The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

2291-24

Joint ICTP-IAEA Course on Science and Technology of Supercritical Water Cooled Reactors

27 June - 1 July, 2011

SCWR CHEMISTRY

Radek NOVOTNY

JRC IE Petten
Westerduinveg 3
1755LE Petten
THE NETHERLANDS

SCWR Chemistry

R. Novotny

JRC IE - Institute for Energy

Petten, The Netherlands

http://ie.jrc.ec.europa.eu/

http://www.jrc.ec.europa.eu/

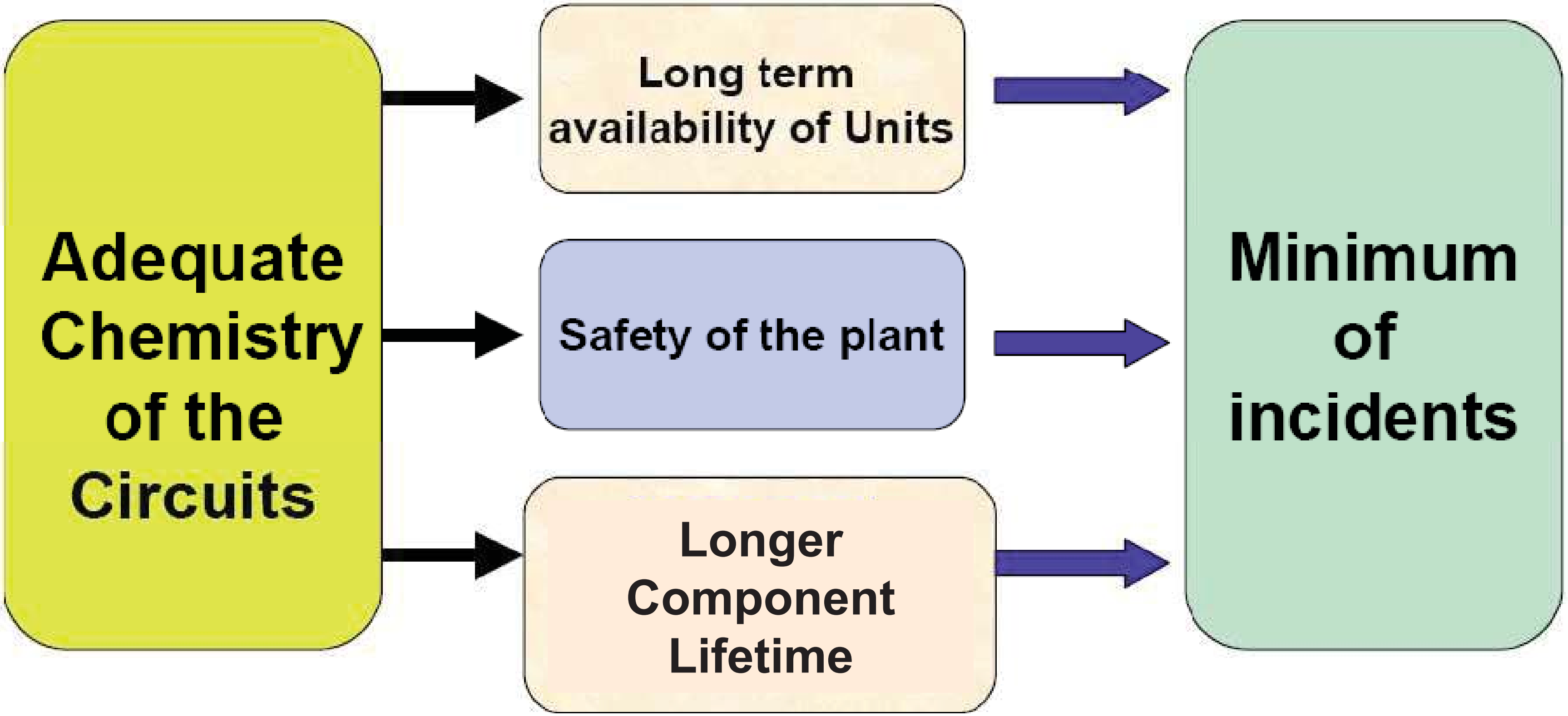
Outline

- **Introduction**
- **Water chemistry in Light Water Reactors (LWR)**
  - Objectives
  - Tasks
  - Historical evolution
  - Reactor specific water chemistry
- **Chemistry in Pressurized Water Reactors (PWR)**
- **Chemistry in Boiling Water Reactors (BWR)**
- **Chemistry for Supercritical Water Reactor (SCWR)**
- **Summary**

Introduction

A poor chemistry may, on a rather long term, induce corrosion

The effect is detrimental for components



Introduction

❑ **Compared to the large body of work on materials testing, little work on SCWR water chemistry has yet been carried out**

❑ **Long-term goal is to specify a suitable water chemistry for the SCWR design**

❑ **Candidate water chemistry regimes and specifications for key chemistry parameters:**

- **pH**
- **dissolved oxygen and hydrogen concentrations**
- **concentrations of any other additives**
- **allowable concentrations of impurities**

SCWR water chemistry must be identified prior to any long-term materials testing

Water chemistry in LWR - Objectives

- Assure material integrity: maintain corrosions at acceptable rates
- Limit mass transfer along circuits to avoid fouling, activity buildup, etc.
- Minimize the impact on the environment (effluents, wastes) and workers

The best chemistry is a compromise

- Different materials have different optimum conditions

- Low dissolved O_2 concentrations are beneficial to low carbon steel FAC, but detrimental to nickel base alloys

- High concentrations of lithium in the primary coolant should reduce steam generators releases, but could also increase risks on fuel cladding and the internals

Water chemistry in LWR - Tasks

- Secure of Integrity of the Reactor Core
- Reactivity Control, Moderation
- Minimization of Metal Release Rates
- Minimization of Occurrence of Local Corrosion Phenomena
- Limitation of Deposits of Corrosion Products on Heat Transferring Surfaces (CRUD)
- Minimization of Contamination of Water Steam Cycle/Primary Circuit
- Removal of Corrosive Species or Compounds
- Removal of Fission and Activation Products from the Circuits
- Control of Activity Built–Up and Transport in the Primary Circuit or Water Steam Cycle

Water Chemistry in LWR – Historical evolution

Institute for Energy

In the past, chemistry was the cause of problems

❑ **1970s:** Major ingress of sea water, oil, ion exchange resins, etc. caused corrosion and fuel problems

- Impurities contributed to IGSCC of BWR piping
- Phosphate dosing of PWR steam generators caused wastages or IGA/SCC, leading to "all-volatile treatment" in 1974, which caused denting

❑ **1980s:** "Purer is Better" was the theme – not sufficient to eliminate problems for Alloy 600

Chemistry advances focus on mitigation of corrosion problems

❑ **1990s:** BWR hydrogen water chemistry, zinc injection, pH control in PWR primary and secondary systems for FAC and SCC

❑ **2000s:** Noble metal chemical addition in BWRs, PWR primary zinc injections, elevated pH or amine in most secondary systems of PWR for SG deposits and FAC mitigation, dispersants trial.

Reactor Water Specific Conditions – BWR, PWR

NWC

Normal Water Chemistry

HWC

Hydrogen Water Chemistry

Parameter	*BWR/NWC*	*BWR/HWC*	PWR
Temperature	274 to 290 °C	274 to 290 °C	290 to 320 °C
Pressure	7.2 MPa	7.2 MPa	16 MPa
Flow rate	1 to 10 m/s	1 to 10 m/s	1 to 10 m/s
$pH_{300\,°C}$	5.65 (neutral)	5.65 (neutral)	6.8 – 7.4 (alkalic)
κ at 25 °C	≤ 0.1 µS/cm	≤ 0.1 µS/cm	10 to 40 µS/cm
Composition	$O_2 + ½\,H_2O_2 > H_2$ High-purity water	$H_2 >> O_2 + ½\,H_2O_2$ High-purity water	$H_2 >> O_2 + ½\,H_2O_2$ H_3BO_3, LiOH
$O_2 + ½\,H_2O_2$	300 to 600 ppb*	< 5 to 50 ppb*	< 10 ppb
H_2	5 – 40 ppb*	50 to 300 ppb* (1 to 2.5 ppm in feedwater)	2 to 5 ppm
Cl^-, SO_4^{2-}	< 1 ppb	< 1 ppb	< 1 to < 50 ppb
ECP (SS)	+50 to −250 mV_{SHE}	-500 to -200 mV_{SHE}**	-700 to -500 mV_{SHE}
ECP (LAS)	-50 to +150 mV_{SHE}	-600 to -200 mV_{SHE}**	-800 to -600 mV_{SHE}

* May strongly depend on reactor design and location within RPV ** In upper plenum always a high ECP of + 150 to +200 mV_{SHE} prevails.

Reactor Specific Water Chemistry

Institute for Energy

Pressurized Water Reactor (PWR)

Primary Circuit:

- *Lithium Hydroxide buffered Boric Acid*
- *Reducing Conditions due to H_2-Dosage*

Secondary Circuit:

- *High All Volatile Treatment*
- *Reducing Conditions due to Hydrazine-Dosage*
- *In the past: Phosphate Treatment (Wastage Build Up in SG)*

Boiling Water Reactor (BWR)

Water Steam Cycle:

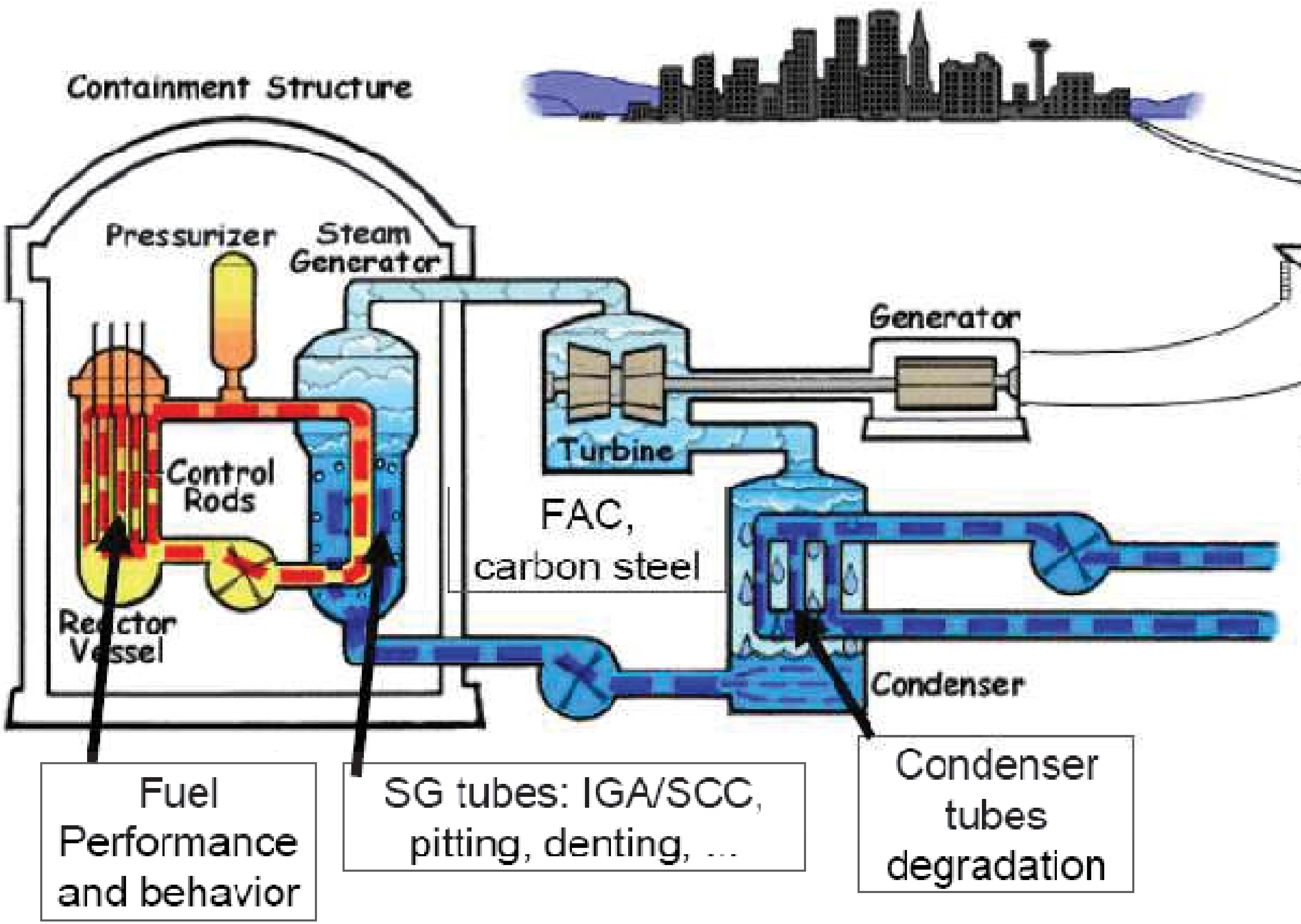
- *Normal Water Chemistry (NWC)*
- *Hydrogen Water Chemistry (HWC)*
- *Noble Metal Chemical Addition (NMCA)*

PWR Chemistry relation with materials degradation and objectives for Corrosion mitigation as well as other purposes.

-

- **Primary system**
  - Lithium, pH, Hydrogen, Zinc
  - Primary Water Stress Corrosion Cracking – PWSCC
  - Fuel behaviour
- **Secondary system**
  - Amine, ammonia, corrosion inhibitors
  - Copper alloys corrosion
  - Intergranular/SCC (mainly Inconel 600 MA)
  - Flow Accelerated Corrosion (FAC) of carbon steel
  - Corrosion products deposition and Flow Induced Vibration

Chemistry in PWR- Main corrosion Issues



Chemistry in PWR - Primary circuit pH control

Boric acid to control neutron flux :

- During full-power operation : power control
- During shutdowns : safety
- To compensate the decreasing fuel reactivity during a cycle

Lithium hydroxide to control pH :

- The target $pH_{300°C}$ is designed to reduce release from steam generators and limit deposition on fuel cladding:

Typical $pH_{300°C}$ range 7.2 to 7.4

- The lithium hydroxide concentration is coordinated with boric acid concentration
- ^{7}Li is used to avoid tritium generation

PWR: Typical Li_{max} = 2.2 or 3.5 ppm

Some cases with even higher values

No benefit expected for PWSCC, but potentially for dosimetry

Li natural : ^{6}Li : 7.42 %

^{7}Li : 92.58 %

$^{6}_{3}Li + ^{1}_{0}n \Rightarrow ^{4}_{2}He + ^{3}_{1}H$ (tritium)

$^{6}Li\ (n, \alpha)\ T$

$\Rightarrow$ use of ^{7}Li enriched to 99.9 %

Chemistry in PWR – Primary circuit Redox control

❑ Primary redox control during operation

Hydrogen :

- Water radiolysis in the core can generate oxidizing species (O_2 , H_2O_2)
- Hydrogen injection prevents oxidizing species generation and ensures a reducing environment
- Typical concentrations are in the range : 2.2-3.1 mg/kg (25-35 cc/kg)

Avoid oxygen ingress

❑ Primary redox control during shutdown/startup

- Avoid hazardous mixtures of H_2 and O_2 (Chemical or physical degassing)
- H_2O_2 injection during shutdown to ensure a quick transient from reducing to oxidizing conditions
- Hydrazine at startup (oxygen scavenger)

Chemistry in PWR - Hydrogen selection puzzle

Hydrogen upper limit ↓

- **Risk of corrosion**
  Laboratory tests not all in agreement. Higher influence on Inconel 600 crack propagation than initiation
- Elimination duration at shutdown
- Gaseous wastes

PWSCC Initiation

Controversial results
Sweden : the lowest the best
e.g. Factor 2 from 20 to 5 cc
EPRI: either low or high but large scatter, limited impact

Hydrogen lower limit ↓

- **Risk of radiolysis**
  5 ml/kg sufficient, always achieved
- **Risk of corrosion** see below
- **Low value control**
  low pressure difficult to keep constant
- Start to decrease before shutdown

PWSCC Propagation

Controversial results
Sweden : select either low < 10 cc or High > 30 cc (low impact)
EPRI: would need <5 impractical thus higher H_2 is better

USA is looking for higher H_2 than present acceptable range (25-50)
Japan is looking for lower H_2 ($\leq$ 10cc) than usual range
Many utilities prefer not to change anything: no risk approach
No need to look for other values without Inconel 600

Chemistry in PWR - Hydrogen effect on PWSCC Propagation

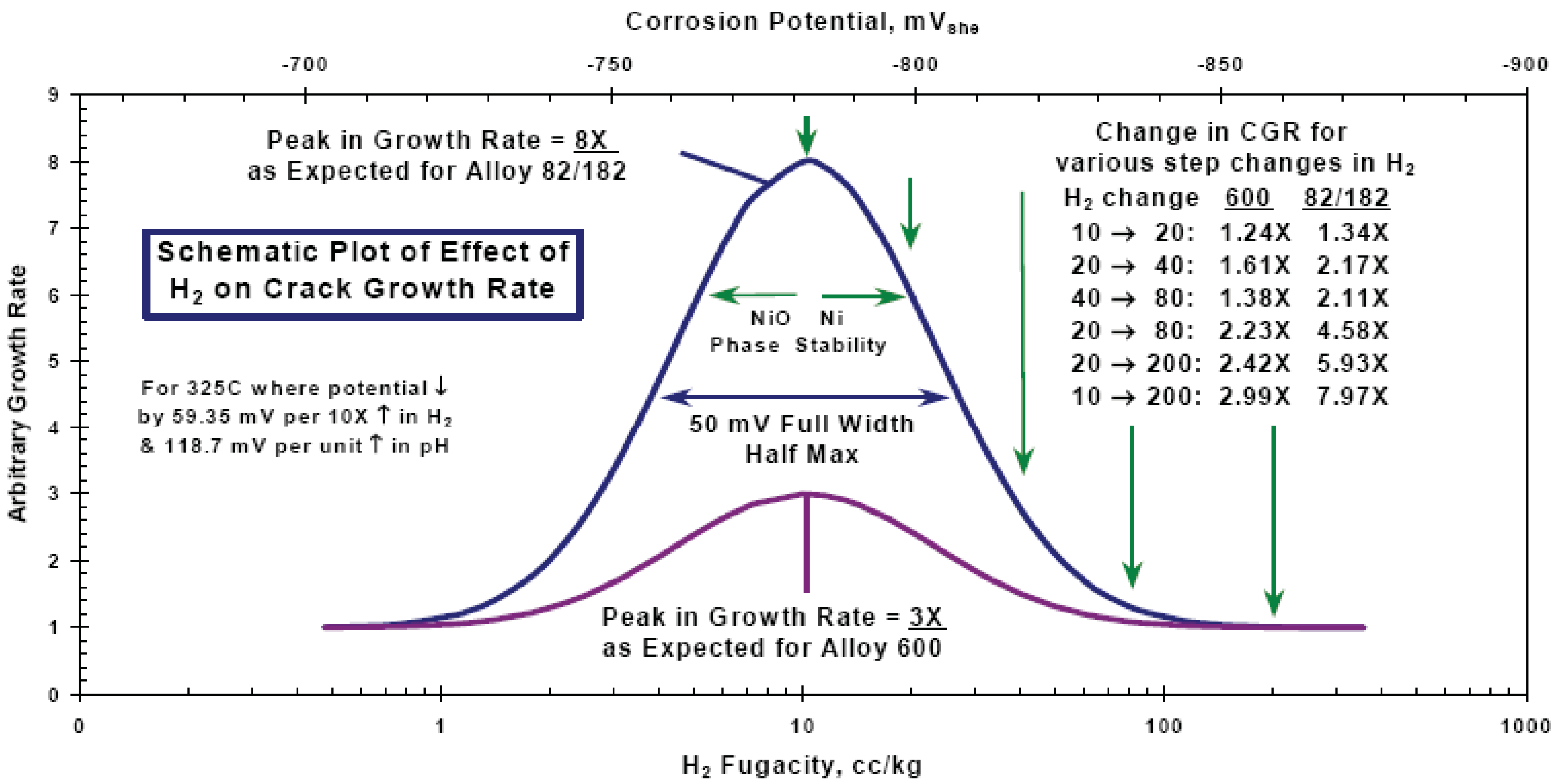


Illustration – position of peak and magnitude depend on temperature and materials

Chemistry in PWR - Impurity control

Primary impurity control

- Continuous purification on filters and ion exchange resins
- Degassing in the volume control tank
- Feed and bleed
- Make-up water and reagents purity

Secondary impurity control

- Non volatile species will concentrate in steam generators
  - Condensate polishing (filter + ion exchange)
  - Blowdown demineralization
- Make-up water and reagent purity
- Avoid cooling water in-leakage

Chemistry in PWR - Secondary Water Chemistry

- pH control in both liquid and vapour phase by a volatile amine

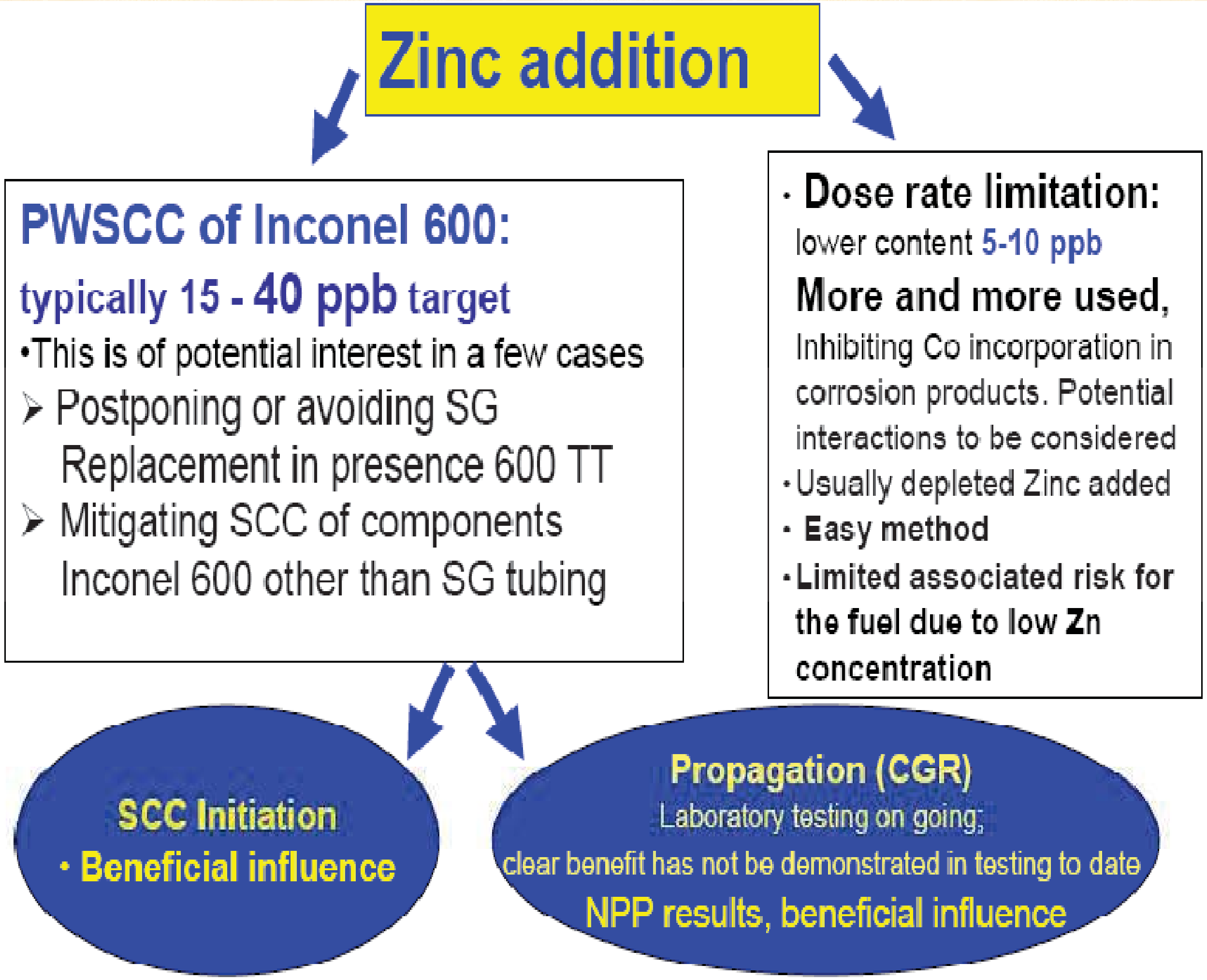
- Redox control by:
  - Hydrazine addition to scavenge oxygen:
    - $N_2H_4 + O_2 \rightarrow N_2 + 2\ H_2O$
    - Thermal decomposition: $N_2H_4 \rightarrow N_2, H_2, NH_3$
  - Limitation of oxygen ingress, degassing

❑ Primary

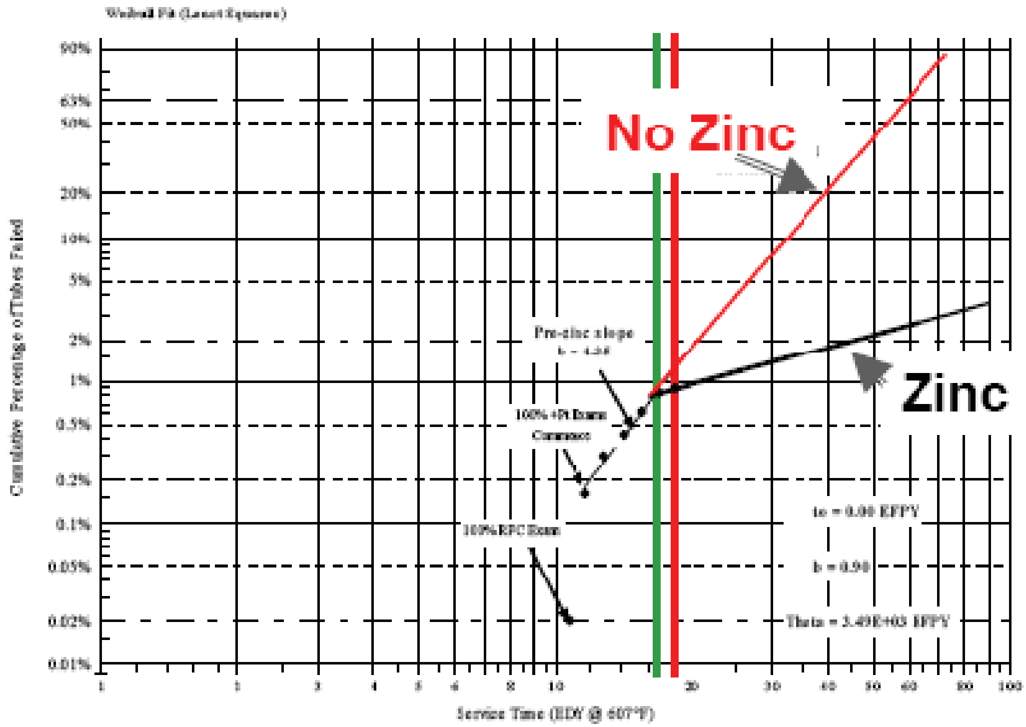
- Zinc injection
- Steam generator tubes with low long term nickel release rate
- New filtration media to improve colloids removal (specific resins, sub-micron filters)

❑ Secondary

- Dispersants injection to increase iron blowdown removal



Chemistry in PWR - Some recent developments



Cumulative % of failed tube versus time with or without 35 ppb Zinc.

Zinc Impact on PWSCC

- What is the impact of zinc injection on PWSCC initiation and crack growth rate(s).
  - 1 US Utility has experienced a 79% reduction in the Weibull Slope with a target zinc level of 35 ppb.
  - A comprehensive EPRI review of US plants consistently demonstrated a significant benefit of zinc
- Reduced crack growth benefit of zinc shown for A600 SG tubes does not necessarily transfer to thick-wall RCS components and to A82/182 welds

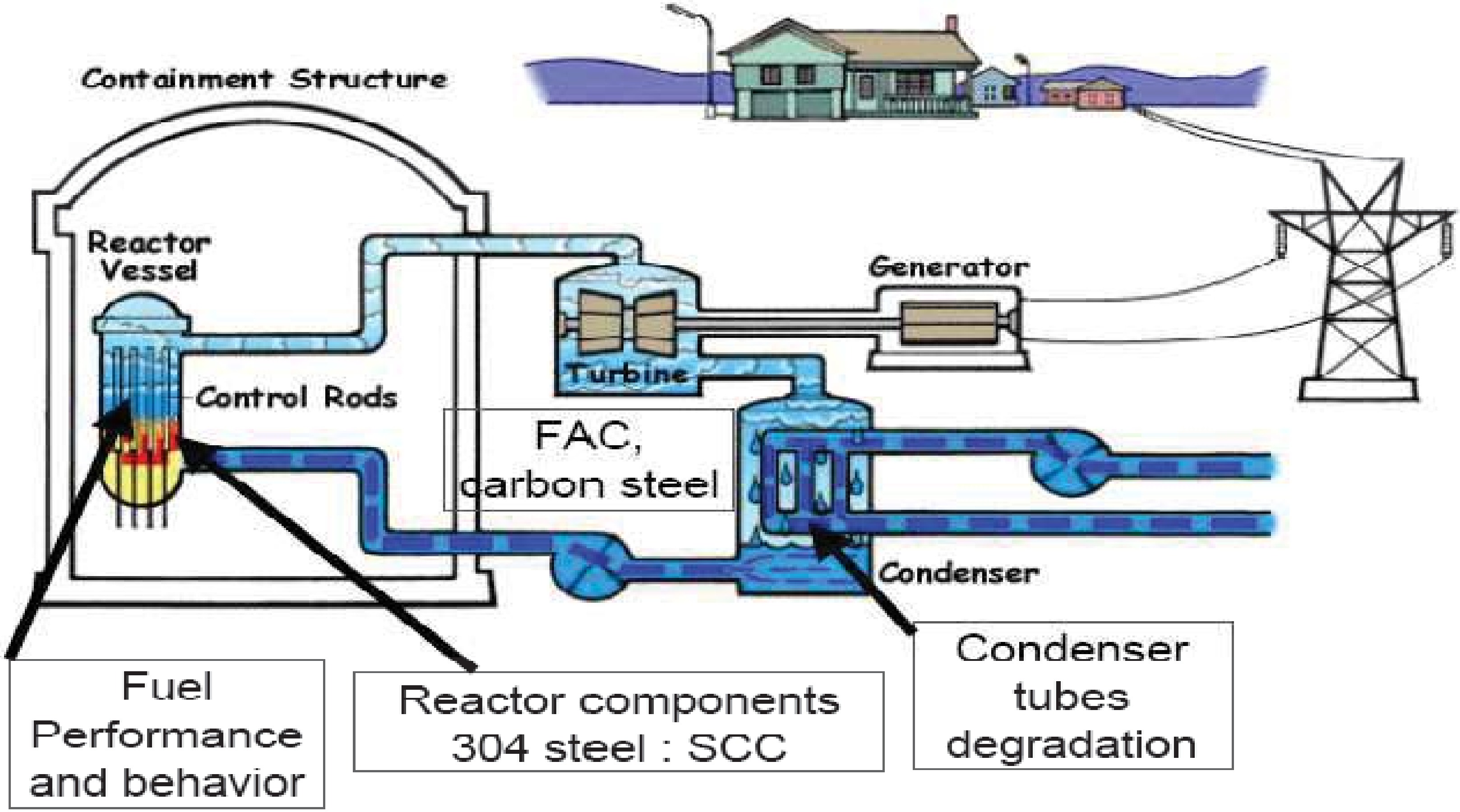
Reactor water during steady state BWR power operation and start-up

Parameter	Steady-state power operation	Start-up
Conductivity [µS/cm]	0.1	1.0 (at 25 °C) $\rightarrow$ 0.1 (steady-state)
Temperature [°C]	270 - 290	25 $\rightarrow$ 270 - 290
pH_T	5.6	5.6 – 8.6 (at 25 °C) $\rightarrow$ 5.6 (steady-state)
O_2 [ppm]	0.2	8.0 $\xrightarrow{150°C}$ 0.02 $\xrightarrow{290°C}$ 0.2 (steady-state)
H_2 [ppm]	0.0125	0 $\rightarrow$ 0. 0125
H_2O_2 [ppm]	0 - 0.4*	0 $\xrightarrow{150°C}$ 1.0 $\xrightarrow{290°C}$ 0 – 0.4*
Cl^- [ppb]	1	< 5 -10
ECP [mV_{SHE}]	-50 bis +200	no reliable measurements available

*Thermal decomposition of H_2O_2 at high temperatures + heterogeneous catalysis of decomposition: $\rightarrow$ Decreasing concentration of H_2O_2 with increasing distance from reactor core.

Chemistry in BWR - Main Corrosion Issues

- ❑ **Water Purity Control – Feedwater/Condensate and Reactor Water**
- ❑ **Depleted Zinc Addition – Dose Control**
- ❑ **Hydrogen and Noble Metal Addition – Intergranular Stress Corrosion Cracking (IGSCC) Mitigation**



Chemistry in BWR – Historical development

BWR Chemistry: 1970s to Today

Note: increasing complexity of BWR chemistry

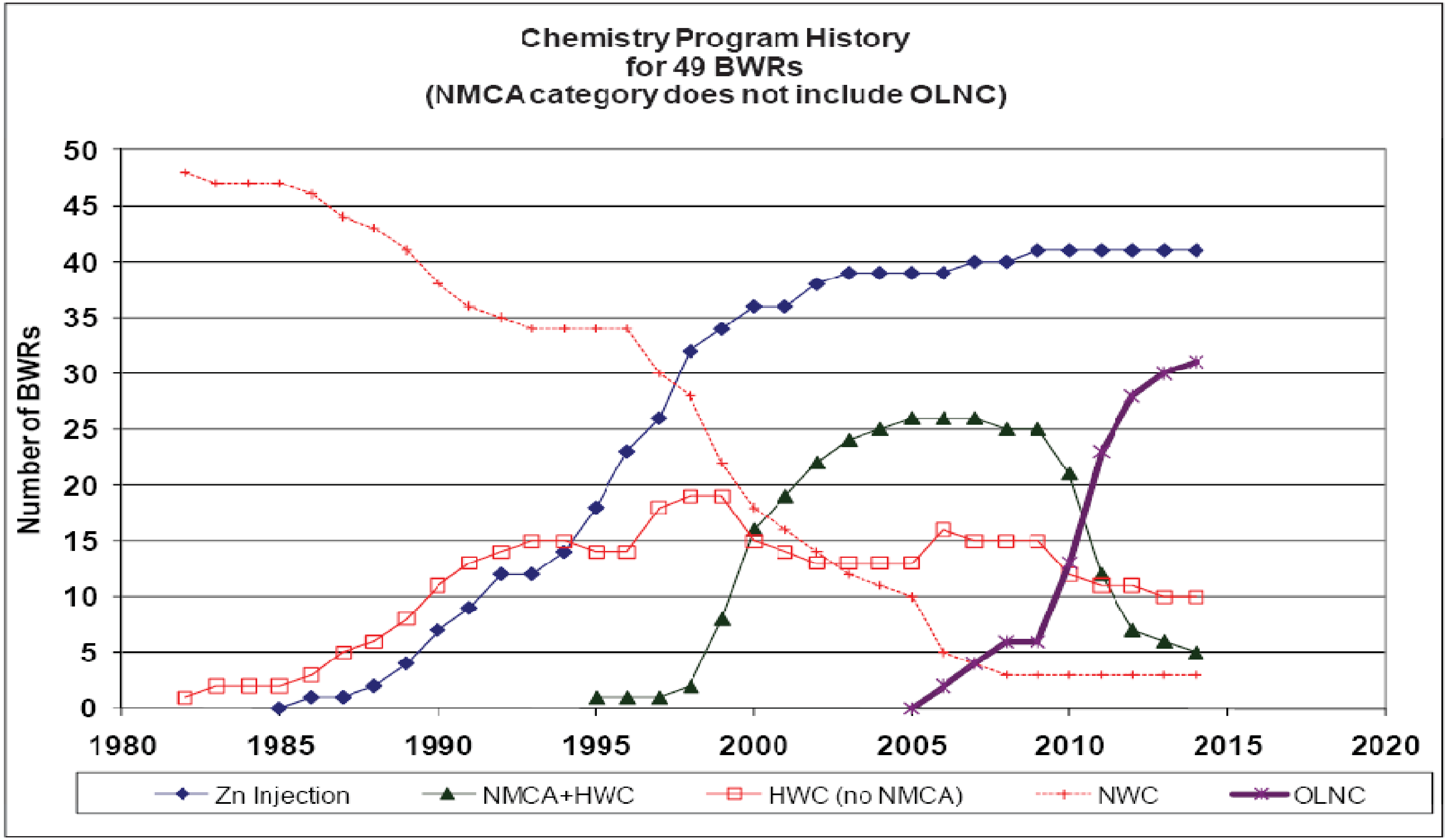
1970s: Neutral, naturally oxygenated water ← *Corrosion, radiation buildup issues*

1980s: Water Purity Control ← *EPRI BWR Water Chemistry Guidelines*

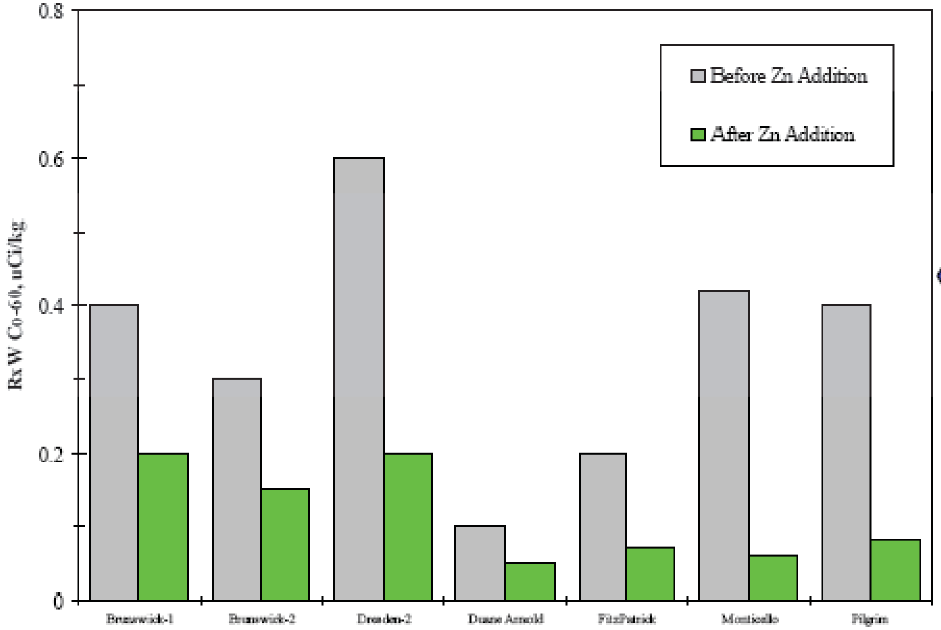
Controlling IGSCC, Radiation Buildup → **Late 1980s - 1990s: Hydrogen, Zinc**

Controlling Internals IGSCC And Reducing Operating Dose Rates → **2000: Noble Metal Chemical Addition (NMCA)**
2006+: Online NobleChem™(OLNC)

BWR Chemistry Regime History and Projections

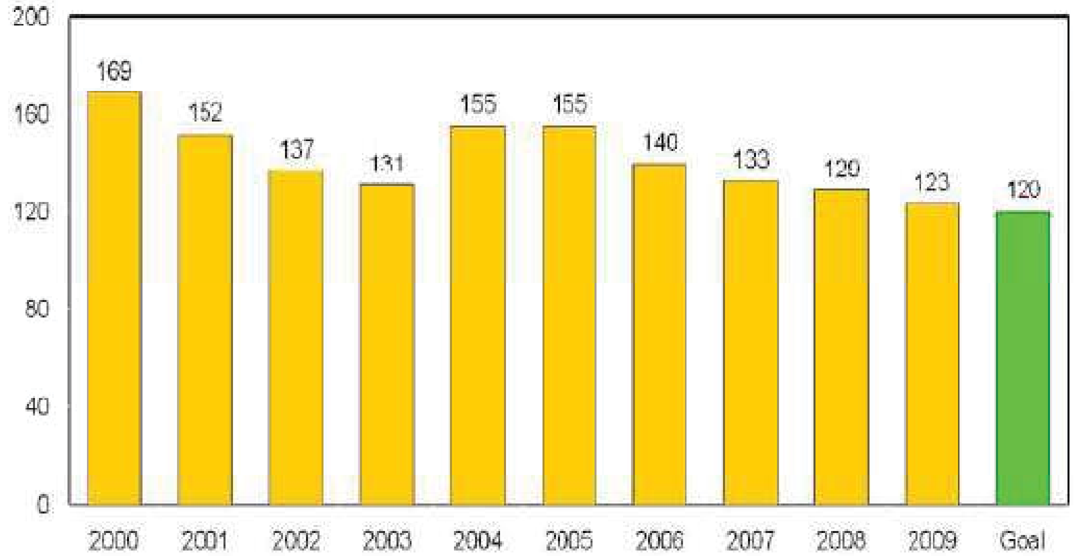


Chemistry in BWR – Dose control



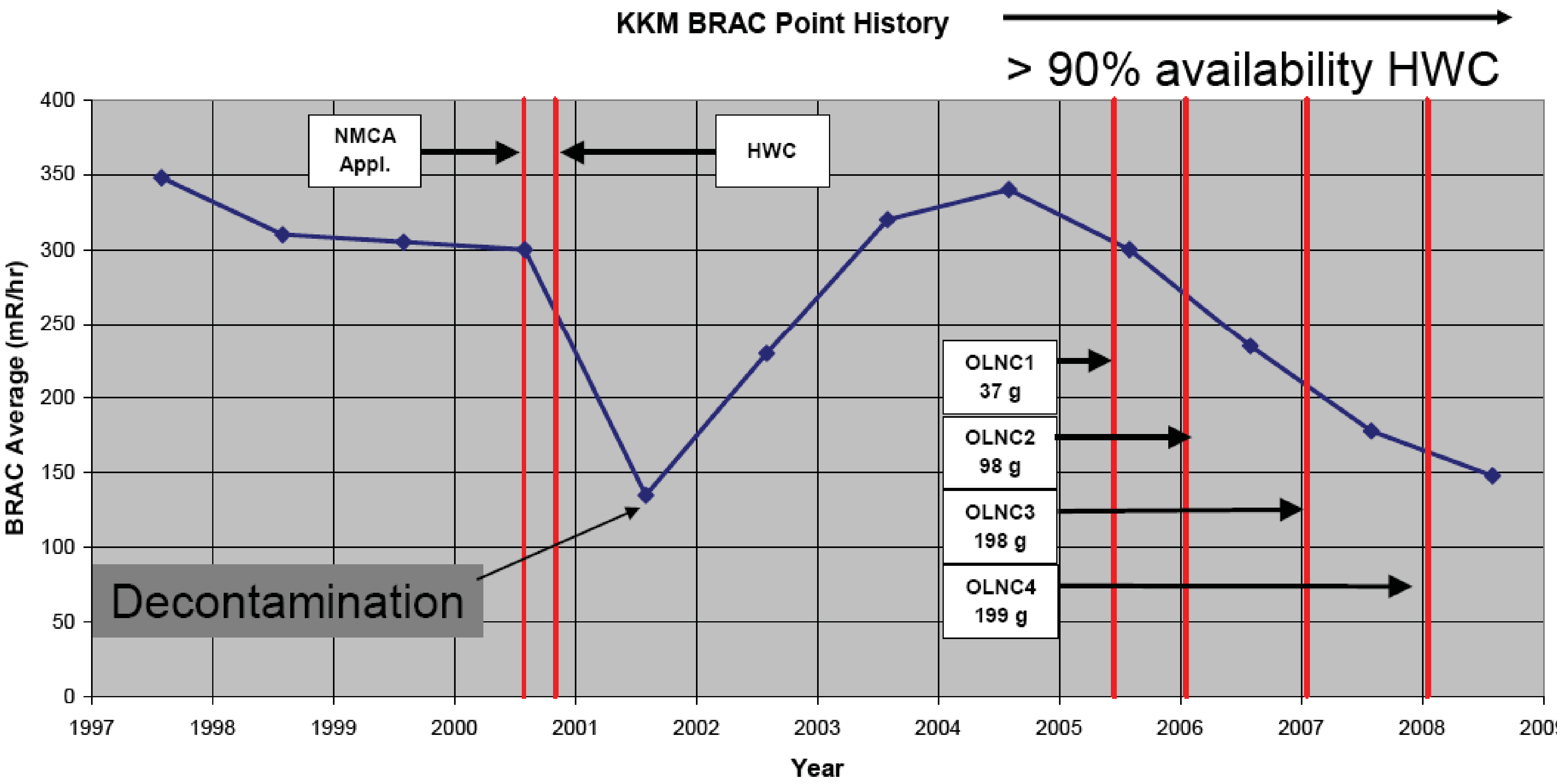
- **RxW Co-60 levels significantly reduced with Zn addition**
- Co-60 is the major dose contributor to BWR shutdown dose rates
- Decontamination of piping was very common in U.S. prior to Zn addition

- U.S. exposures on decreasing trend since 2005
- Implementation of Zn addition in U.S. is a key contributor
- Other factors include crud reduction and optimized use of hydrogen injection and noble metal addition



Chemistry in BWR– Dose control

Online Noble Metal Impact on Piping Dose Rates



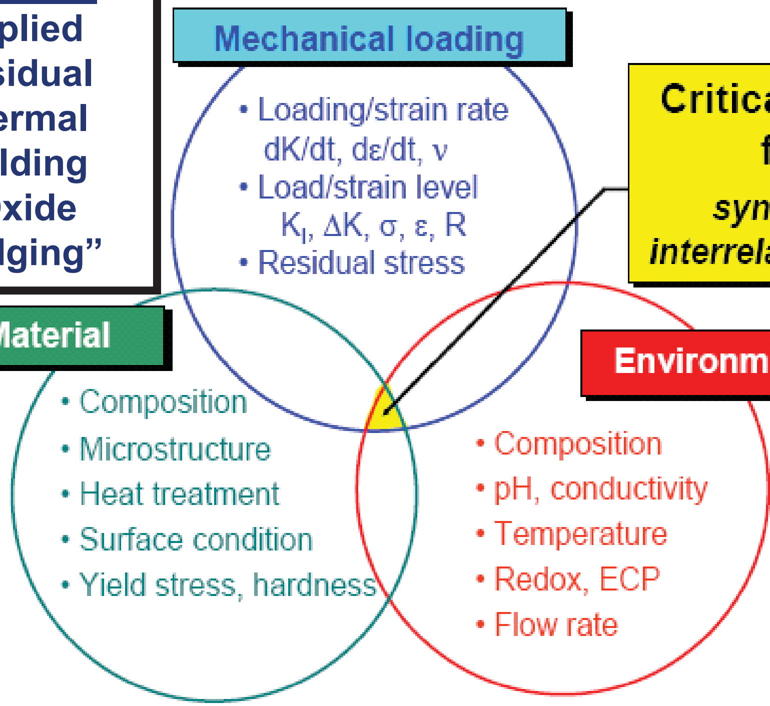
Applications Dose rates have decreased >50% since OLNC applications

Chemistry in BWR - BWR IGSCC Overview

Institute for Energy

- Stress Corrosion Cracking (SCC)
- Radiolysis in the BWR
- Corrosion rates – with and without hydrogen injection
- Reduction technologies:
  - Hydrogen injection
  - Noble metals (NMCA, OLNC, LTNC)
  - Others
- Application of IGSCC technologies at startup and shutdown (lower temp. operation)

Tensile stress:
Applied
Residual
Thermal
Welding
"Oxide Wedging"

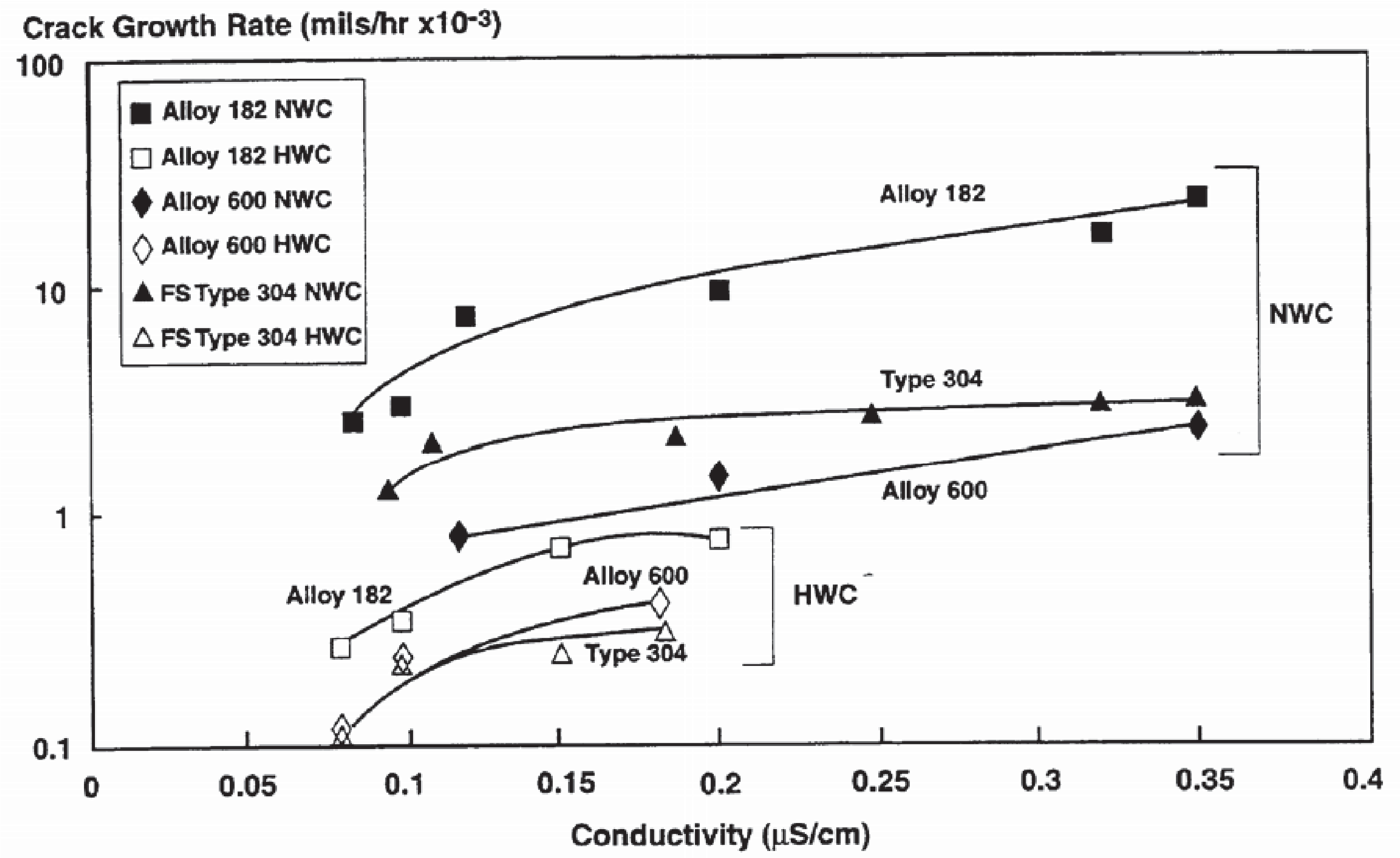


Critical conditions for SCC
synergistic and interrelated parameters

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

Chemistry in BWR - IGSCC and conductivity

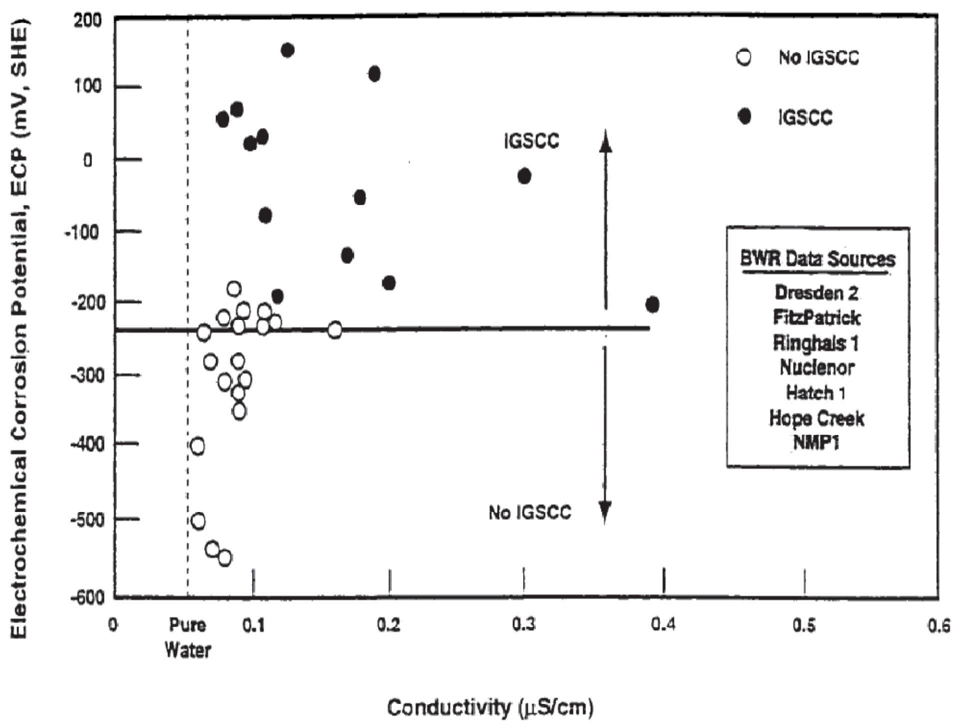


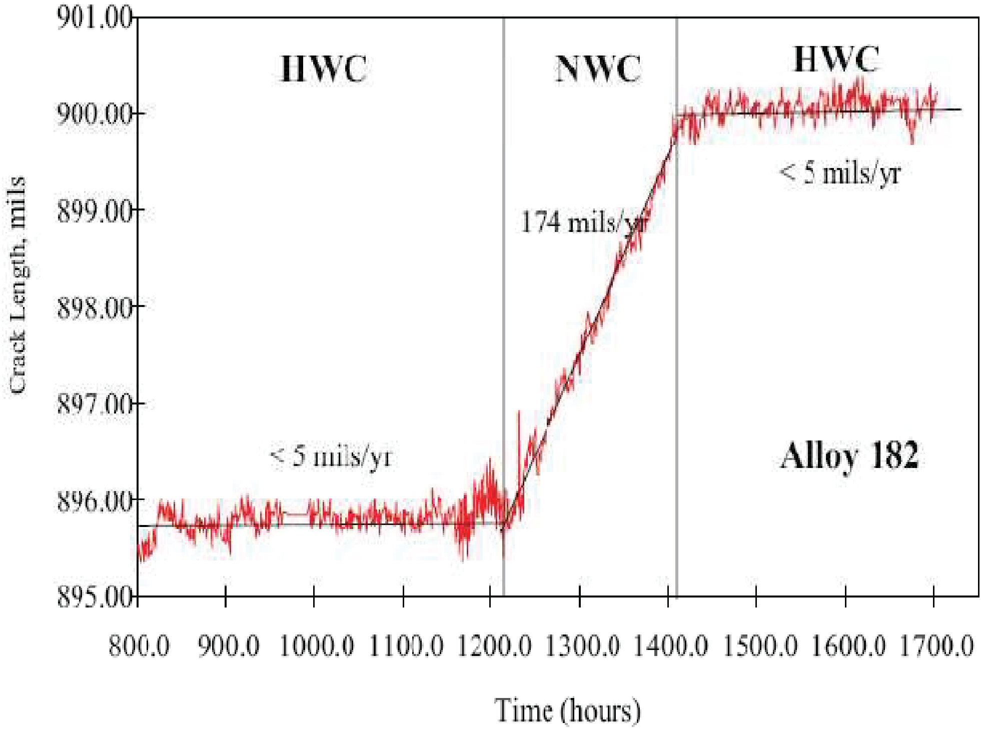
Even the PUREST water will NOT provide IGSCC immunity in the BWR - good water quality delays initiation, but IGSCC still occurs.

Chemistry in BWR - IGSCC and HWC

SCC has been observed since the early 70's in BWRs (e.g. austenitic piping, core components, core shroud, etc.)

- Influence of a oxidizing regime as a pre-condition for SCC is proven
- HWC was invented in the early 80's for BWRs (Sweden, USA)
- Main aim of hydrogen dosage: Decrease of corrosion potentials to negative levels (≤-230 mV SHE)

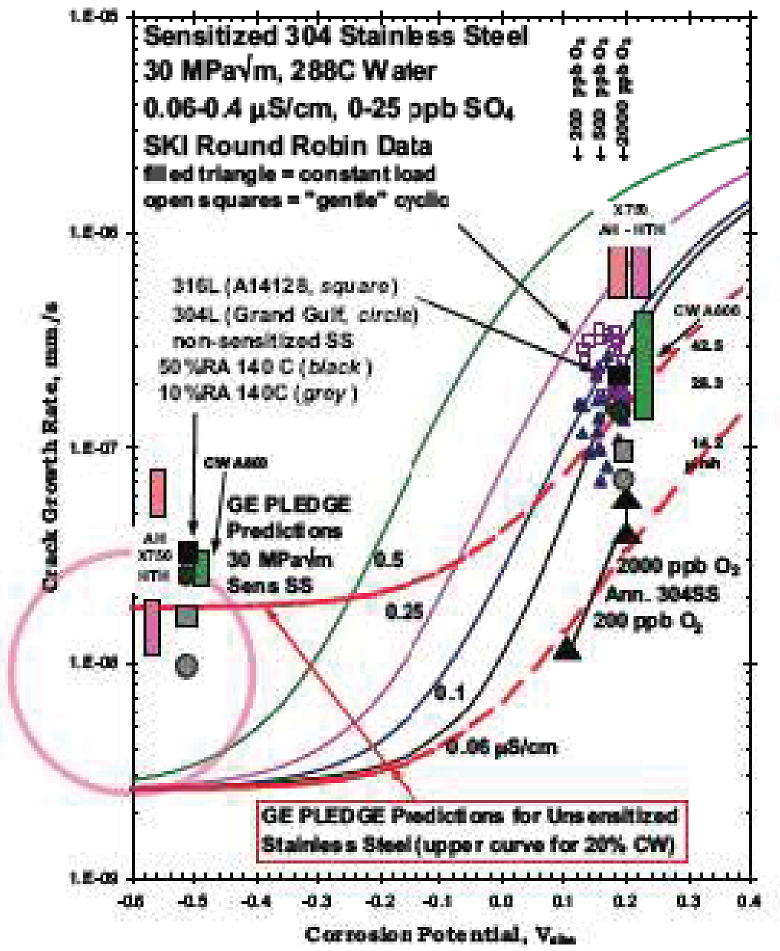


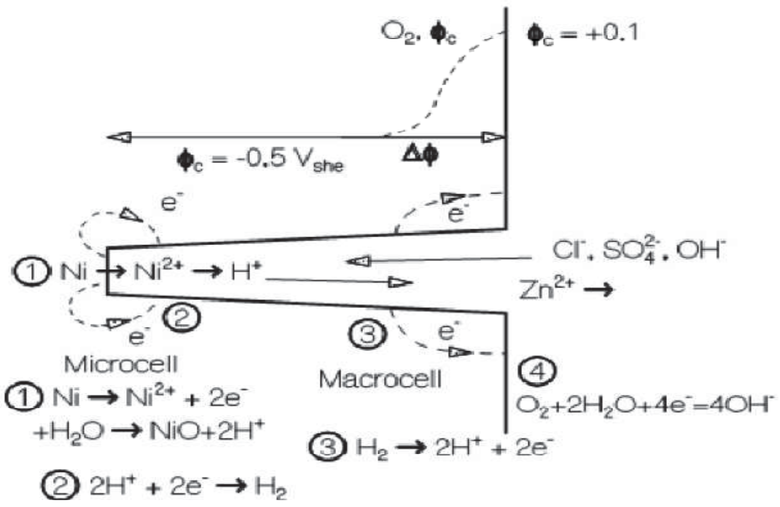


Chemistry in BWR - IGSCC and HWC

A 30-fold concentration (above the bulk water) will occur in a crack under NWC conditions:

- Hydrogen injection reduces the corrosion potential (ECP) of the material by changing the bulk chemistry
- Noble metal on surfaces (with the presence of hydrogen) will catalyze the oxidation-reduction reaction thus reducing ECP





$$J_A = -D_A \Delta C_A - z\mu C_A F \Delta\phi + C_A V$$

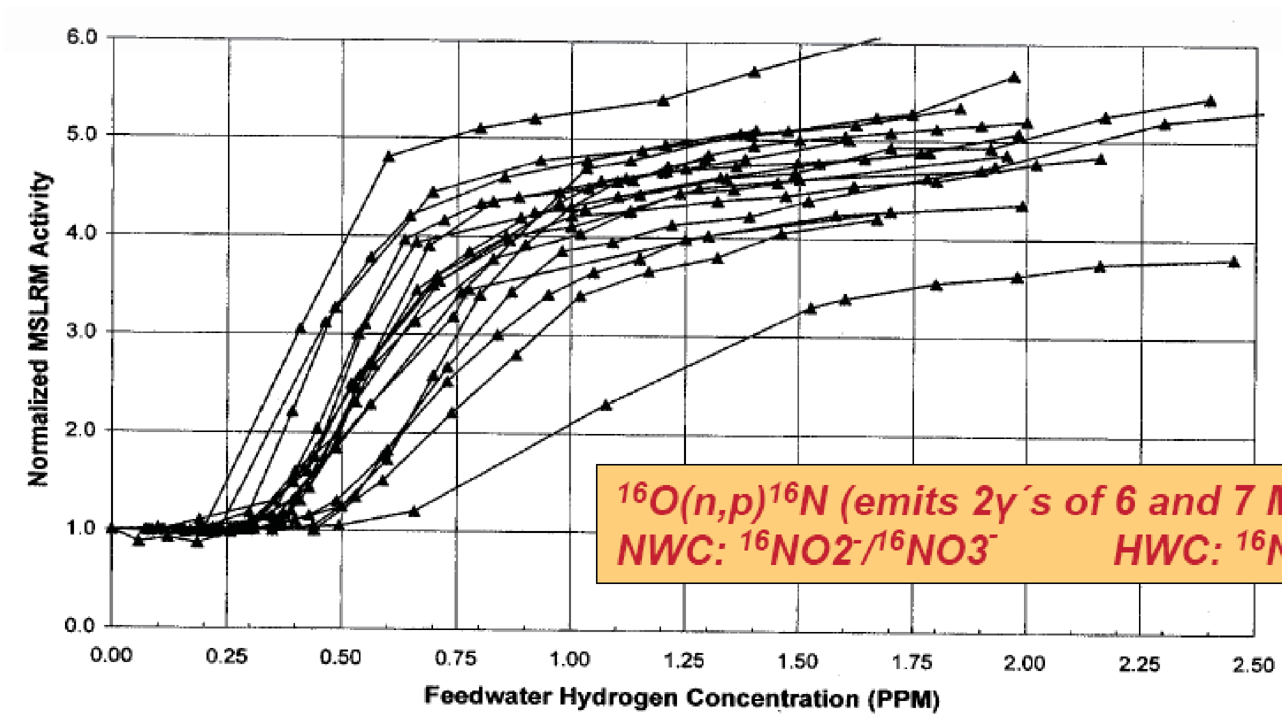
flux = diffusion + ϕ-driven + convection

Chemistry in BWR – "Sky Shine" effect

"Sky Shine", i.e. significant increase of does rate at the main steam line due to steam volatile ^{16}N-compounds at high hydrogen dosages.

Countermeasures:

- Shielding of machine room
- Catalysis of H_2-oxidation due doting of reactor surfaces with noble metals (Pt, Rh) ("Noble Metal Chemical Addition" NMCA)



$^{16}O(n,p)^{16}N$ (emits 2γ´s of 6 and 7 MeV), $t_{1/2}$ = 7s
NWC: $^{16}NO2^-/^{16}NO3^-$ HWC: $^{16}NH3$

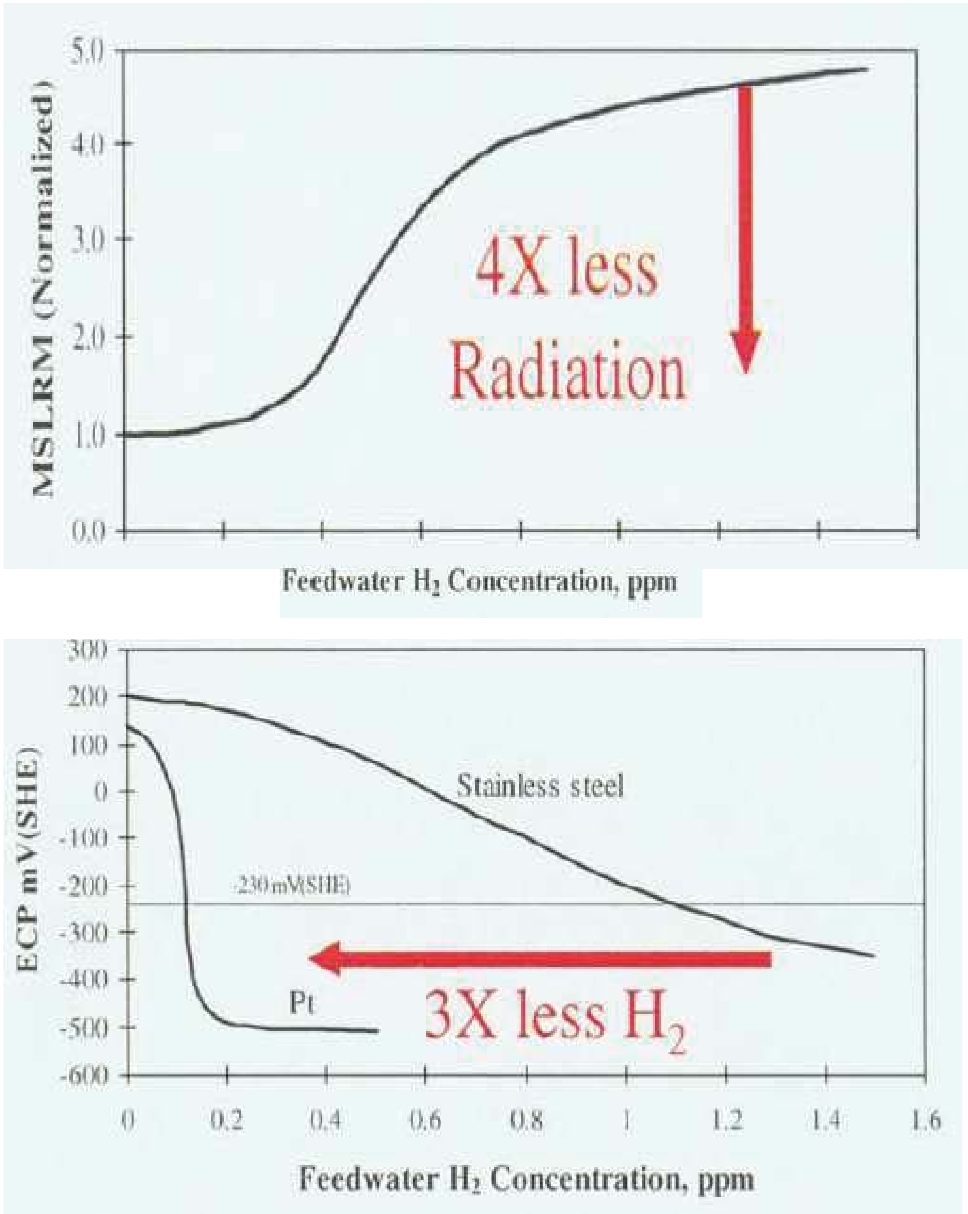
Chemistry in BWR– NMCA

Intentions of NMCA-Treatment (GE-Patent):

- ❑ Avoidance of dose rate increase of main steam line
- ❑ Increase of efficiency of H_2-oxidation (avoidance of SCC)

Principle:

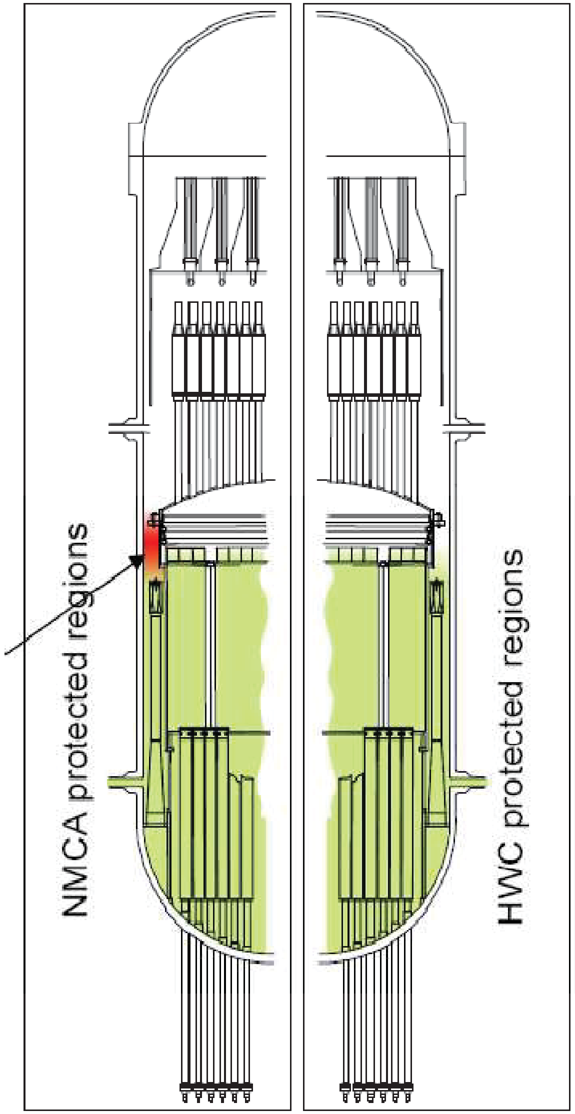
- ❑ Doting of oxide layers of reactor core components with noble metals (Pt, Rh) enables the decrease of hydrogen feed water concentration
- ❑ Typical H_2-concentration in the feed water ~ 0.2 ppm
- ❑ To date enormous costs for NMCA-Treatment



Chemistry in BWR – HWC and NMCA

NMCA + HWC

- ECP reduction as soon as feedwater and separator/dryer return flow are fully mixed to create >2:1 H_2 to oxidant molar ratio
- Additional areas of protection with NMCA – upper, outer shroud regions (red region)
- Hydrogen injection rate is < 0.3 ppm



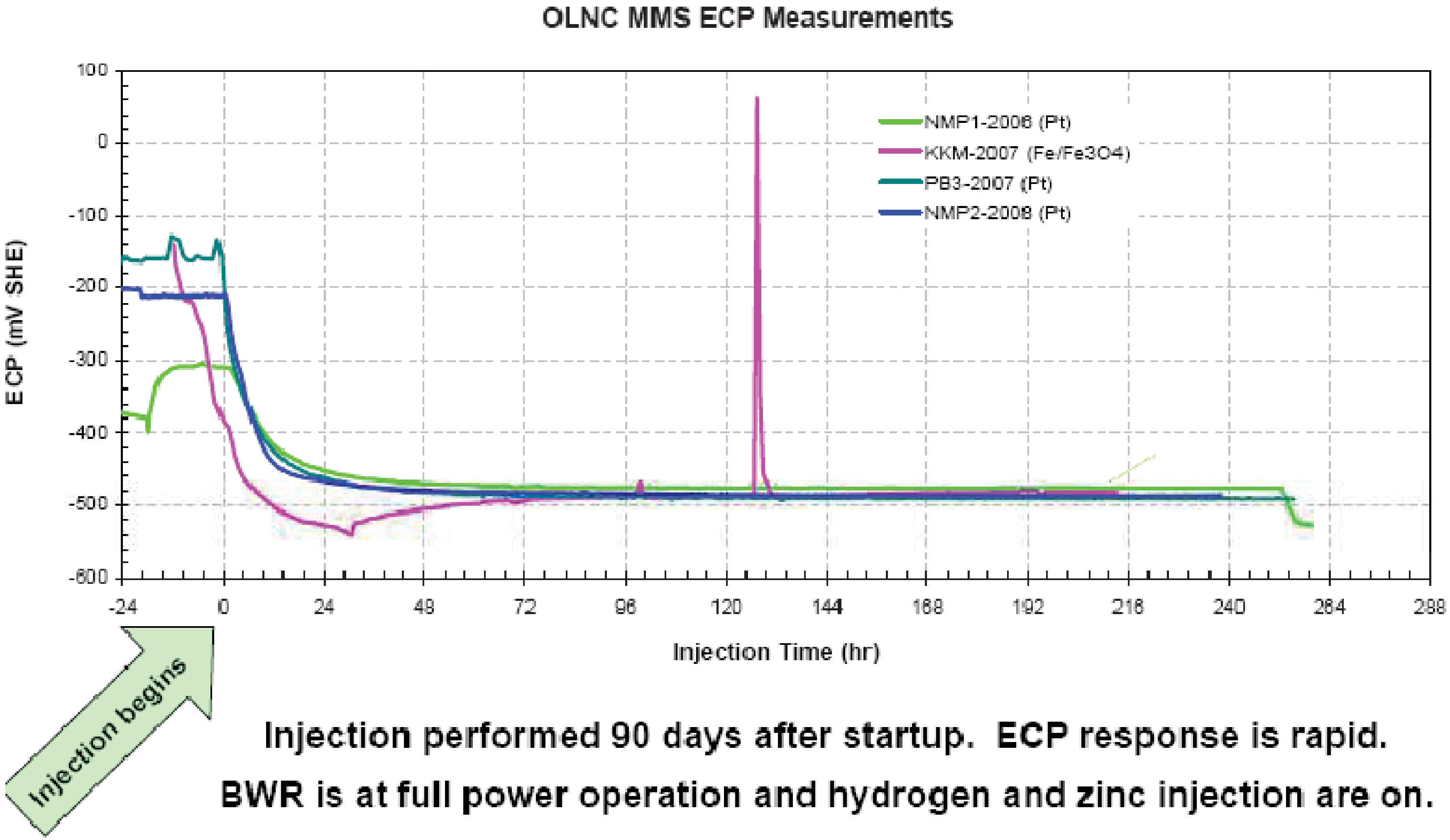
HWC-Moderate

- ECP reduction in the upper shroud annulus as gamma from the core recombines H_2 and O_2
- ECP reduction depends on H_2 injection amount
- Typically < -230 mV (SHE) around upper jet pump
- Hydrogen injection rates are >1ppm

Critical Differences Between NobleChem™ and On-Line NobleChem™

NobleChem™	On-Line NobleChem™
During hot shutdown	During reactor operation
Application Temperature > 235°F	Application Temperature > 540°F
Noble Metals, Pt & Rh	Noble Metal, Pt only
Sodium and nitrate ions 100s to 1000s ppb in reactor water during application	Sodium ions < 20 ppb, and no nitrate ions added during the application
Reactor water clean-up in operation	Reactor water clean-up in operation
Reactor water cleaned up prior to plant startup	Reactor water cleaned up during plant operation
Core Flow – minimum	Core Flow > 85% (>75% for MELLLA plants)
Hydrogen injection Off	Hydrogen injection On
Zinc injection Off	Zinc injection On
Application period – 48 hrs	Application period – 1 to 3 weeks

ECP behaviour during On-line Noble Metal (OLNC) application



Injection performed 90 days after startup. ECP response is rapid.

BWR is at full power operation and hydrogen and zinc injection are on.

Chemistry in BWR - HWC, NMCA summary

- ❑ **HWC effective for IGSCC Mitigation (all US 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 BWRs now apply noble metal (29 of 35 to date)**
- ❑ **….but hydrogen is not always being injected at BWRs**

BWR Chemistry – Summary

Actual Status of BWR Water Chemistry Regimes

- ❑ Ca. 60 BWR's are injecting hydrogen
- ❑ Ca. 40 BRW's are injecting zinc
- ❑ Ca. 30 BWR's apply NMCA-Treatment
- ❑ Further increase of plants applying NWC is to be expected in the next years (ca. 70 –75)
- ❑ European BWR's with NWC treatment (at present 14 plants) represent about 15 % of all BWR's
- ❑ On going discussions on the efficiency of HWC/NMCA treatment in plants on line ("crack flanking effect")
- ❑ On going discussions on the effects of the fuel cladding of NMCA treatment
- ❑Costs

BWR Chemistry – Summary

Objective 1: Control IGSCC of Piping Systems

Hydrogen Water Chemistry
Low levels controls piping IGSCC

Objective 2: Mitigate IGSCC of Reactor Internals

Moderate HWC
Increases N-16 in Turbine

Noble Metals
Refuel Outage Application

Objective 3: Control Radiation Fields

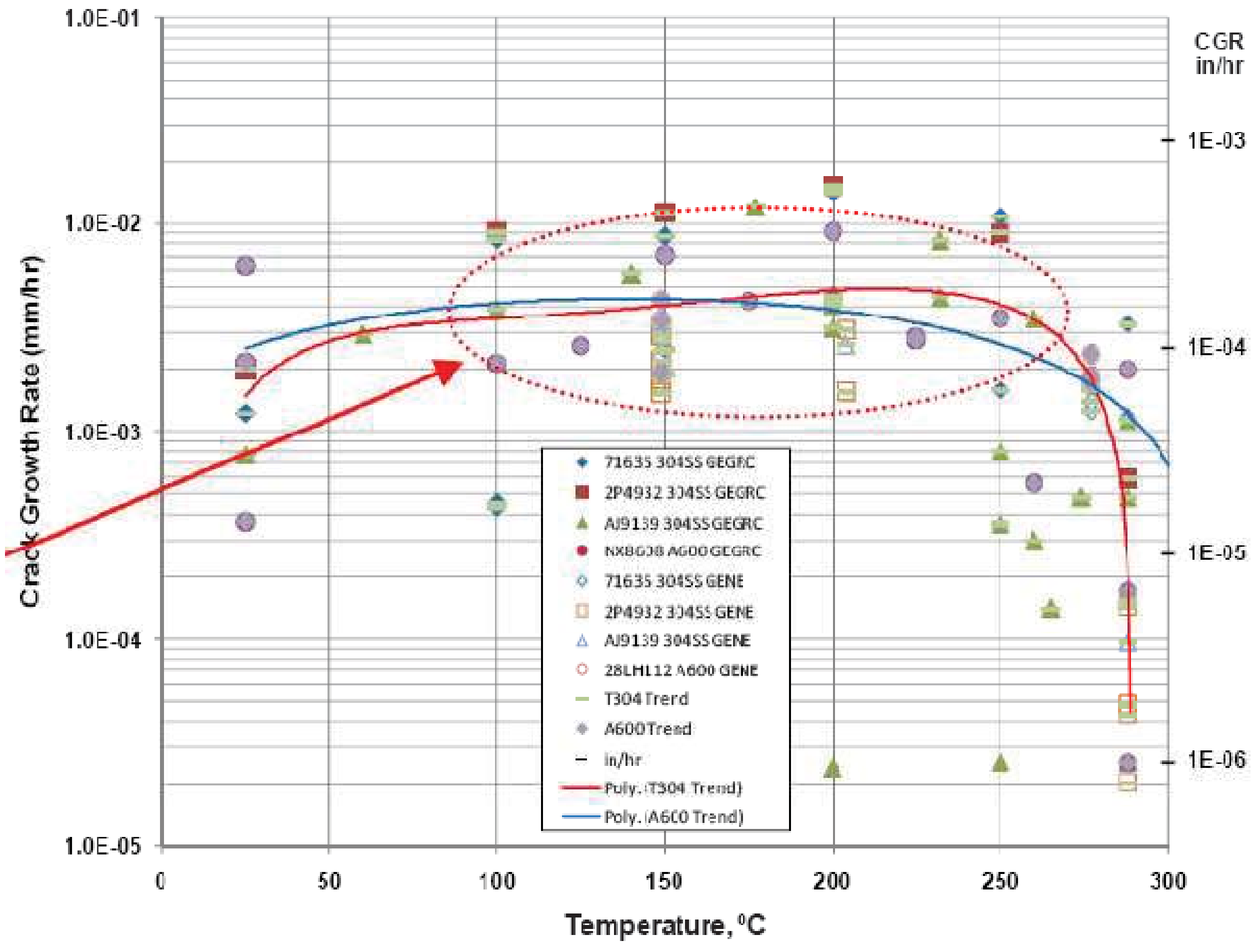
Zinc Injection

Objective 4: Avoid Fuel Crud Concerns

Limit Feedwater Zinc and Reduce Iron Ingress

BWR Startup ECP Reduction – Action Needed

- ❑ Current H2 injection systems have limitations for early injection (often delayed until >20% power)
- ❑ Crack initiation can occur at startup
- ❑ Elevated ECP during startup due to high oxygen levels
- ❑ CGR higher at intermediate temperatures
- ❑ Earlier hydrogen injection being evaluated for plant startup



Chemistry for SCWR – Introduction

- **The idea of using a supercritical water (SCW) coolant in a water-cooled reactor dates back to the 1960s**

- **More recently, two types of supercritical water-cooled reactor (SCWR) concept have evolved from existing light water reactor (LWR) and pressurized heavy water reactor (PHWR) designs:**

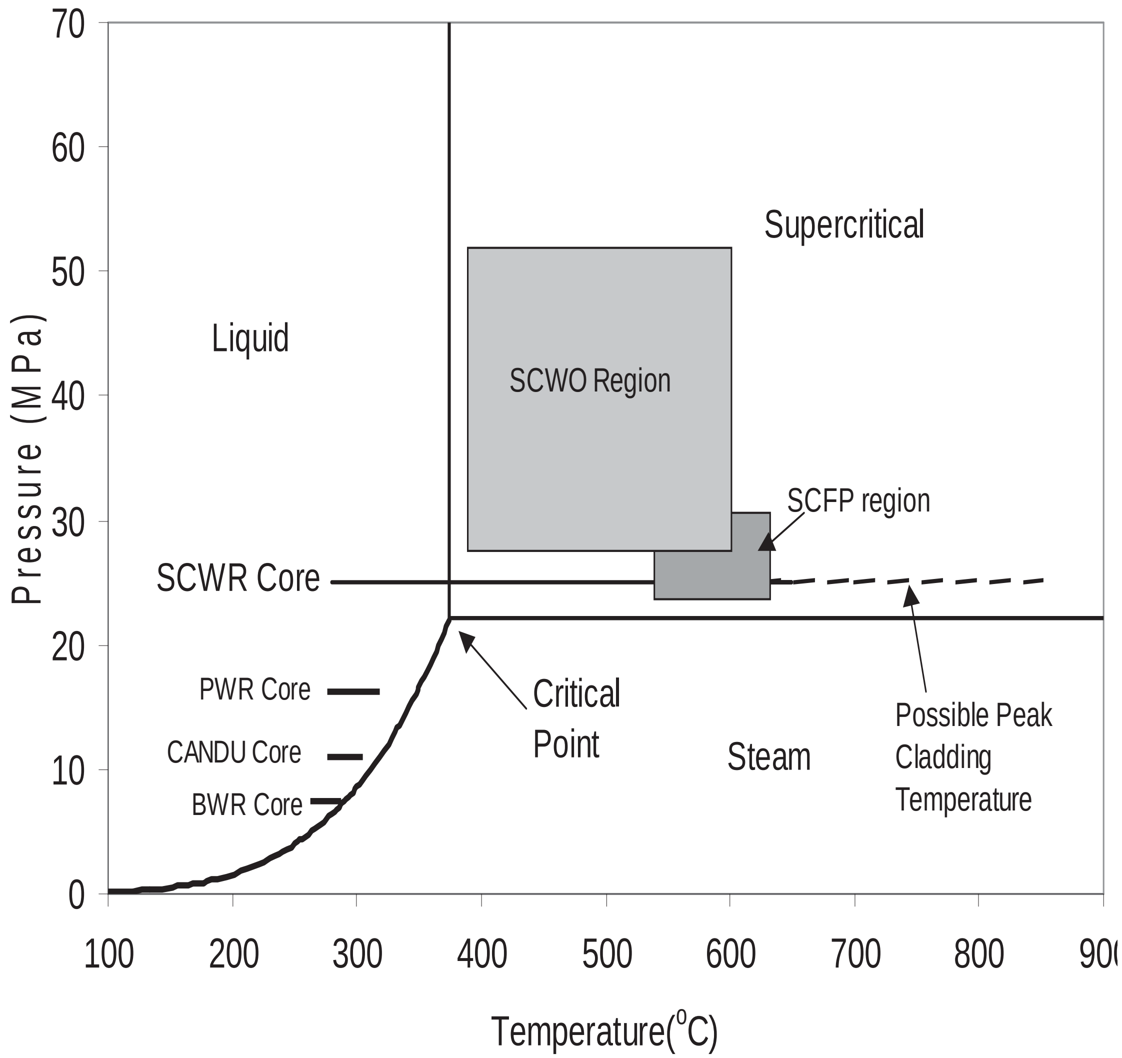
  - designs consisting of a large reactor pressure vessel containing the reactor core (fueled) heat source, analogous to conventional Pressurized Water Reactor (PWR) and Boiling Water Reactor (BWR) designs

  - designs with distributed pressure tubes or channels containing fuel bundles, analogous to conventional CANDU® and RBMK (*reaktor bolshoy moshchnosti kanalniy* - High Power Channel Type Reactor)

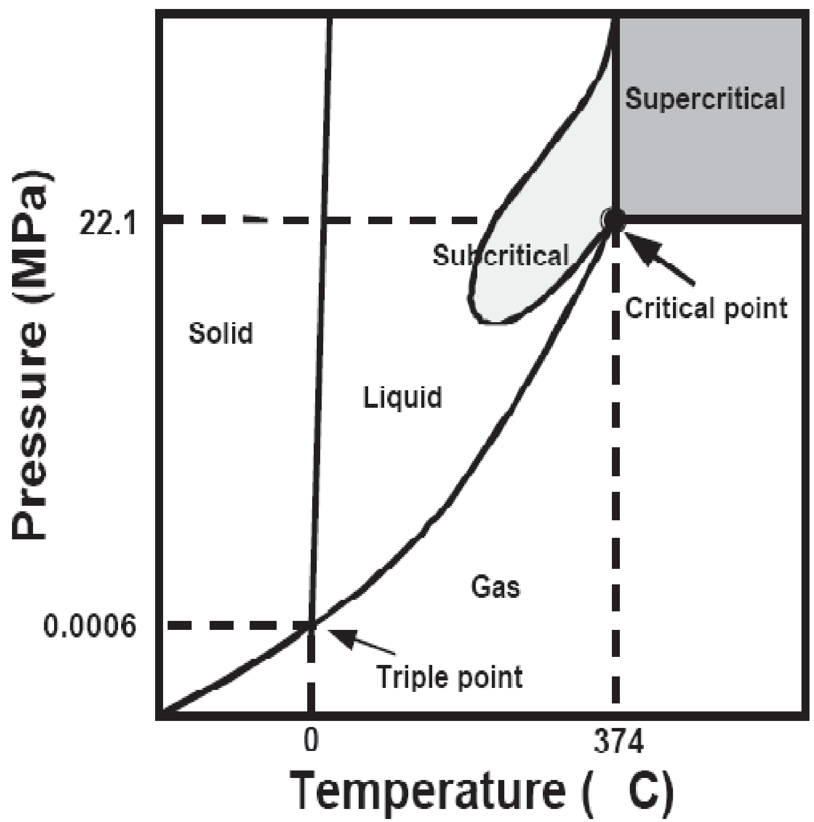
  - Out-of-core portions of both concepts are similar to existing fossil-fired generators

Chemistry for SCWR – Introduction

What is supercritical water (SCW) ?

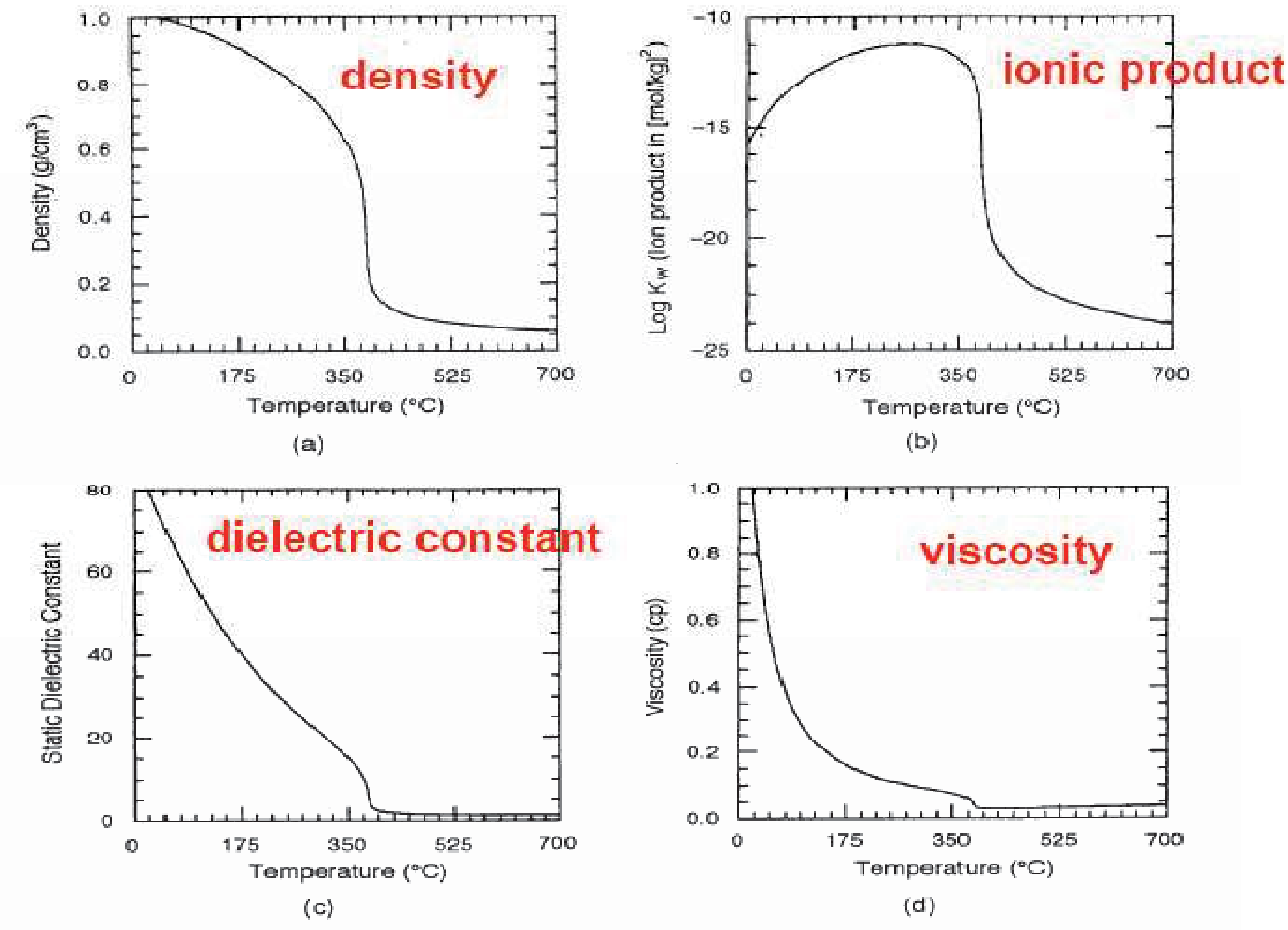


$T_c > 374\ °C$, $P_c > 22.1$ MPa



Chemistry for SCWR – Introduction

Temperature dependence of some water properties at 250 bar



Chemistry for SCWR – Introduction

The GIF SCWR Materials and Chemistry Provisional Project Management Board (PPMB) has identified two major challenges that must be overcome to ensure the safe and reliable performance of an SCWR:

1. Insufficient data are available for any single alloy to unequivocally ensure its performance in an SCWR, especially for alloys to be used for in-core components

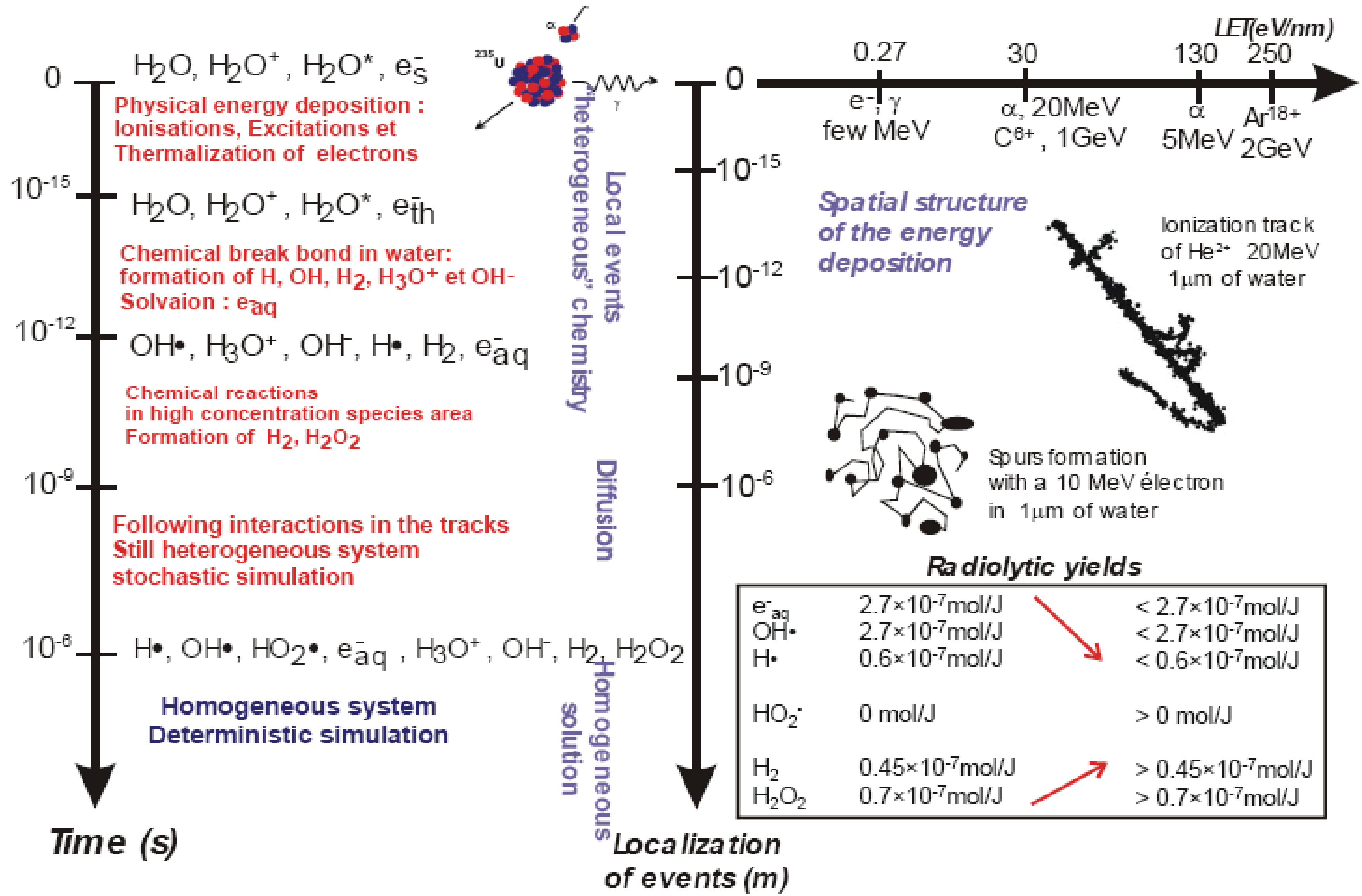
2. Current understanding of SCW chemistry is inadequate to specify a chemistry control strategy, as the result of the large changes in physical and chemical properties of water through the critical point, coupled with the as yet poorly understood effects of water radiolysis

Chemistry for SCWR – Introduction

Four key issues identified for SCWR:

- Radiolysis of SCW
- Understanding Corrosion Product Transport and Deposition
- Specification of Water Chemistry for Detailed Testing
- Identification of Methods for Chemistry Monitoring and Control

Chemistry for SCWR – Radiolysis



Radiolytic yields

e^-_{aq}	2.7×10^{-7}mol/J	< 2.7×10^{-7}mol/J
$OH\bullet$	2.7×10^{-7}mol/J	< 2.7×10^{-7}mol/J
$H\bullet$	0.6×10^{-7}mol/J	< 0.6×10^{-7}mol/J
$HO_2^\bullet$	0 mol/J	> 0 mol/J
H_2	0.45×10^{-7}mol/J	> 0.45×10^{-7}mol/J
H_2O_2	0.7×10^{-7}mol/J	> 0.7×10^{-7}mol/J

Chemistry for SCWR – Radiolysis

Radiolytic production of oxidizing species (e.g., ·OH, H_2O_2, O_2, $HO_2\cdot/O_2^{-}\cdot$) can increase corrosion of reactor components as well as affect corrosion product transport and deposition

A critical Importance: $OH + H_2 \rightarrow H + H_2O$

- To convert the oxidizing radical, OH, into the reducing radical, H
- Suppression oxidative corrosion in the primary heat transport systems

Current PWRs and PHWRs limit formation of oxidizing species by ensuring the presence of excess hydrogen at concentrations sufficient to chemically lower the net production of oxidizing species by radiolysis

- Insufficient data to determine whether this strategy would be effective in an SCWR
- Coolant could be very oxidizing immediately downstream of the core

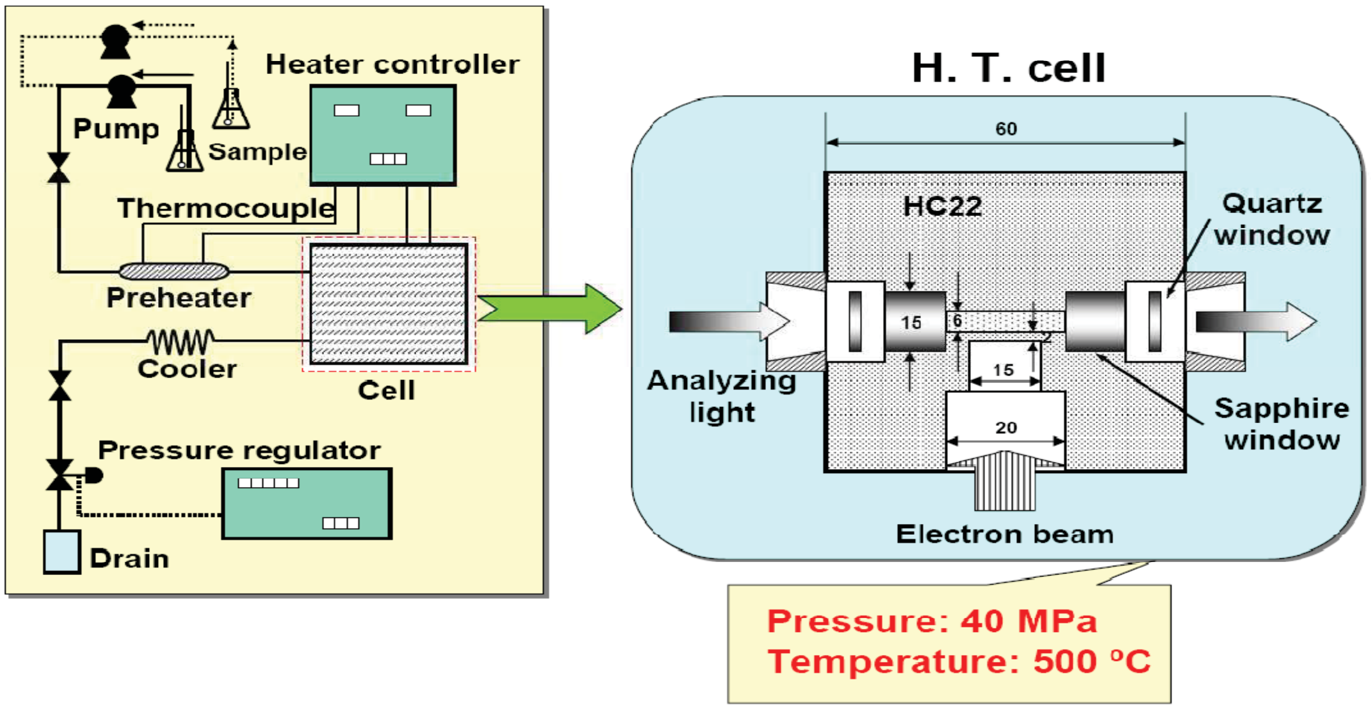
Work is on-going to develop an improved understanding of SCW radiolysis through a combination of experiment and modeling

Chemistry for SCWR - Radiolysis experimental

- ❑ **Direct measurements of chemistry in reactor cores is extremely difficult**
- ❑ **Theoretical calculations and chemical models have been used**
- ❑ **Laboratory measurements:**

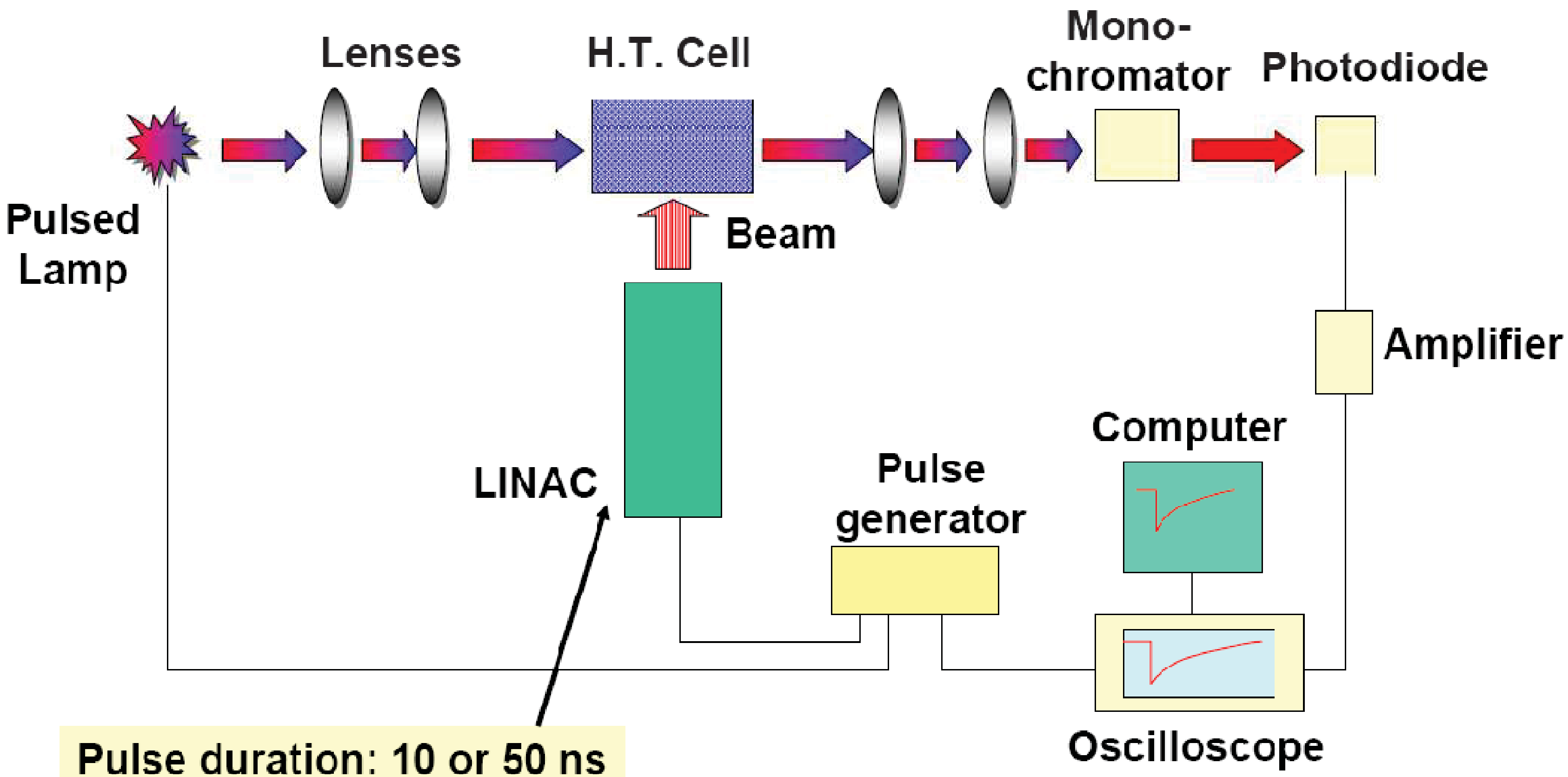
To evaluate the concentrations of the radicals primary yield of each radical (G-value) and rate constants of chemical reactions by means of:

Pulse radiolysis



Pulse Radiolysis System

Pulse radiolysis with photo-spectroscopic detection method



Pulse duration: 10 or 50 ns
Dose per pulse: 10 ~ 60 Gy

Chemistry for SCWR - Radiolysis experimental

Pulse Radiolysis System

- ❑ Chemical reagents are used as Scavengers of radicals
- ❑ Detected by Absorbance measurement
- ❑ Methyl-viologen to determine G-value of:

- Hydrated electron G (e_{aq}^-)
- Water decomposition G (e_{aq}^- + OH + H)

e^-_{aq}, H, OH

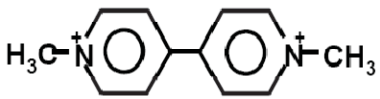
absorption band: temperature dependent

absorption coefficient: not known

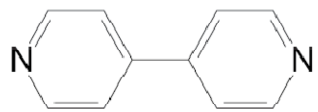
MV•+

BPYH•

MV^{2+}

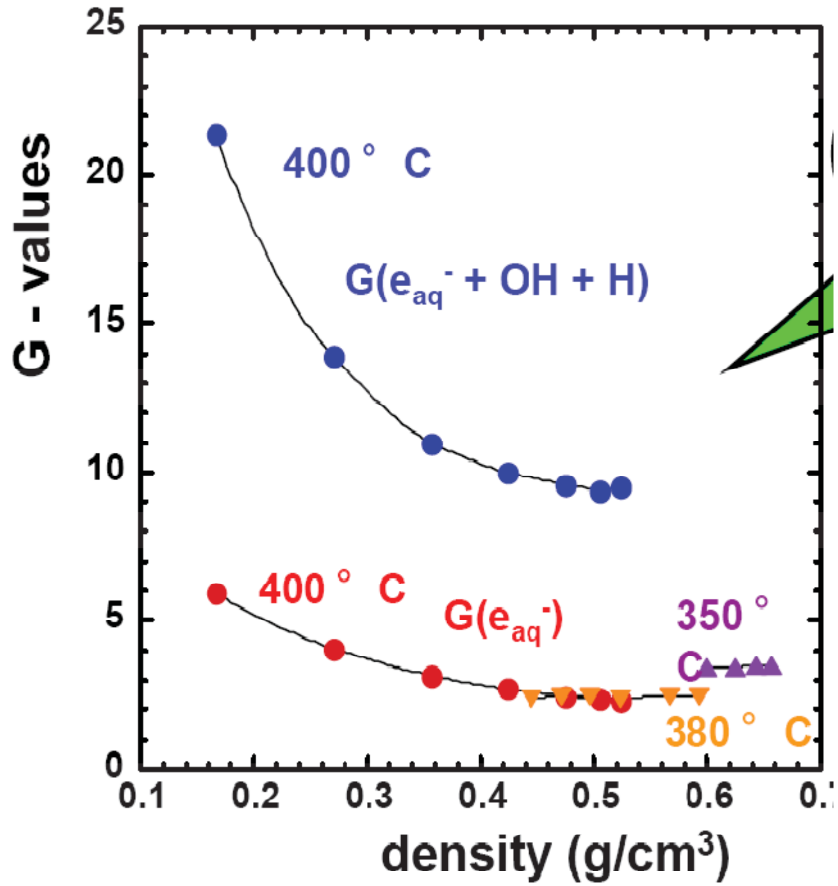


4,4'-bpy



Temperature independent

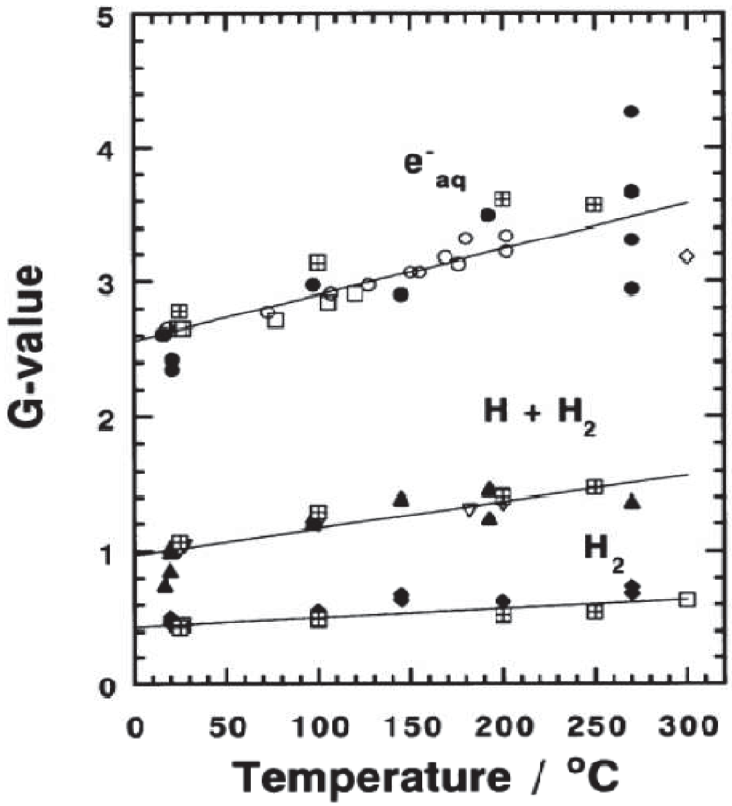
absorption band & coefficient

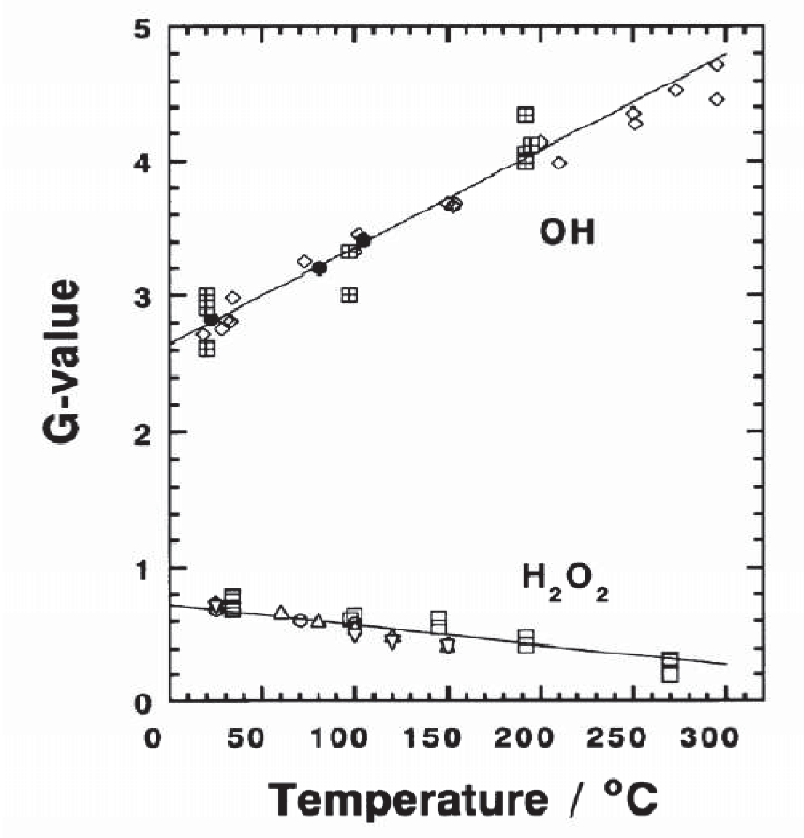


Chemistry for SCWR - Radiolysis experimental

Pulse Radiolysis System - Results

Data on kinetics of radiolytic reactions and chemical yields (G-values) of decomposition products are obtained

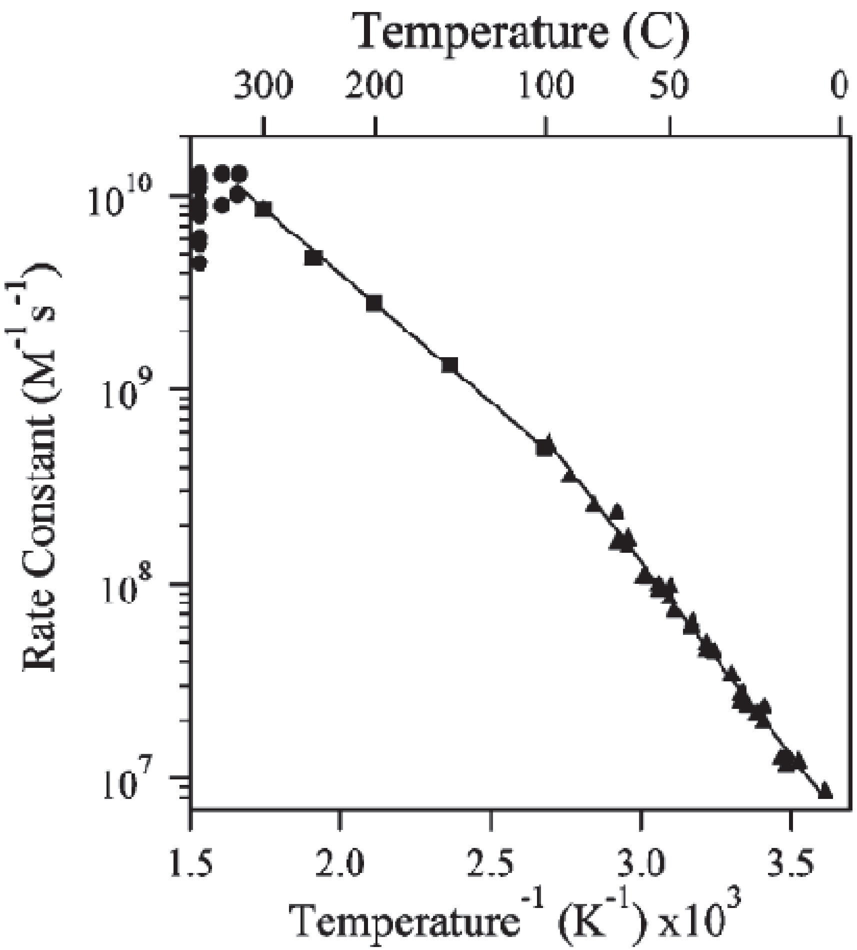




Data can be used for development of a radiolysis model

Pulse Radiolysis System – Results

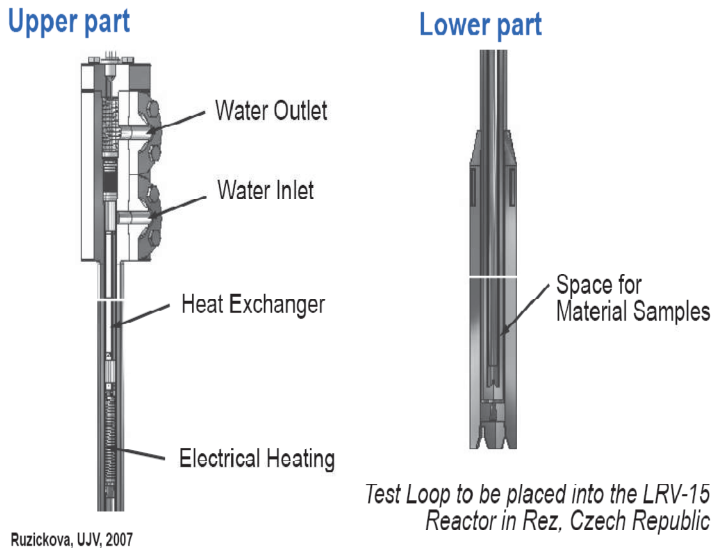
The rate constant for the reaction of hydrogen atoms (H^*) with hydroxide ions (OH^-) in aqueous solution has been measured from 100 to 300 ℃ by direct measurement of the hydrated electron (e_{aq}^-) product growth rate.



Supercritical Water Loop –SCWL (Research Center Rez)

Main targets:

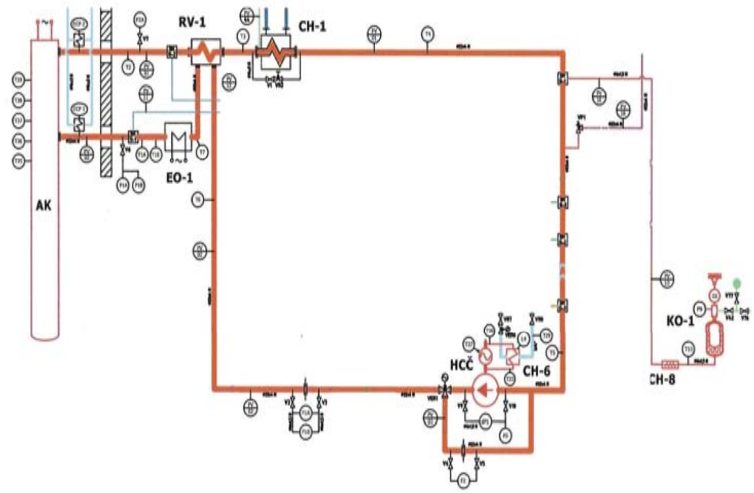
- ❑ Corrosion studies
- ❑ Testing and optimization of suitable water chemistry
- ❑ Coolant radiolysis studies
- ❑ Development and testing of sensors



Test Loop to be placed into the LRV-15 Reactor in Rez, Czech Republic

LOOP: MAIN PARAMETERS:

- PRESSURE: 25MPa; max. 32MPa.
- TEMPERATURE: max. in active channel 600°C; max. in loop 390°C.
- FLOWRATE IN ACTIVE CHANNEL: 200kg/h.
- FLOWRATE IN LOOP: 200kg/h.
- TOTAL VOLUME: 42dm3.
- FILTRATION RATE: 30kg/h.
- SAMPLING: 0.2kg/h.
- ON-LINE MEASUREMENT: 2 x 12kg/h (HIGH-PRESSURE AND LOW-PRESSURE CIRCUITS).



The radiolytic model will be verified in SCWL

Chemistry for SCWR – Corrosion Product Transport

- **Release and transport of corrosion products from surfaces of system components a serious concern for all water-cooled nuclear power plants**

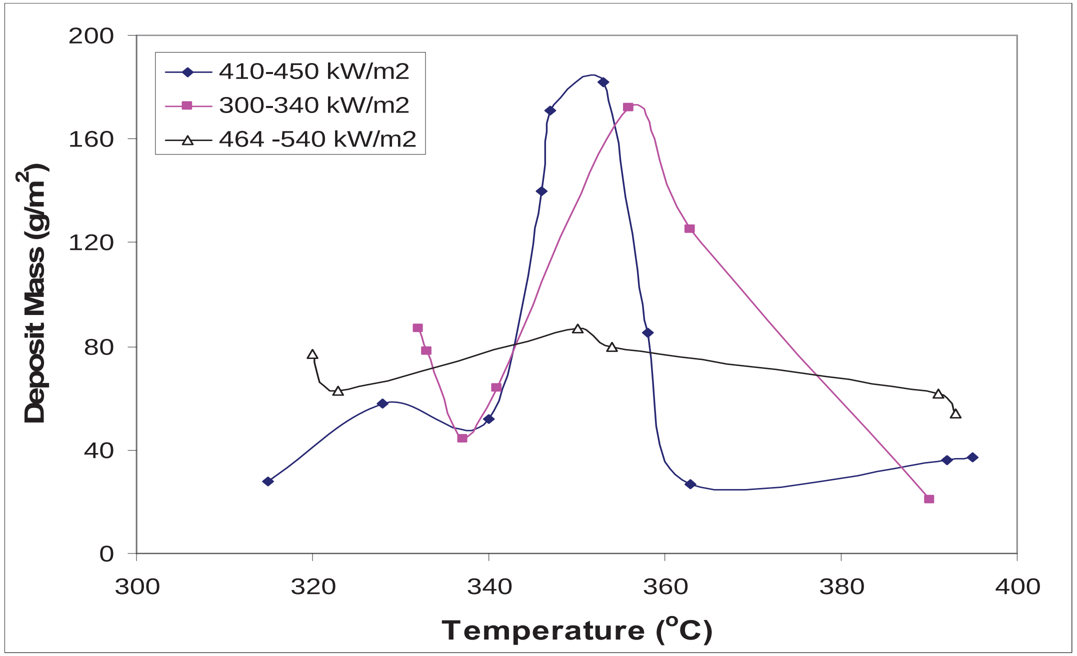
- **High levels of corrosion product transport can result in:**
  - **Increased deposition on fuel cladding surfaces, leading to reduced heat transfer and the possibility of fuel failures**
  - **Increased production of radioactive species by neutron activation, ultimately increasing out-of-core radiation fields and worker dose**
  - **In addition, nuclear and thermal power stations experience deposition of copper and silica species (which are volatile in steam) on turbines at levels that can cause turbine failure**

- **Supercritical thermal stations experience suggests corrosion product deposition could be significant in an SCWR**

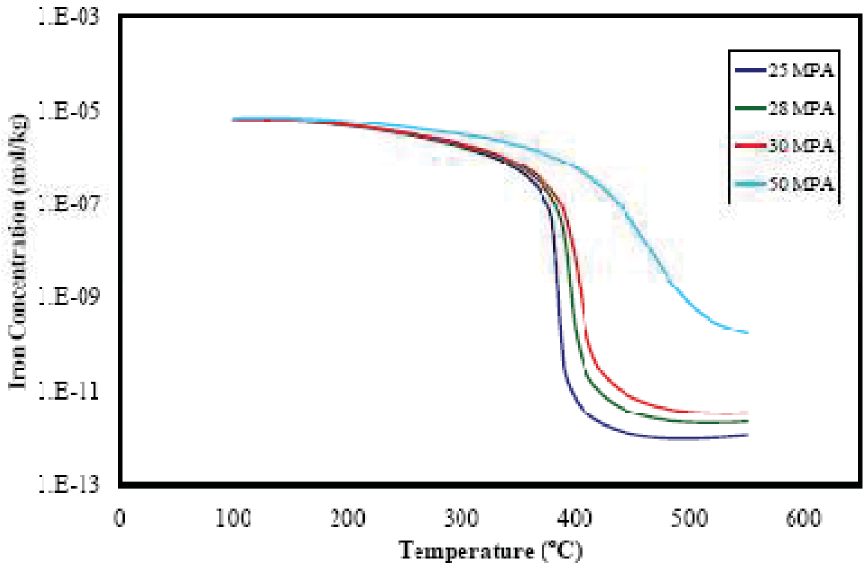
Chemistry for SCWR – Corrosion Product Transport

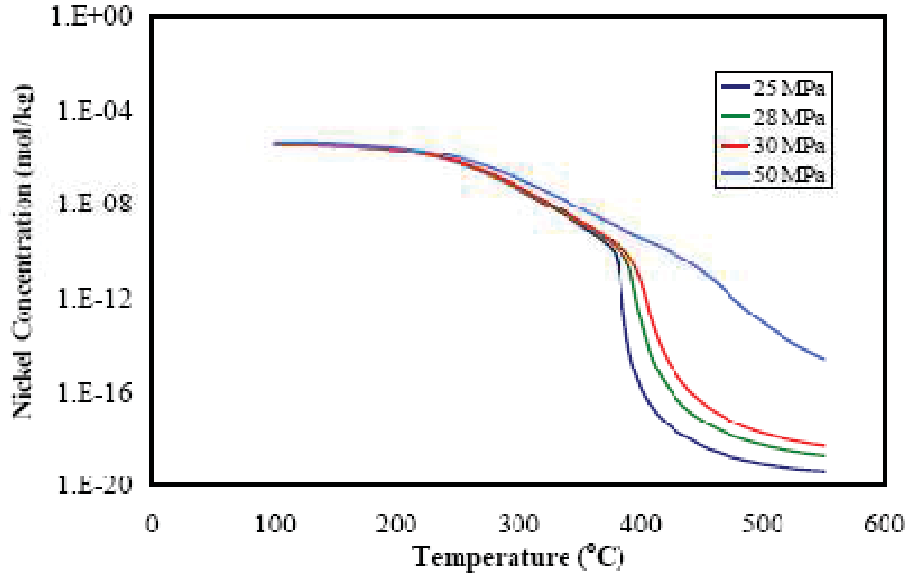
Distribution of deposits in a fossil-fired SCW boiler

- Lower radiant section
- 8400 h operation
- Hydrazine water treatment at pH 8.0-8.5



Predicted solubility of (a) magnetite and (b) nickel (II) oxide as a function of temperature and pressure.





Chemistry for SCWR – Chemistry monitoring

- **Relevant chemistry parameters (e.g., conductivity, pH, ECP, concentrations of dissolved H_2 and O_2) must be monitored and controlled in an SCWR and in in-reactor test loops**

- **Existing methods of chemistry monitoring are predominantly:**
  - **ex-situ (cooled and de-pressurized)**
  - **off-line (batch laboratory analysis of grab samples)**

- **These will be inadequate in an SCWR, as a result of the large changes in water chemistry around the critical point**

- **Reliable monitoring of key chemistry parameters will likely require development of in-situ or on-line probes**
  - **need for more work on this topic**

Most experimental work on SCWR materials has been carried out using a limited range of water chemistries

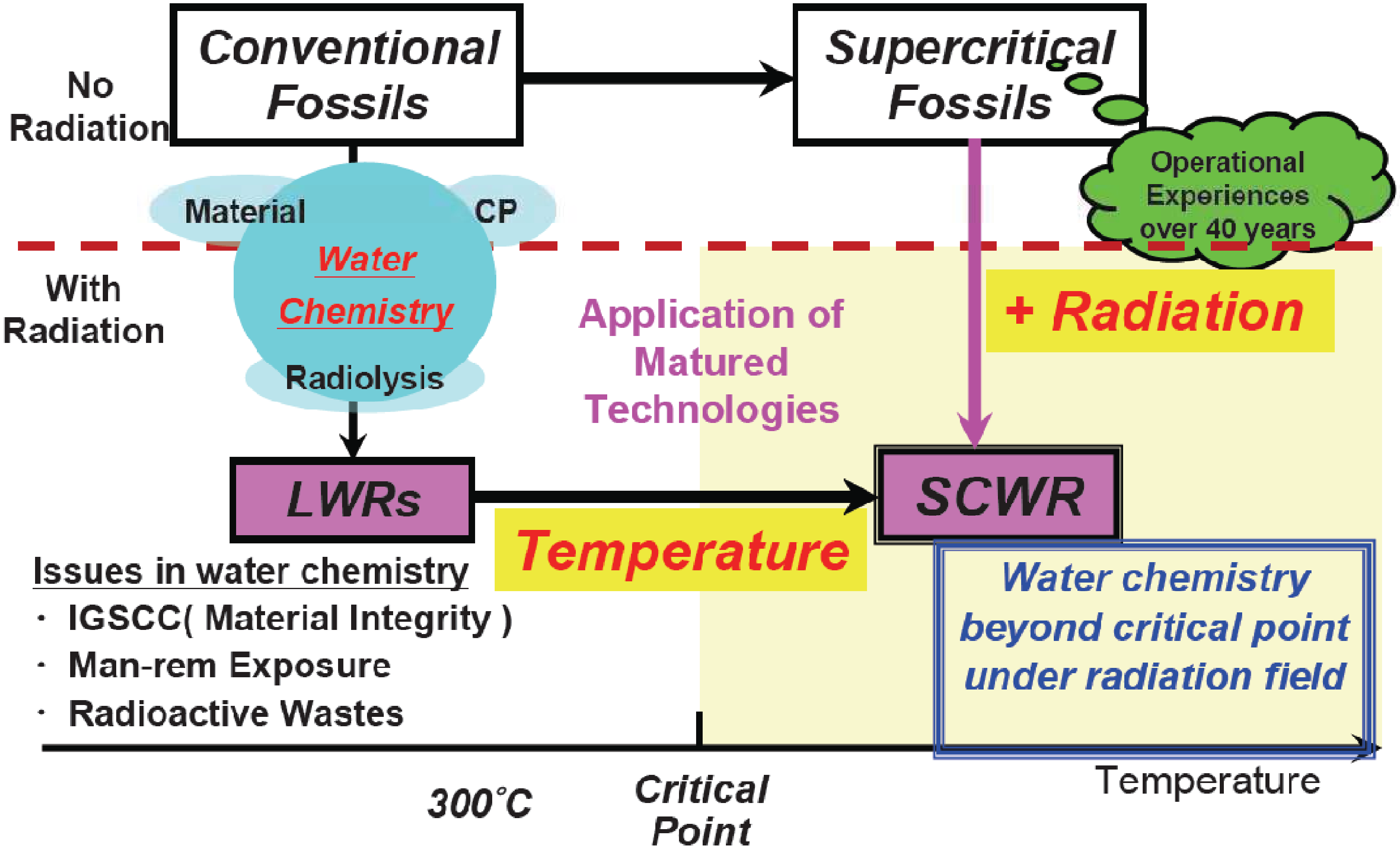
- Pure water
- Pure water with added oxygen (50 - 8000 ppb)
- Hydrogen water chemistry (H_2 concentration ~ 30 cm^3/kg water).

Thinking 'outside the box' may be helpful in devising novel water chemistries (e.g., LiOH addition)

Water Treatments used in Supercritical Water Fossil-Fired Power Plants

Water Chemistry	pH at 25ºC	Comments
$NH_3 + N_2H_4$	**8.5 – 9.6**	
N_2H_4 only	**7.7 – 8.5**	**60-100 µg/kg N_2H_4**
Chelant + $NH_3 + N_2H_4$		**0 µg/kg chelant, 0.8 mg/kg NH_3, 0.2 mg/kg N_2H_4**
pH 7 with O_2	**6.5 – 7.3**	**50-200 µg O_2/kg, conductivity <0.1 µS/cm**
Combined Mode	**8 – 8.5**	**NH_3+O_2 - NH_3 provides slight pH buffering**

Chemistry for SCWR - Summary



Chemistry for SCWR - Summary

While the pace has not been as rapid, some progress in understanding water chemistry issues such as radiolysis and corrosion product transport in SCW has been made

First water chemistry specifications

- **SCWR technologically similar to BWR**

⟶ similar water chemistry: NWC or HWC.

- **But! Higher temperature gradient.**

- **HWC in PWR:**

recent tests and calculations showed that currently used doses of hydrogen 30-60Nml/kg are overestimated; doses of 10x lower should do.