National Analytical Management Program (NAMP)
U.S. Department of Energy Carlsbad Field Office

Radiochemistry Webinars

Nuclear Fuel Cycle Series

- *Chemistry and Radiochemistry of the Reactor Coolant System*

In Cooperation with our University Partners

Meet the Presenter… *Dr. Robert Litman*

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

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TRAINING AND EDUCATION SUBCOMMITTEE

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

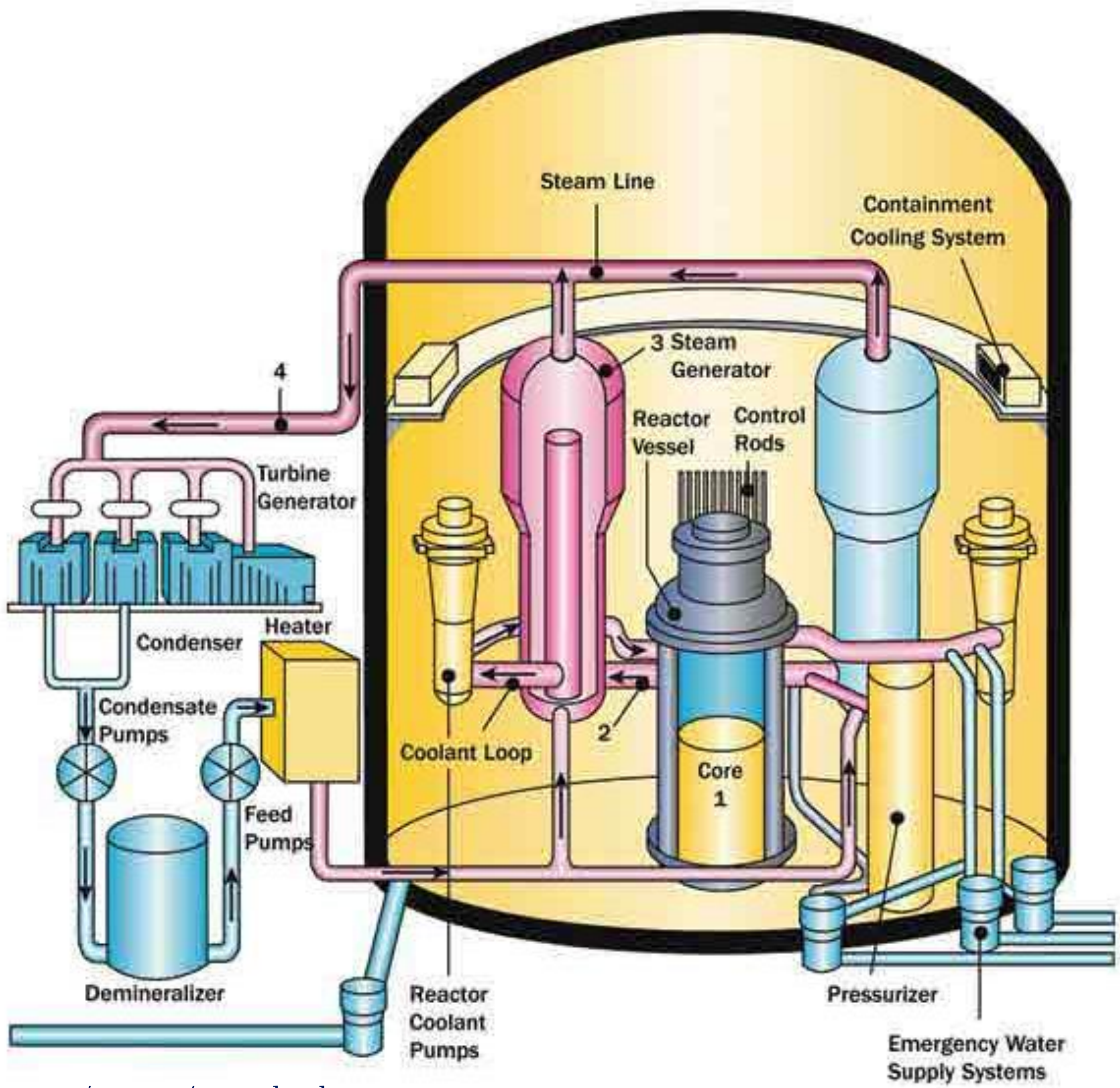


Diagram from http://www.nrc.gov/reactors/power.html

Typical U-Tube Steam Generator

Purified steam

U-bend region

Tube bundle with support plates

Hot leg inlet to SG tubes

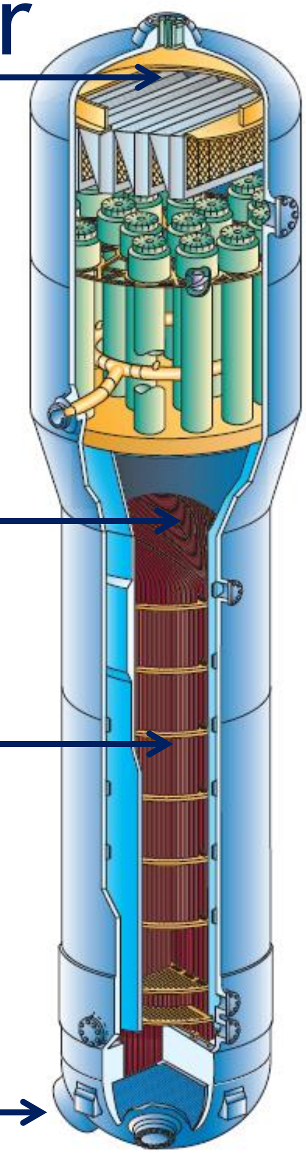
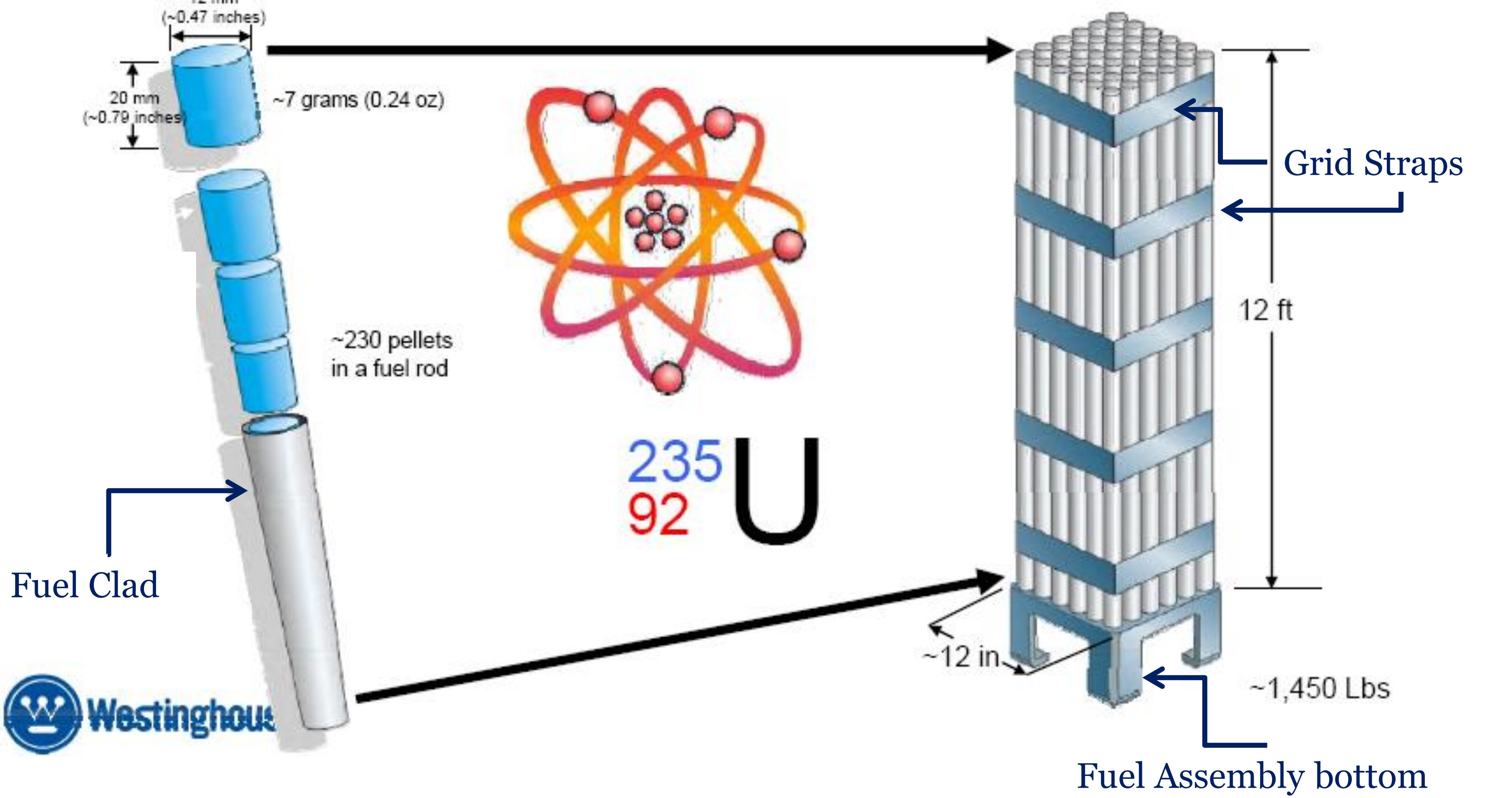


Diagram from http://westinghousenuclear.com/Operating-Plants/PWR/Products-and-Services/cid/54/Steam-Generators

A PWR Fuel Assembly



Courtesy of Westinghouse at http://intergoogle.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

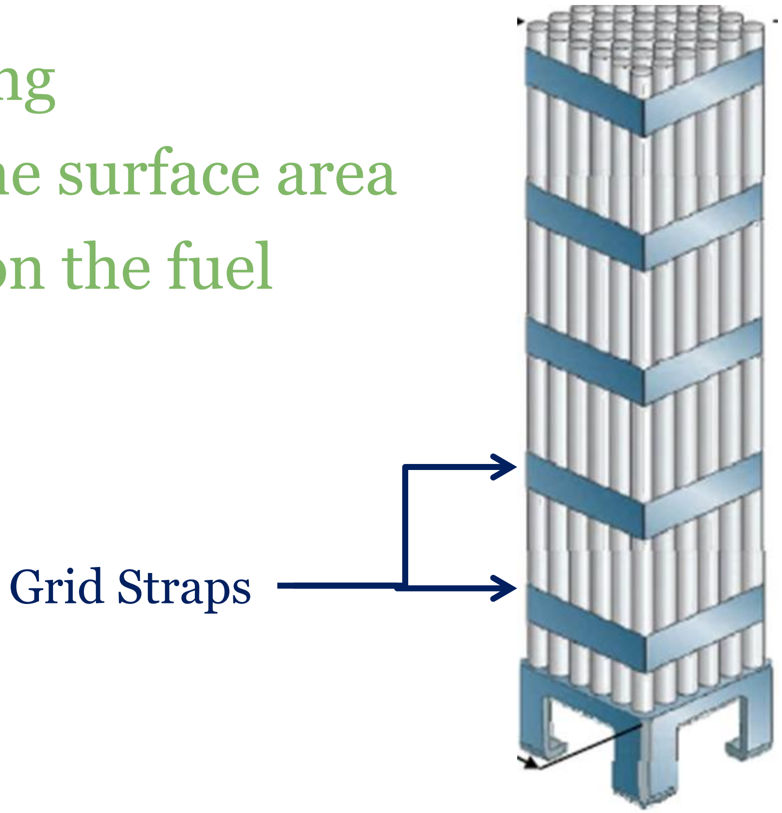
- Stainless Steel
  - Accounts for ~5% of surface area in RCS
  - Contains ~18% chromium, ~8% nickel, ~74% iron
  - Has the highest general corrosion rate of all internal RCS surface materials (10^{-3} to 10^{-5} mil/yr)
  - Forms two different layers of corrosion during initial power cycle

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

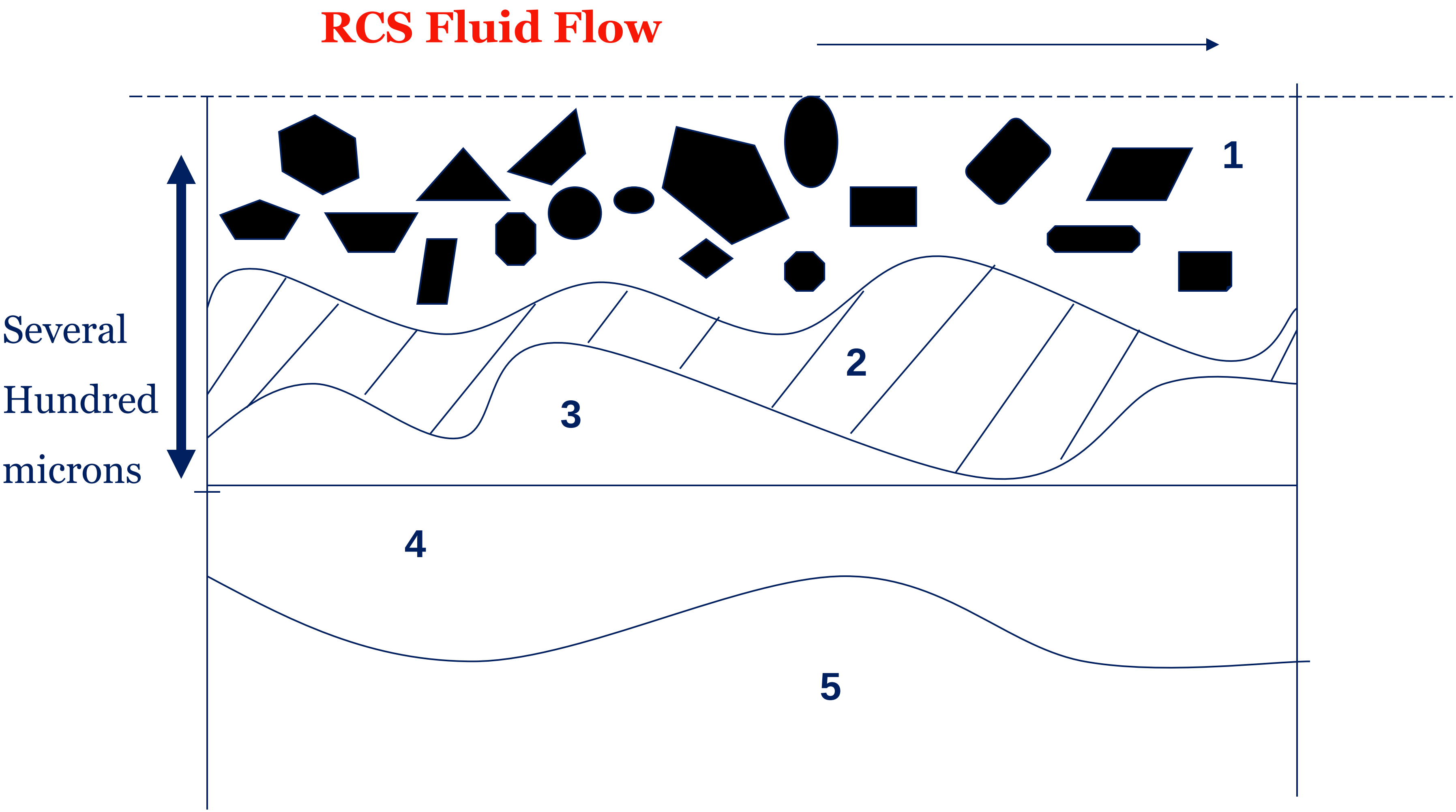
Contaminants

- Oxygen(<5 ppb)
- Anionic
  - Cl (<150 ppb)
  - F (<150 ppb)
  - 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 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

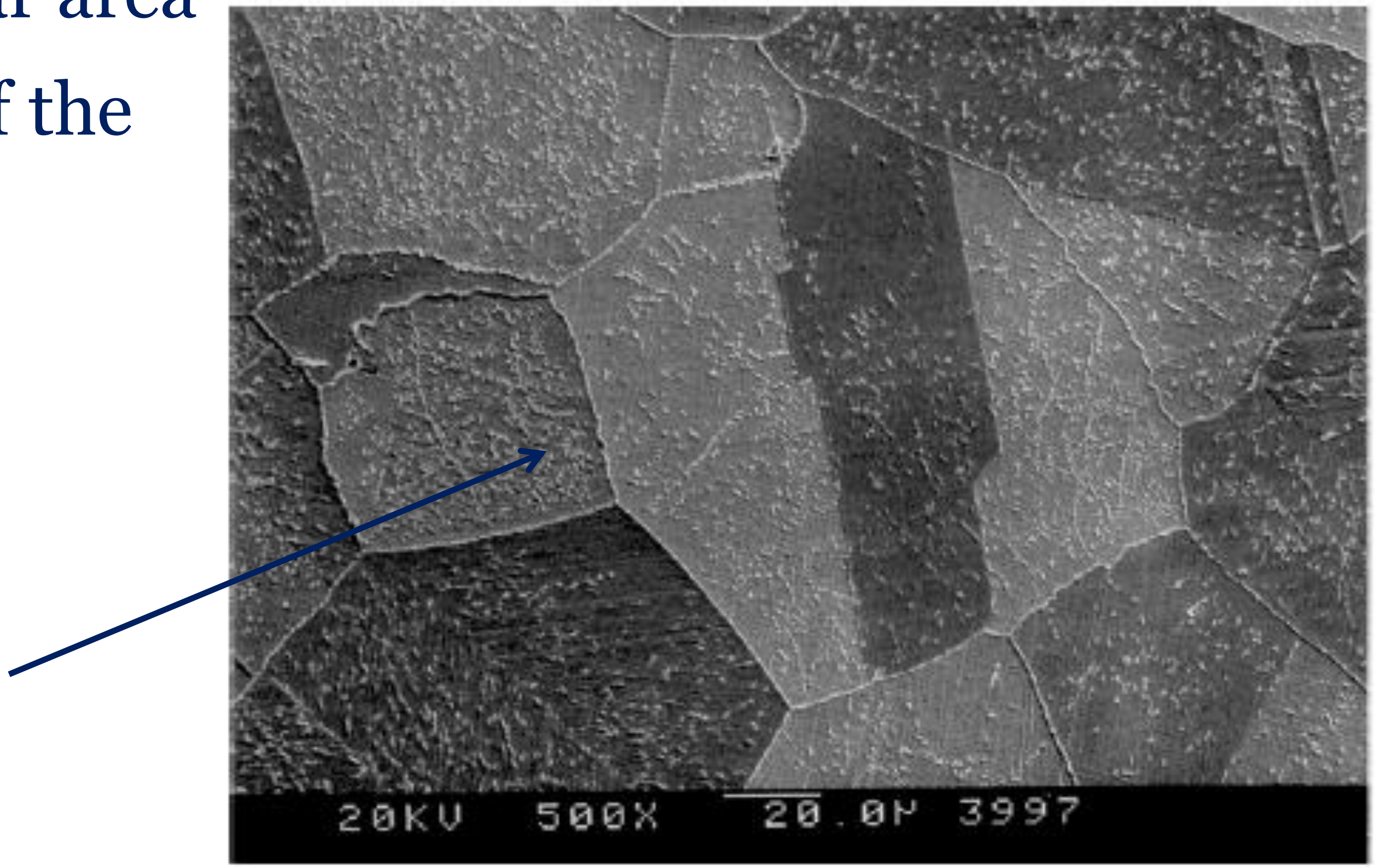
RCS Metal Alloys

- 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:

$$Fe + O_2 \leftrightarrow FeO \qquad (1)$$

No Water!

$$Fe + H_2O \leftrightarrow FeO + H_2 \qquad (2)$$

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 O•, •OH, •OOH, O_2•

$$2H_2O \leftrightarrow 2H_2 + O_2$$

$$H_2 + \bullet OH \leftrightarrow H\bullet + H_2O$$

etc.

Hydrogen

- Hydrogen maintains metals in *lower* oxidation states:

$$Ni_xFe_YO_Z + H_2 \rightarrow Ni_xFe_YO_{Z-1} + H_2O$$

- Electrochemical potential
- Controls oxide form of Fe and Ni

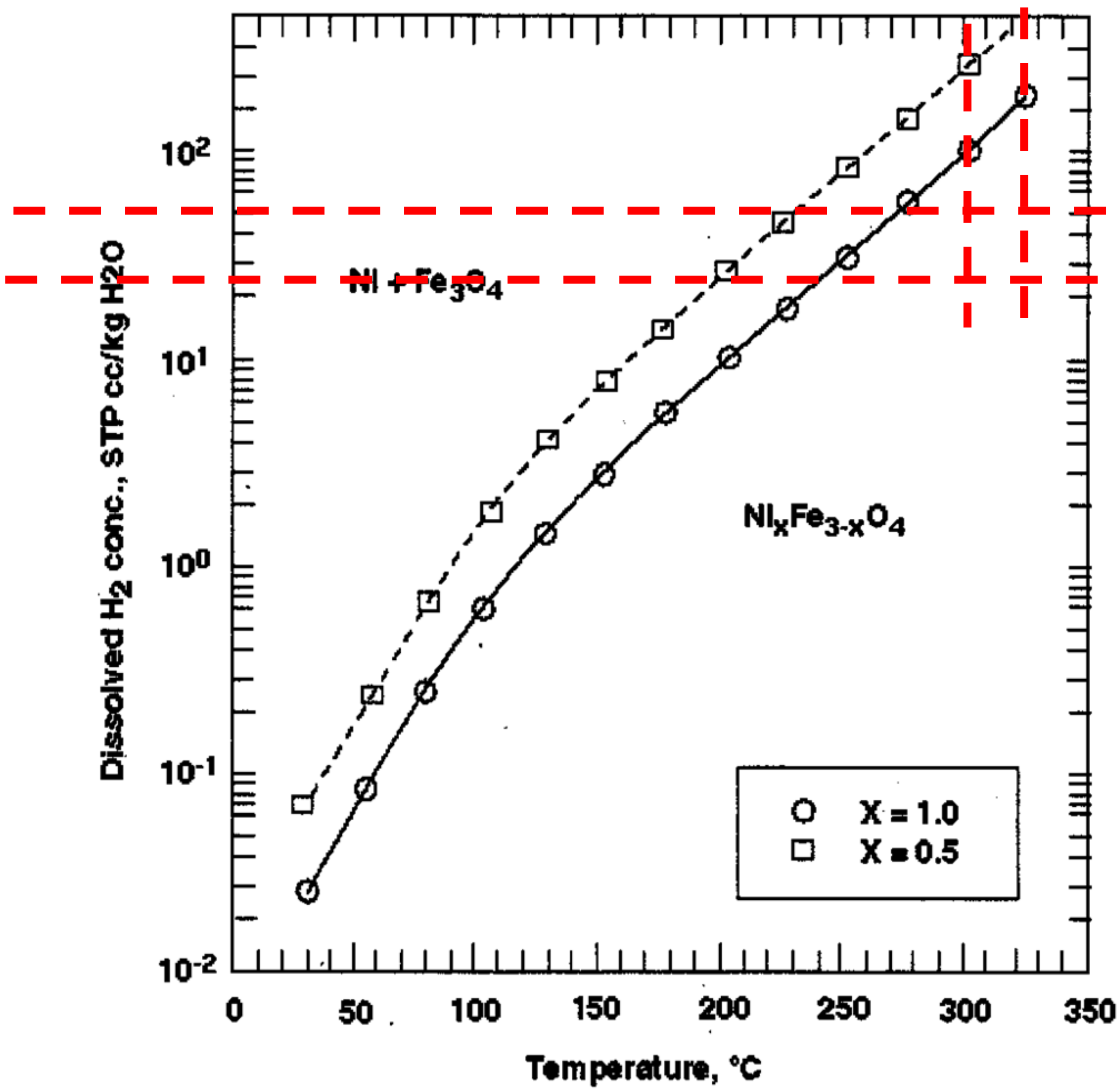
Hydrogen

Too much hydrogen will hydride fuel cladding

$$Zr^0 + 2H_2 \xrightarrow{\text{Excess}} ZrH_4$$

and also will destabilize CRUD layers

Effect of Hydrogen on CRUD



Boric Acid

- Soluble neutron absorber is ^{10}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:
  - $^{10}B(n,\alpha)^{7}Li$
    - Cross section is ~3900 barns
    - ~0.15 ppm/day/1000 ppm boron
  - $^{11}B(n,\gamma)^{12}B \rightarrow {}^{12}C$
    - Cross-section is 5 mb

Control of RCS at pH_{Tavg} is “Critical”

- Boric acid makes the RCS acidic
- LiOH is added - pH_{Tavg} to about 7.2
  - Neutrality for pH_{Tavg} 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}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
  - $^{10}B(n,\alpha)^{7}Li$ reaction
  - Cross section is ~3900 barns
  - ~0.15 ppm/day/1000 ppm boron

- Used up by
  - $^{7}Li(n,n\alpha)^{3}H$
    - This is NOT a significant contributor to RCS ^{3}H
  - $^{7}Li(n,\gamma)^{8}Li \rightarrow {}^{8}Be + \beta^{-}$

    $^{8}Be \rightarrow 2\alpha$

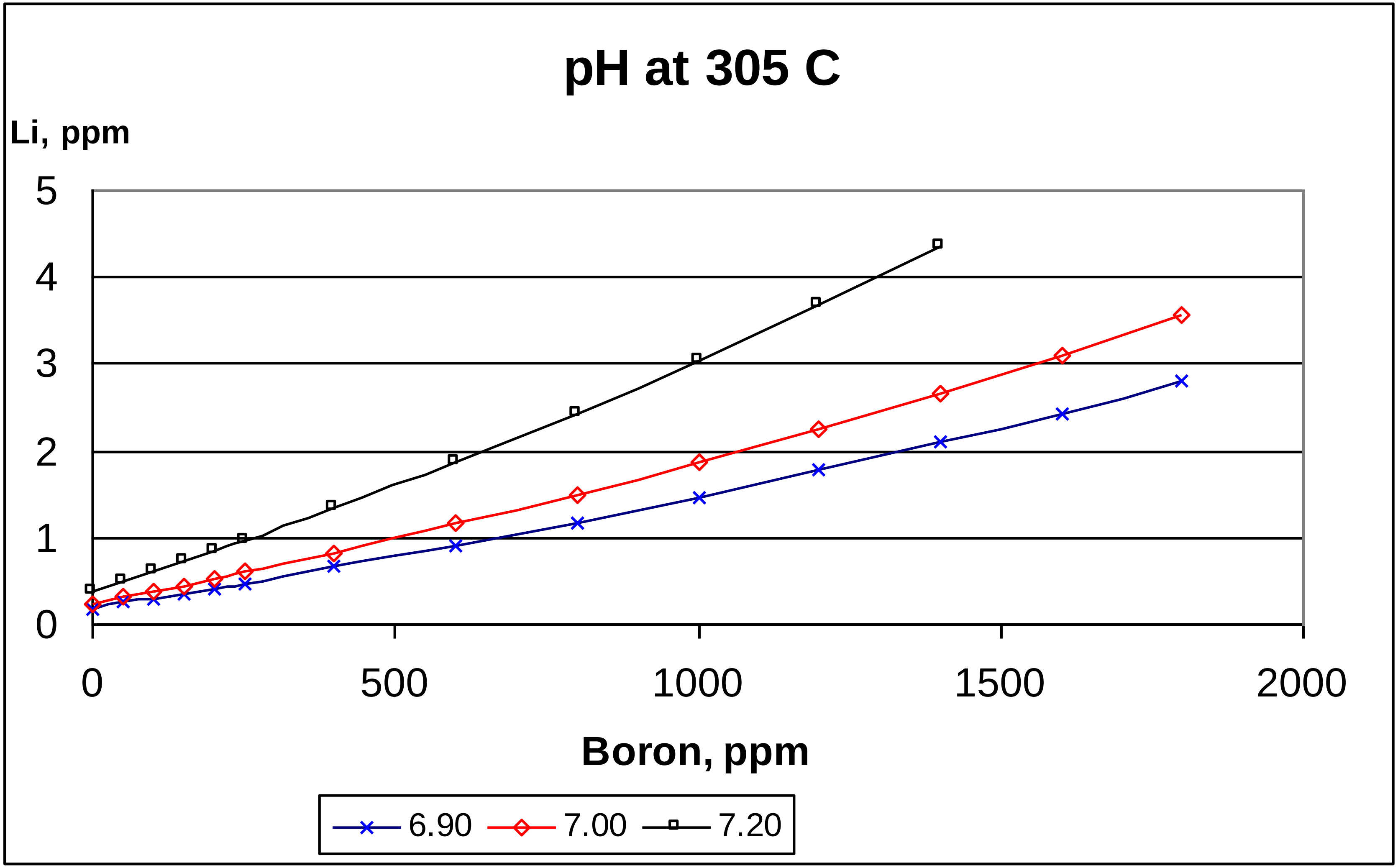
(^{8}Li $t_{1/2}$ = 840 ms) (^{8}Be $t_{1/2}$ = $7x10^{-17}$ s)

What About 6Li?

- Natural lithium is 7.6% ^{6}Li
  - PWR lithium is enriched to 99.5+% ^{7}Li
  - Minimizes production of tritium
    - $^{6}Li(n,\alpha)^{3}H$

Lithium and Boron Effects

(Constant Temperature)



Hydrazine

- Added during start-up from refueling outages
- Reacts with oxygen
  - $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$
- Decomposes
  - $N2H4 \rightarrow 2H2 + N2$
  - $2N2H4 \rightarrow N2 + 2NH3 + H2$

Hydrogen Peroxide

- Transient corrosion layer
- Decomposes into H_2O and O_2
- Provides an oxidizing environment to solubilize ions

Activation Products: Corrosion and Contaminants

Radionuclide Product	Half-Life	Nuclear Reaction	Source of Target Material	Principal Gamma Rays (keV)
^{56}Mn	2.6 h	^{55}Mn(n, γ)	Corrosion	**847**
^{24}Na	15 h	^{23}Na(n, γ)	MUW, SAT	**1369, 2754**
^{41}Ar	1.8 h	^{40}Ar(n, γ)	Air contaminant	**1294**
^{58}Co	71 d	^{58}Ni(n, p)	Nickel alloys	**811**
^{122}Sb	2.7 d	^{121}Sb(n, γ)	Start up source, RCP bearing	**564**
^{89}Zr	3.3 d	^{90}Zr(n, 2n)	Fuel cladding	**909**
^{187}W	24 h	^{186}W(n, γ)	Weld rod residue, satellite	**686**
^{51}Cr	28 d	^{50}Cr(n, γ)	Stainless steel, nickel alloys	**320**
^{54}Mn	312 d	^{54}Fe(n, p)	Stainless steel	**835**
^{60}Co	5.3 a	^{59}Co(n, γ)	Cobalt bearing components	**1332, 1173**
^{38}Cl	37 m	^{37}Cl(n, γ)	MUW, H_3BO_3, contaminants	**2168, 1642**
^{124}Sb **^{125}Sb**	60 d 2.8 a	^{123}Sb(n, γ) ^{124}Sb(n, γ)	Start-up source, RCP bearing alloy, fuel clad	**603, 1691** **428, 601**
^{110m}Ag **^{108m}Ag**	250 d 420 a	^{109}Ag(n, γ) ^{107}Ag(n, γ)	Control rod wear	**658, 885** **723, 434**
^{94}Nb	2 x 10^{4} a	^{93}Nb (n, γ), Fission Product	Fuel clad, fuel	**871, 703**
^{46}Sc	84 d	^{45}Sc(n, γ)	Trace element in zirc cladding	**1120, 889**
^{57}Co	272 d	^{57}Fe(p, n)	Stainless steel	**122, 137**
^{109}Cd **^{115m}Cd**	461 d 45 d	^{108}Cd(n, γ) ^{114}Cd(n, γ)	Control rod	**88** **934, 1291**

Radionuclides: Activation of Water and Chemicals

Radionuclide Product	Half Life	Nuclear Reaction	Source of Target Material	Principal Gamma Rays (keV)
^{7}Be	53 d	$^{7}Li(p, n)$, Fission Product	Li	**478**
^{3}H	12.3 a	$^{10}B(n,2\alpha)$, Fission Product $^{6}Li(n,\alpha)$	H_3BO_3, fuel, Li	**None (β^- emitter)**
^{11}C	20 m	$^{11}B(p, n)$	Boric Acid	**511 (See Note)**
^{14}C	5715 a	$^{14}N(n, p)$, $^{17}O(n, \alpha)$	RCS, MUW	**No gamma**
^{13}N	10 m	$^{16}O(p, \alpha)$	Reactor Coolant	**511 (See Note)**
^{16}N	7.1 s	$^{16}O(n,p)$	Reactor Coolant	**6129, 7115**
^{18}F	109 m	$^{18}O(p,n)$	Water	**511 (See Note)**
^{65}Zn	244 d	$^{64}Zn(n, \gamma)$	Zinc acetate or oxide	**1115**
^{69m}Zn	14 h	$^{68}Zn(n, \gamma)$	Zinc acetate or oxide	**439**
^{71m}Zn	4 h	$^{70}Zn(n, \gamma)$	Zinc acetate or oxide	**387**

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

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

Radionuclides Formed from the Activation of Fuel

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

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
  - http://intergoogle.westinghousenuclear.com/search?q=fuel+assembly&site=default_collection&client=westinghouse_frontend&proxystylesheet=westinghouse_frontend&output=xml_no_dtd
  - www.nrc.gov/reactors/power.html

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NAMP website http://www.wipp.energy.gov/namp/