics (stainless steel)

• Region 1 - a transient solid layer

• Region 1 stability affected by:
  – Reactor power (i.e., temperature)
  – pH
  – Hydraulic flow
  – Other chemicals/contaminants in the RCS

• Refueling outage effects
RCS Metal Alloys

- Highly resistant to general corrosion
- Metal alloys are a mixture

The microstructural unit – the “grain”
Metal Grains

- No specific size or shape
- Grain boundary
- Intergranular area
- Annealing of the alloy
Stress

• Caused by the inexact alignment of the grain boundaries
  – Somewhat relieved by annealing
  – Can be increased by the result of “cold work” of metals

• Present to some extent in all alloys

• Eventually causes stress corrosion cracking (SCC)
What Chemicals are Used in the RCS?

- Water
- Hydrogen
- Boric acid
- Lithium hydroxide
- Hydrazine
- Hydrogen peroxide
Oxygen

The effect of oxygen on ferrous materials:

\[ \text{Fe} + \text{O}_2 \leftrightarrow \text{FeO} \]  \hspace{1cm} (1)

No Water!

\[ \text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{FeO} + \text{H}_2 \]  \hspace{1cm} (2)

No Oxygen!

Because the RCS operates with water, (2) is the one we focus on.
Hydrogen

- Hydrogen is principally used to suppress the radiolytic cleavage of water by gamma radiation. Radiolysis produces oxygen and reactive radical species such as $\text{O}^\cdot$, $\text{•OH}$, $\text{•OOH}$, $\text{O}_2^\cdot$

$$2\text{H}_2\text{O} \leftrightarrow 2\text{H}_2 + \text{O}_2$$
$$\text{H}_2 + \text{•OH} \leftrightarrow \text{H}^\cdot + \text{H}_2\text{O}$$

etc.
Hydrogen

- Hydrogen maintains metals in lower oxidation states:
  \[
  \text{Ni}_x\text{Fe}_y\text{O}_z + \text{H}_2 \rightarrow \text{Ni}_x\text{Fe}_y\text{O}_{z-1} + \text{H}_2\text{O}
  \]
- Electrochemical potential
- Controls oxide form of Fe and Ni
Hydrogen

Too much hydrogen will hydride fuel cladding

\[
\text{Excess} \\
Zr^0 + 2H_2 \rightarrow ZrH_4
\]

and also will destabilize CRUD layers
Effect of Hydrogen on CRUD

![Graph showing the effect of temperature on dissolved hydrogen concentration for different compositions of Ni<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub>](image)

- **Ni<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub>**
  - Closed circles: \( x = 1.0 \)
  - Open squares: \( x = 0.5 \)

**Graph Details:**
- **Y-axis:** Dissolved H<sub>2</sub> conc., STP cc/kg H<sub>2</sub>O
- **X-axis:** Temperature, °C
- **Logarithmic scale for the Y-axis**
Boric Acid

- Soluble neutron absorber is $^{10}\text{B}$ (19.9 %)
- Start of fuel cycle: 1200-1700 ppm B
- End of fuel cycle: 0 ppm B
- The “at temperature” pH of RCS is acidic without a pH control agent
Boric Acid Reactions

• Both isotopes of boron undergo nuclear reactions:
  
  - $^{10}\text{B}(n,\alpha)^7\text{Li}$
    - Cross section is $\sim$3900 barns
    - $\sim$0.15 ppm/day/1000 ppm boron
  
  - $^{11}\text{B}(n,\gamma)^{12}\text{B} \rightarrow ^{12}\text{C}$
    - Cross-section is 5 mb
Control of RCS at $pH_{T_{avg}}$ is “Critical”

- Boric acid makes the RCS acidic
- LiOH is added - $pH_{T_{avg}}$ to about 7.2
  - Neutrality for $pH_{T_{avg}}$ is about 6.9
- Ratio of B/Li - maintained by Chemistry and Operations groups
Why Lithium?

- No long-lived activation products
- Easily enriched to the $^7\text{Li}$ isotope
- Small amount in mass required to adjust pH
- It is produced by boron reaction
Lithium Concentration During Power Operation

- Lithium is also “used up” by:
  - RCS bleed and feed
    - To maintain power level by diluting out B
  - Chemistry sampling
  - Cation bed in service
  - RCP seal leak off

- Certain operational changes require addition of lithium
Lithium Concentration During Power Operation

- **Produced by**
  - $^{10}\text{B}(n,\alpha)^{7}\text{Li}$ reaction
  - Cross section is $\sim 3900$ barns
  - $\sim 0.15$ ppm/day/1000 ppm boron

- **Used up by**
  - $^{7}\text{Li}(n,\alpha)^{3}\text{H}$
    - This is NOT a significant contributor to RCS $^{3}\text{H}$
  - $^{7}\text{Li}(n,\gamma)^{8}\text{Li}\rightarrow^{8}\text{Be} + \beta^{-}$
    - $^{8}\text{Li} t_{1/2} = 840$ ms
    - $^{8}\text{Be} t_{1/2} = 7 \times 10^{-17}$ s
What About $^6$Li?

- Natural lithium is 7.6% $^6$Li
  - PWR lithium is enriched to 99.5+% $^7$Li
  - Minimizes production of tritium
    - $^6$Li(n,α)$^3$H
Lithium and Boron Effects
(Constant Temperature)
Hydrazine

- Added during start-up from refueling outages
- Reacts with oxygen
  \[ \text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \]
- Decomposes
  \[ \text{N}_2\text{H}_4 \rightarrow 2\text{H}_2 + \text{N}_2 \]
  \[ 2\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{NH}_3 + \text{H}_2 \]
Hydrogen Peroxide

- Transient corrosion layer
- Decomposes into $\text{H}_2\text{O}$ and $\text{O}_2$
- Provides an oxidizing environment to solubilize ions
### Activation Products: Corrosion and Contaminants

<table>
<thead>
<tr>
<th>Radionuclide Product</th>
<th>Half-Life</th>
<th>Nuclear Reaction</th>
<th>Source of Target Material</th>
<th>Principal Gamma Rays (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{56}\text{Mn}$</td>
<td>2.6 h</td>
<td>$^{55}\text{Mn}(n, \gamma)$</td>
<td>Corrosion</td>
<td>847</td>
</tr>
<tr>
<td>$^{24}\text{Na}$</td>
<td>15 h</td>
<td>$^{23}\text{Na}(n, \gamma)$</td>
<td>MUW, SAT</td>
<td>1369, 2754</td>
</tr>
<tr>
<td>$^{41}\text{Ar}$</td>
<td>1.8 h</td>
<td>$^{40}\text{Ar}(n, \gamma)$</td>
<td>Air contaminant</td>
<td>1294</td>
</tr>
<tr>
<td>$^{58}\text{Co}$</td>
<td>71 d</td>
<td>$^{58}\text{Ni}(n, p)$</td>
<td>Nickel alloys</td>
<td>811</td>
</tr>
<tr>
<td>$^{122}\text{Sb}$</td>
<td>2.7 d</td>
<td>$^{121}\text{Sb}(n, \gamma)$</td>
<td>Start up source, RCP bearing</td>
<td>564</td>
</tr>
<tr>
<td>$^{89}\text{Zr}$</td>
<td>3.3 d</td>
<td>$^{90}\text{Zr}(n, 2n)$</td>
<td>Fuel cladding</td>
<td>909</td>
</tr>
<tr>
<td>$^{187}\text{W}$</td>
<td>24 h</td>
<td>$^{186}\text{W}(n, \gamma)$</td>
<td>Weld rod residue, satellite</td>
<td>686</td>
</tr>
<tr>
<td>$^{51}\text{Cr}$</td>
<td>28 d</td>
<td>$^{50}\text{Cr}(n, \gamma)$</td>
<td>Stainless steel, nickel alloys</td>
<td>320</td>
</tr>
<tr>
<td>$^{54}\text{Mn}$</td>
<td>312 d</td>
<td>$^{54}\text{Fe}(n, p)$</td>
<td>Stainless steel</td>
<td>835</td>
</tr>
<tr>
<td>$^{60}\text{Co}$</td>
<td>5.3 a</td>
<td>$^{59}\text{Co}(n, \gamma)$</td>
<td>Cobalt bearing components</td>
<td>1332, 1173</td>
</tr>
<tr>
<td>$^{38}\text{Cl}$</td>
<td>37 m</td>
<td>$^{37}\text{Cl}(n, \gamma)$</td>
<td>MUW, $\text{H}_3\text{BO}_3$, contaminants</td>
<td>2168, 1642</td>
</tr>
<tr>
<td>$^{124}\text{Sb}$</td>
<td>60 d</td>
<td>$^{123}\text{Sb}(n, \gamma)$</td>
<td>Start-up source, RCP bearing alloy, fuel clad</td>
<td>603, 1691, 428, 601</td>
</tr>
<tr>
<td>$^{125}\text{Sb}$</td>
<td>2.8 a</td>
<td>$^{124}\text{Sb}(n, \gamma)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{110\text{m}}\text{Ag}$</td>
<td>250 d</td>
<td>$^{109}\text{Ag}(n, \gamma)$</td>
<td>Control rod wear</td>
<td>658, 885</td>
</tr>
<tr>
<td>$^{108\text{m}}\text{Ag}$</td>
<td>420 a</td>
<td>$^{107}\text{Ag}(n, \gamma)$</td>
<td></td>
<td>723, 434</td>
</tr>
<tr>
<td>$^{94}\text{Nb}$</td>
<td>$2 \times 10^4$ a</td>
<td>$^{93}\text{Nb}(n, \gamma)$, Fission Product</td>
<td>Fuel clad, fuel</td>
<td>871, 703</td>
</tr>
<tr>
<td>$^{46}\text{Sc}$</td>
<td>84 d</td>
<td>$^{45}\text{Sc}(n, \gamma)$</td>
<td>Trace element in zirc cladding</td>
<td>1120, 889</td>
</tr>
<tr>
<td>$^{57}\text{Co}$</td>
<td>272 d</td>
<td>$^{57}\text{Fe}(p, n)$</td>
<td>Stainless steel</td>
<td>122, 137</td>
</tr>
<tr>
<td>$^{109}\text{Cd}$</td>
<td>461 d</td>
<td>$^{108}\text{Cd}(n, \gamma)$</td>
<td>Control rod</td>
<td>88</td>
</tr>
<tr>
<td>$^{115\text{m}}\text{Cd}$</td>
<td>45 d</td>
<td>$^{114}\text{Cd}(n, \gamma)$</td>
<td></td>
<td>934, 1291</td>
</tr>
</tbody>
</table>
### Radionuclides: Activation of Water and Chemicals

<table>
<thead>
<tr>
<th>Radionuclide Product</th>
<th>Half Life</th>
<th>Nuclear Reaction</th>
<th>Source of Target Material</th>
<th>Principal Gamma Rays (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^7)Be</td>
<td>53 d</td>
<td>(^7)Li(p, n), Fission Product</td>
<td>Li</td>
<td>478</td>
</tr>
<tr>
<td>(^3)H</td>
<td>12.3 a</td>
<td>(^{10})B(n,2(\alpha)), Fission Product (^6)Li(n,(\alpha))</td>
<td>(\text{H}_3\text{BO}_3), fuel, Li</td>
<td>None ((\beta^+) emitter)</td>
</tr>
<tr>
<td>(^{11})C</td>
<td>20 m</td>
<td>(^{11})B(p, n)</td>
<td>Boric Acid</td>
<td>511 (See Note)</td>
</tr>
<tr>
<td>(^{14})C</td>
<td>5715 a</td>
<td>(^{14})N(n, p), (^{17})O(n, (\alpha))</td>
<td>RCS, MUW</td>
<td>No gamma</td>
</tr>
<tr>
<td>(^{13})N</td>
<td>10 m</td>
<td>(^{16})O(p, (\alpha))</td>
<td>Reactor Coolant</td>
<td>511 (See Note)</td>
</tr>
<tr>
<td>(^{16})N</td>
<td>7.1 s</td>
<td>(^{16})O(n,p)</td>
<td>Reactor Coolant</td>
<td>6129, 7115</td>
</tr>
<tr>
<td>(^{18})F</td>
<td>109 m</td>
<td>(^{18})O(p,n)</td>
<td>Water</td>
<td>511 (See Note)</td>
</tr>
<tr>
<td>(^{65})Zn</td>
<td>244 d</td>
<td>(^{64})Zn(n, (\gamma))</td>
<td>Zinc acetate or oxide</td>
<td>1115</td>
</tr>
<tr>
<td>(^{69m})Zn</td>
<td>14 h</td>
<td>(^{68})Zn(n, (\gamma))</td>
<td>Zinc acetate or oxide</td>
<td>439</td>
</tr>
<tr>
<td>(^{71m})Zn</td>
<td>4 h</td>
<td>(^{70})Zn(n, (\gamma))</td>
<td>Zinc acetate or oxide</td>
<td>387</td>
</tr>
</tbody>
</table>

Note: This is positron annihilation radiation because \(^{11}\)C, \(^{13}\)N and \(^{18}\)F decay by positron emission. The positron interacts with an electron, and two 511 keV gamma rays are emitted. There is no direct gamma ray associated with \(^{11}\)C, \(^{13}\)N or \(^{18}\)F decay.
Fission Product Radionuclides

<table>
<thead>
<tr>
<th>Short Half-life</th>
<th>$t_{1/2}$</th>
<th>Intermediate Half-life</th>
<th>$t_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{85m}$Kr</td>
<td>4.5 h</td>
<td>$^{131}$I</td>
<td>8.0 d</td>
</tr>
<tr>
<td>$^{87}$Kr</td>
<td>1.3 h</td>
<td>$^{133}$Xe</td>
<td>5.2 d</td>
</tr>
<tr>
<td>$^{88}$Kr</td>
<td>2.8 h</td>
<td>$^{99}$Mo</td>
<td>2.7 d</td>
</tr>
<tr>
<td>$^{99m}$Tc</td>
<td>6.0 h</td>
<td>$^{106}$Ru</td>
<td>1.0 y</td>
</tr>
<tr>
<td>$^{97}$Nb</td>
<td>1.2 h</td>
<td>$^{95}$Zr</td>
<td>64 d</td>
</tr>
<tr>
<td>$^{135m}$Xe</td>
<td>15 min</td>
<td>$^{95}$Nb</td>
<td>35 d</td>
</tr>
<tr>
<td>$^{135}$Xe</td>
<td>9.1 h</td>
<td>$^{137}$Cs</td>
<td>30 y</td>
</tr>
<tr>
<td>$^{138}$Xe</td>
<td>14.1 min</td>
<td>$^{134}$Cs</td>
<td>2.1 y</td>
</tr>
<tr>
<td>$^{97}$Zr</td>
<td>17 h</td>
<td>$^{136}$Cs</td>
<td>13.1 d</td>
</tr>
<tr>
<td>$^{132}$I</td>
<td>2.3 h</td>
<td>$^{133m}$Xe</td>
<td>2.2 d</td>
</tr>
<tr>
<td>$^{133}$I</td>
<td>21 h</td>
<td>$^{140}$La</td>
<td>1.7 d</td>
</tr>
<tr>
<td>$^{134}$I</td>
<td>53 min</td>
<td>$^{140}$Ba</td>
<td>12.8 d</td>
</tr>
<tr>
<td>$^{135}$I</td>
<td>6.6 h</td>
<td>$^{103}$Ru</td>
<td>39 d</td>
</tr>
<tr>
<td>$^{88}$Rb</td>
<td>18 min</td>
<td>$^{147}$Nd</td>
<td>11 d</td>
</tr>
</tbody>
</table>
# Radionuclides Formed from the Activation of Fuel

<table>
<thead>
<tr>
<th>Radionuclide Product</th>
<th>Half-Life of Radionuclide Product</th>
<th>Nuclear Reaction</th>
<th>Source of Target Material</th>
<th>Principal Gamma Rays (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{241}$Am</td>
<td>433 a</td>
<td>MNC</td>
<td>$^{238}$U</td>
<td>59</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>$2.4 \times 10^4$ a</td>
<td>MNC</td>
<td>$^{238}$U</td>
<td>None detectable at RCS concentrations</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>$6.6 \times 10^3$ a 14 a</td>
<td>MNC</td>
<td>$^{238}$U</td>
<td>None detectable at RCS concentrations</td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td></td>
<td>MNC</td>
<td>$^{238}$U</td>
<td>None detectable at RCS concentrations</td>
</tr>
<tr>
<td>$^{242}$Cm</td>
<td>163 d</td>
<td>MNC</td>
<td>$^{238}$U</td>
<td>None detectable at RCS concentrations</td>
</tr>
<tr>
<td>$^{243}$Cm</td>
<td>29.1 a</td>
<td>MNC</td>
<td>$^{238}$U</td>
<td>None detectable at RCS concentrations</td>
</tr>
<tr>
<td>$^{239}$U</td>
<td>23 m</td>
<td>$^{238}$U(n, $\gamma$)</td>
<td>$^{238}$U</td>
<td>None detectable at RCS concentrations</td>
</tr>
<tr>
<td>$^{239}$Np</td>
<td>2.4 d</td>
<td>Decay of $^{239}$U</td>
<td>$^{238}$U</td>
<td>106,278</td>
</tr>
</tbody>
</table>
Fuel Defect
Summary

- Corrosion in a PWR RCS is minimized to:
  - Maintain component integrity
  - Maintain good fuel performance
  - Minimize the activation of corrosion products
- Control of contaminants and pH help to achieve these objectives
References

- EPRI, “Pressurized Water Reactor Primary Water Chemistry Guidelines” (Volume 1, Revision 6)
- **Data Source for Half-lives and Cross Sections:** National Nuclear Data Center, Brookhaven National Laboratory, based on ENSDF and the Nuclear Wallet Cards, www.nndc.bnl.gov/chart
- Diagrams from:
  - http://westinghousenuclear.com/Operating-Plants/PWR/Products-and-Services/cid/54/Steam-Generators
  - www.nrc.gov/reactors/power.html
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NAMP website http://www.wipp.energy.gov/namp/