

Material Aging Institute

International Conference on Plants Materials Degradations

Chemical conditioning of Light Water reactors Systems

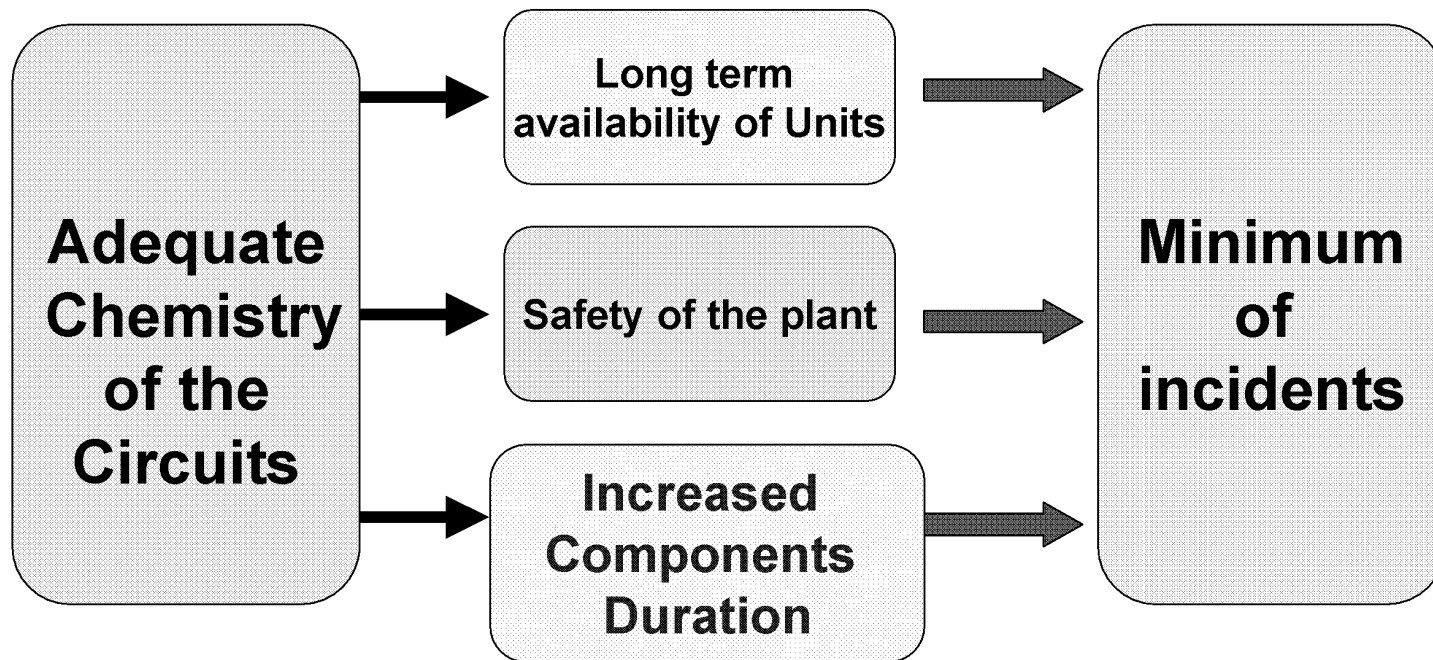
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Acknowledgment and many thanks to Keith Fruzzetti (EPRI) for having provided several data and very valuable comments on this document.

1.1 Introduction: Chemistry Objectives

A poor chemistry may, on a rather long term, induce corrosion
The effect is detrimental for components



1.2 Introduction - Issues Objectives

The NPP strategy is adding new challenges to the most crucial previous weakness of Alloy Inconel 600: SCC (Stress Corrosion Cracking).

- Optimization of the primary water chemistry for dose rates minimization and high performance fuel operation (PWR and BWR).
- Economical, environmentally sustainable and reliable operation of the circuits
- Very high safety and availability levels of the NPP
- Long term behavior of components for a longer life
This still requires corrosion mitigation

1.3 Introduction- Challenges evolution

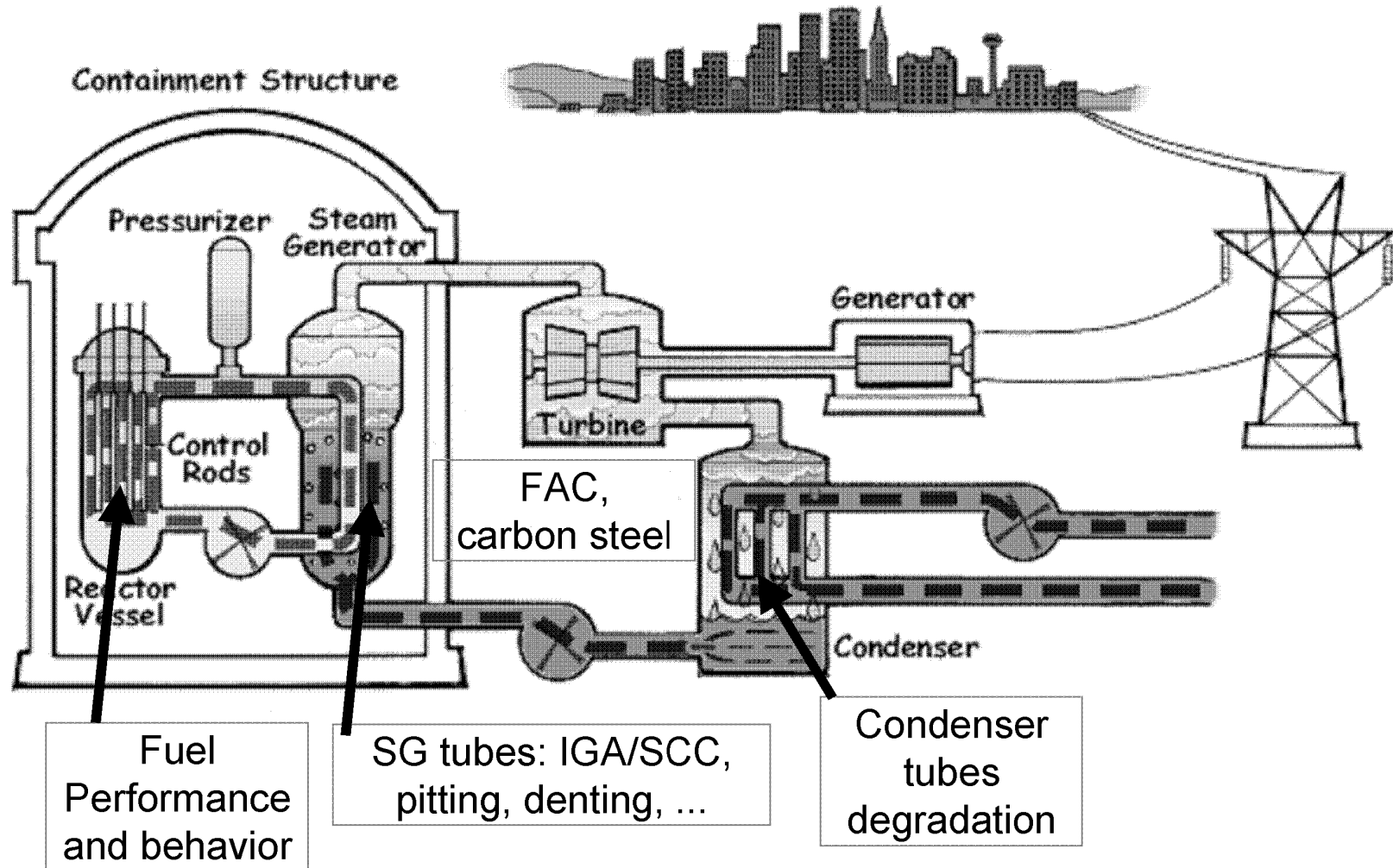
In the early days, chemistry was the cause of problems

- 1970s: Major ingresses 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 wastage or IGA/SCC, leading to “all-volatile treatment” in 1974, which caused denting.
- 1980s: “Purer is Better” was the theme – it helped a lot but was not sufficient to eliminate problems in presence of Alloy 600.

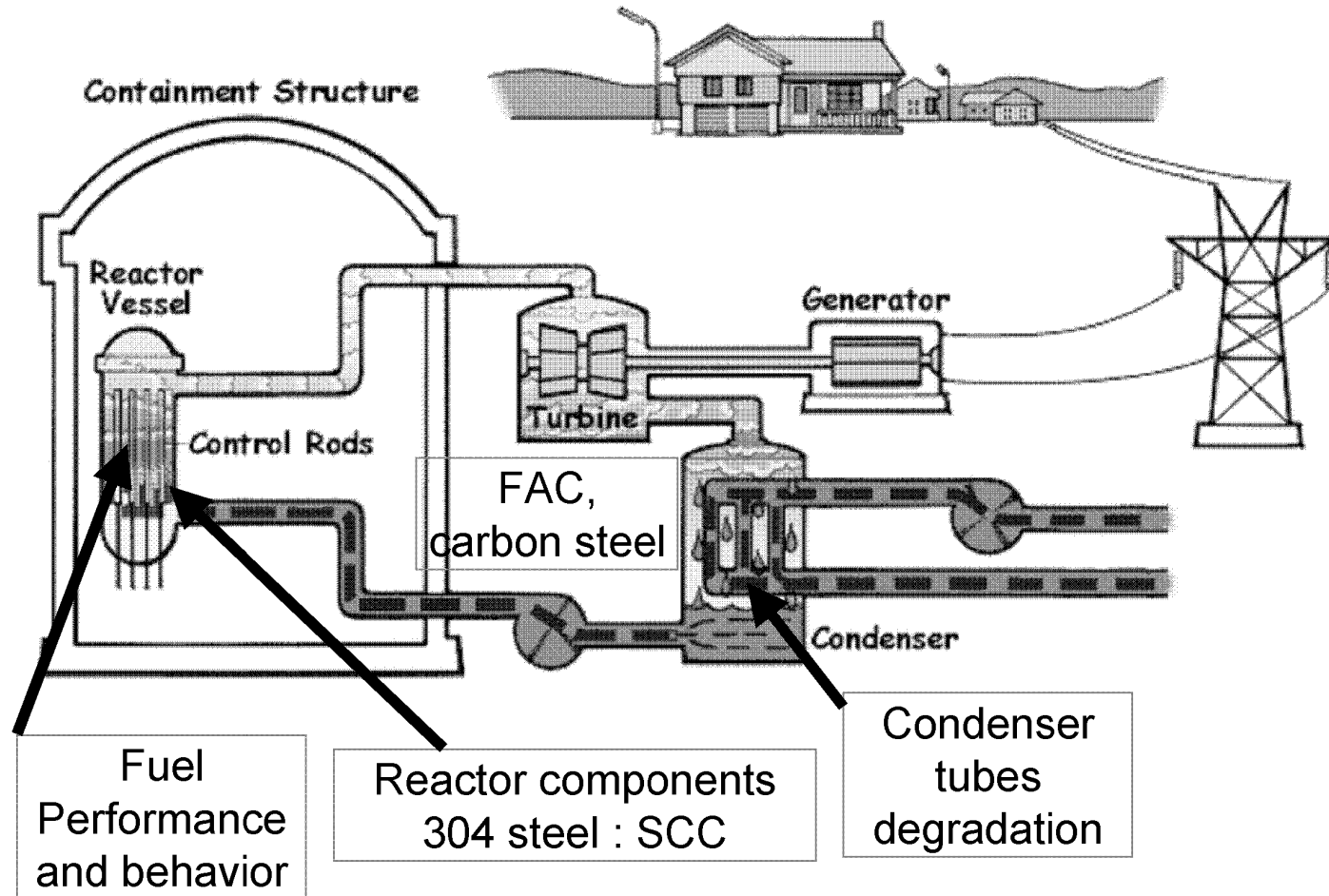
Chemistry advances focus on mitigation of corrosion problems

- 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 injection, elevated pH or amine in most secondary systems of PWR for SG deposits and FAC mitigation, dispersants trial.

1.4 PWR Chemistry- Main corrosion Issues



1.5 BWR Chemistry- Corrosion Issues



2.1. PWR Chemistry

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

Primary system

- Lithium, pH, Hydrogen, Zinc
- PWSCC, fuel behavior

Secondary system

- Amine, ammonia, corrosion inhibitors
- Copper alloys corrosion
- IGA/SCC (mainly Inconel 600 MA), **Flow Accelerated Corrosion** of carbon steel, corrosion products deposition and **Flow Induced Vibration**

2.2 Lithium hydroxide

Objective :

Neutralization of Boric acid
in order to be in a slightly alkaline environment

Optimum pH

Low generalized corrosion

- minimize generation and transport of corrosion products
- minimize dose rates

Alkaline reagent selection

- $\text{NaOH} \Rightarrow {}^{24}\text{Na}$
 - $\text{KOH} \Rightarrow {}^{42}\text{K}$
- Acceptable, used in VVER
- NH_4OH low stability
 - **LiOH** : Low corrosion risk due to limited solubility and concentration
Li-7 also produced from boron neutronic reaction ${}^{10}\text{B} (n, \alpha) {}^7\text{Li}$

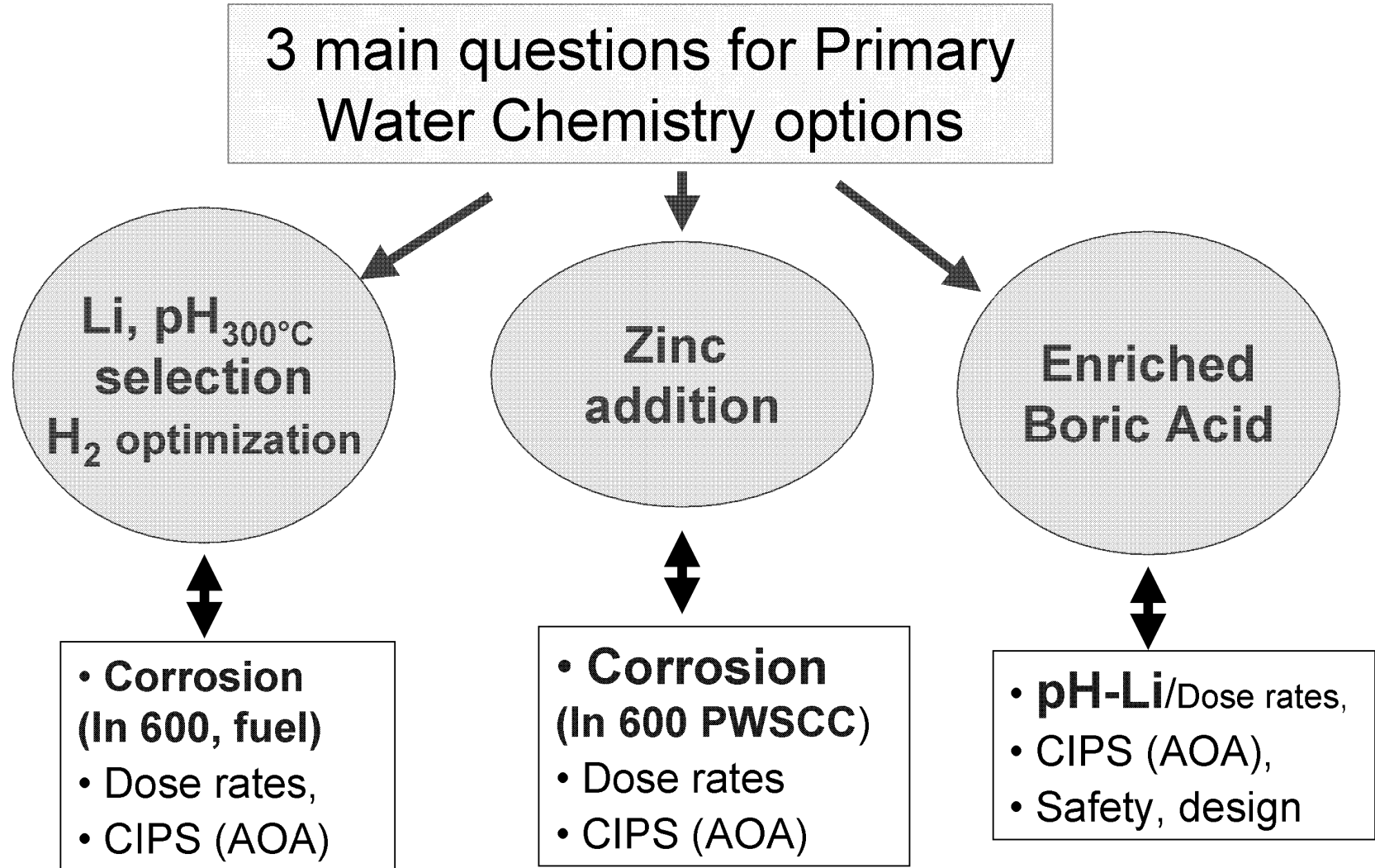
Radiochemistry

Li natural : ${}^6\text{Li}$: 7.42 %
 ${}^7\text{Li}$: 92.58 %



${}^6\text{Li} (n, \alpha) \text{T}$
 \Rightarrow use of ${}^7\text{Li}$ enriched to 99.9 %

2.3 Primary Water Chemistry - Main concerns



2.4 Primary Water Chemistry - pH/Li

Typical pH_{300°C} range 7.2 to 7.4

Upper value limited by



- **Li concentration**, mainly at BOC, potential impact on fuel and Inconel
⇒ Fuel vendor limitation
- **pH influence on PWSCC**, mainly Inconel 600, small effect in this range
- **risk of CIPS**
Boron-Li precipitation, other factors (Ni)
- **K (VVER) versus Li difference**, under investigation (IAEA/FUWAC)

Lower value limited by



- **Dose rate Impact**,
Target pH has been progressively increased in many cases, (calculation codes, feedback)
Limited impact within this range
- **But more impact if pH too low**
- **Compromise with ⁷Li cost**
(load follow, transients, shutdown)

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

2.5 Primary Water Chemistry - pH/Li

Many discussions on the upper maximum [Li], crucial at Beginning Of Cycle, mainly with new fuel options requiring higher [Boron] \Rightarrow Li even >5 ppm for $\text{pH}_{300^\circ\text{C}}$ 7.2

- Historically 2.1 ppm Li for risk of fuel cladding corrosion
- Fuel vendors reluctant to increase Li > 3.5 ppm, which is mainly motivated by Utilities for \searrow dose rates
- Many studies on impact of Li - pH - B on PWSCC
 - \Rightarrow No major influence in this Li - pH range
 - ☐ Very limited influence on propagation (CGR)
 - ☐ May decrease initiation time (factor ~ 2 for Li: 2 \nearrow 4 ppm)
- Fuel vendor limitation: even more cautious with Zn
- Most vendors and regulatory bodies now accept at least 3.5 ppm Li

Typical $\text{Li}_{\text{max}} = 2.2$ or 3.5 ppm, some cases higher

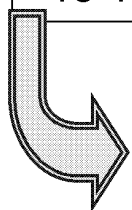
No benefit of higher value expected for PWSCC, but potentially for dosimetry

2.6 CIPS (AOA) - Fuel behaviour

CIPS influenced by



- **Subcooled nucleate boiling** and associated **crud deposits**
- **Boron content + Li**
Impact of new fuel options, longer fuel cycles \Rightarrow Higher B at BOC
Boron precipitation in crud.
- **pH influence** on corrosion product transport, deposition, crud thickness
 \Rightarrow **fuel corrosion risk**
- **Nickel content in Materials**
Inconel 600 the worse. 690 better.
Incoloy 800 (Germany) satisfying
18-10 (VVER) the best.



Inconel 600:
sensitive to SCC
+ risk for fuel

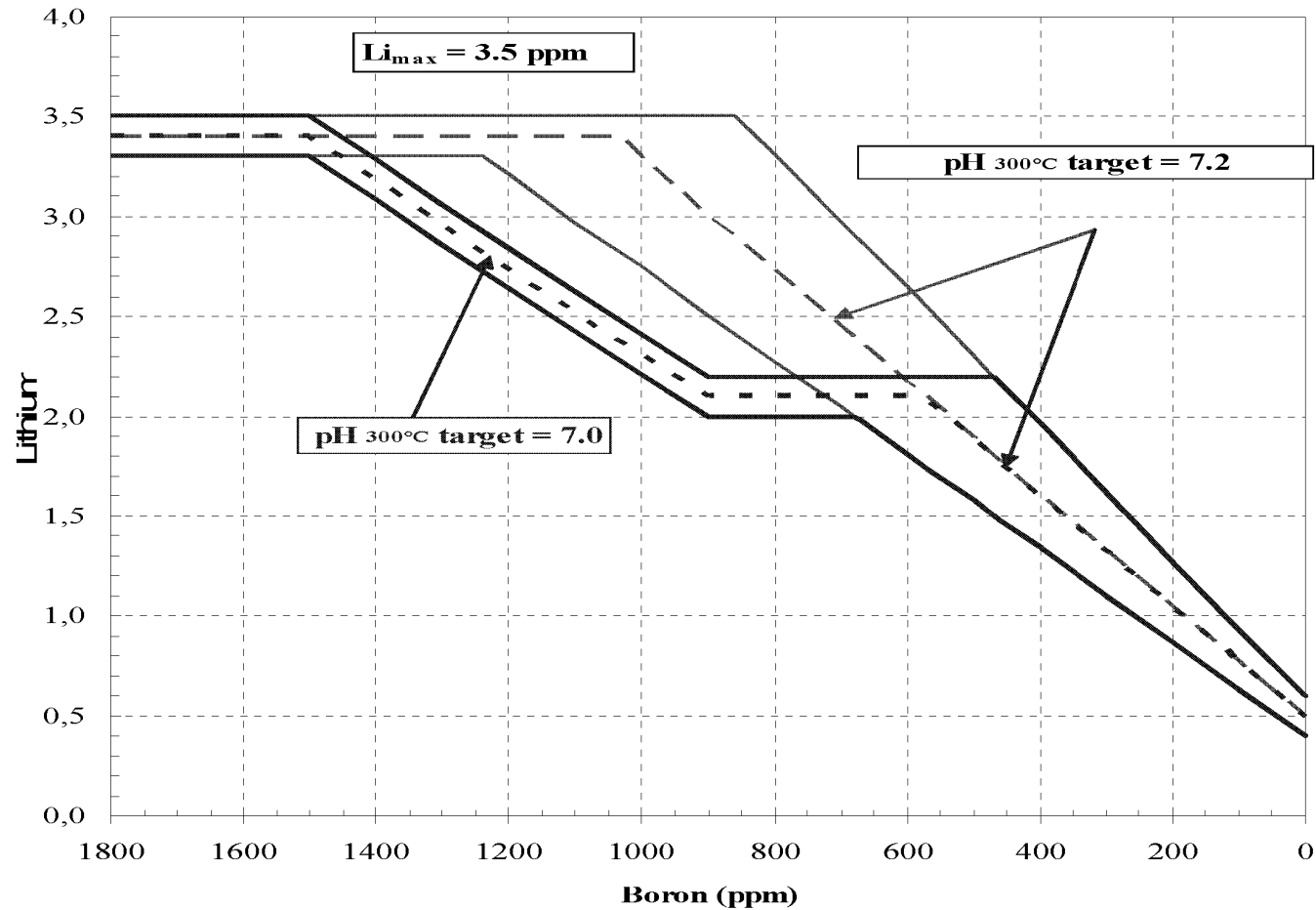
Enriched Boric Acid use



- **Optimum pH** with limited B
 \Rightarrow Li also limited
- May avoid design modification
- Highly advisable to consider for new plants
- **Minor impact on corrosion** although more beneficial relative to zircaloy corrosion and \searrow B in crud

**Many options
and parameters
are connected**

2.7 pH - Li Chemistry on French PWRs

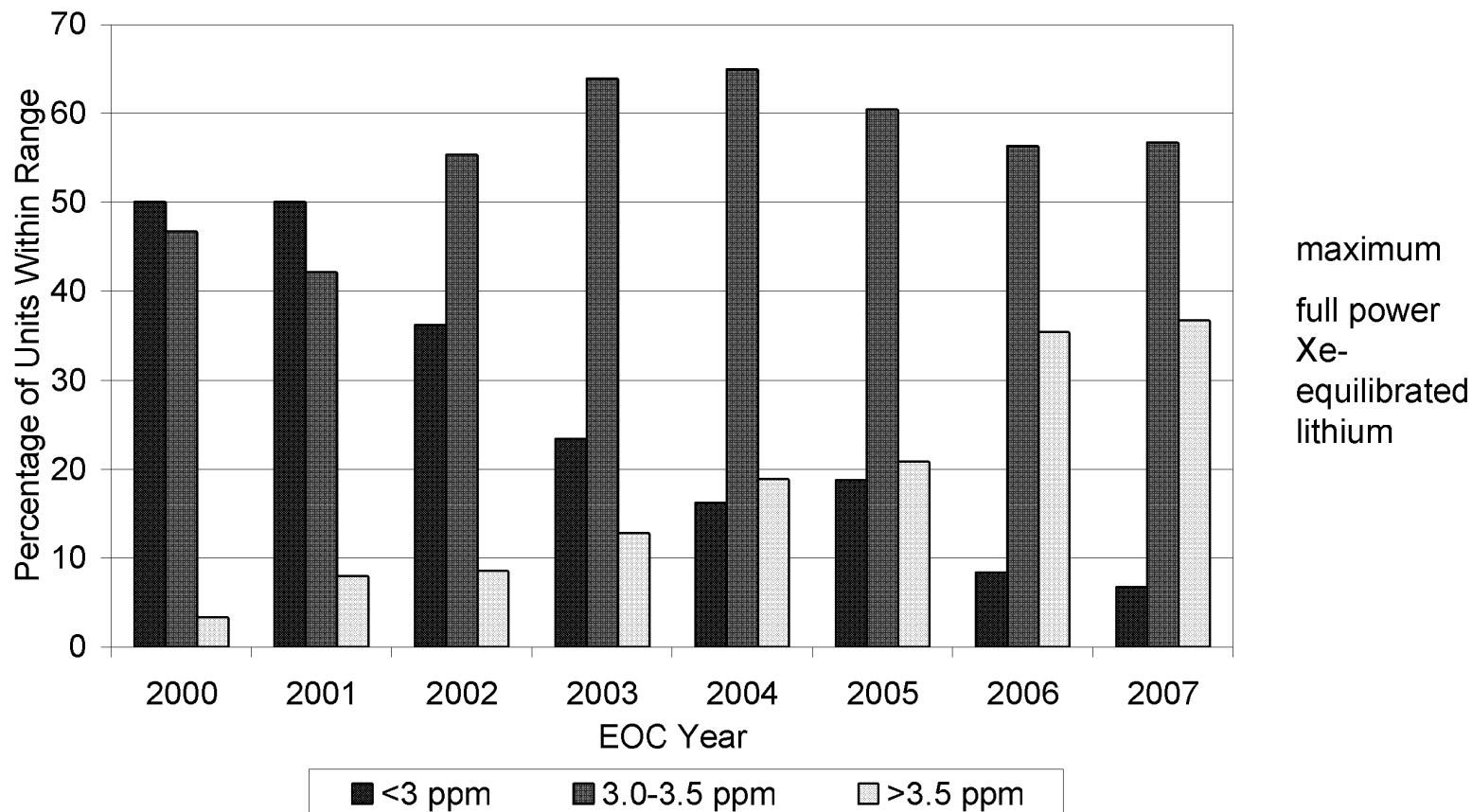


Modified Chemistry (DUO)

High Li Chemistry

Under implementation on 4 EDF units (1450Me Alcade)

2.8 1ry Coolant pH Trends 2000 - 2006 in US Units



- Number of US plants using higher Li concentrations increasing
- No cladding failures have been reported due to rising Li levels

2.9 Zinc addition

Zinc addition

PWSCC of Inconel 600:

typically 15 - 40 ppb target

- This is of potential interest in a few cases
 - Postponing or avoiding SG Replacement in presence 600 TT
 - Mitigating SCC of components Inconel 600 other than SG tubing

• Dose rate limitation:

lower content 5-10 ppb

More and more used,

Inhibiting Co incorporation in corrosion products. Potential interactions to be considered

- Usually depleted Zinc added
- **Easy method**
- **Limited associated risk for the fuel due to low Zn concentration**

SCC Initiation

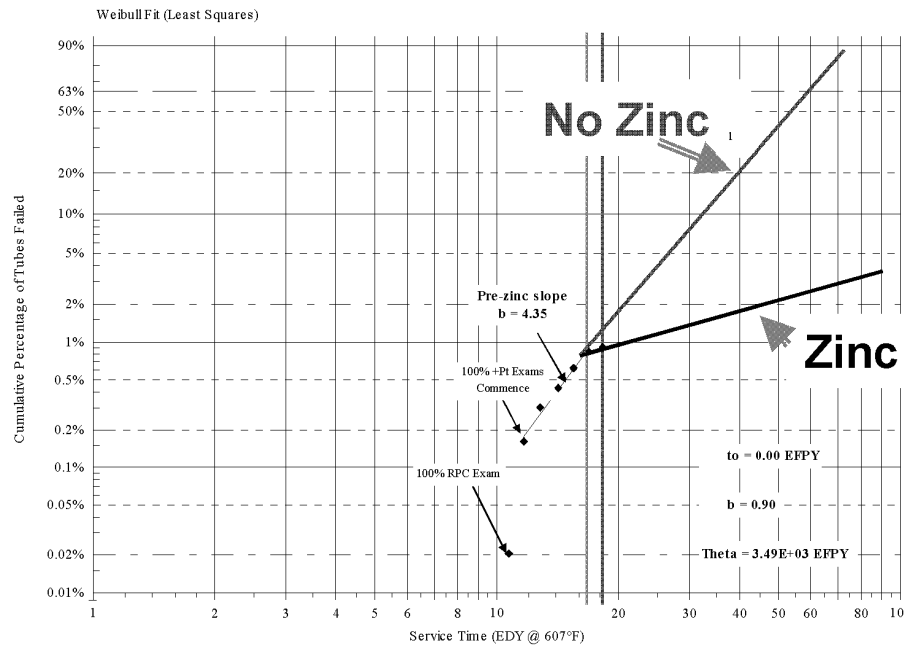
- **Beneficial influence**

Propagation (CGR)

Laboratory testing on-going;

clear benefit has not been demonstrated in testing to-date
NPP results, beneficial influence

2.10 Zinc for PWSCC of Inconel (US results)



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

2.11 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 H₂ is better

USA is looking for higher H₂ than present acceptable range (25-50)

Japan is looking for lower H₂ (≤ 10 cc) than usual range

Many utilities prefer not to change anything: no risk approach

No need to look for other values without Inconel 600

2.12 EPRI conclusion on chemical factors for PWSCC

- pH, Lithium and Boron effects are minimal
- Zinc is Beneficial
 - Increases PWSCC initiation time, but beneficial effect on crack growth rates is uncertain
 - May need to remove hydrogen sooner in shut down process
 - ❑ Going to lower hydrogen may increase crack propagation at lower RCS temperatures (e.g. 290°C)
 - ❑ Operation at low hydrogen increases the risk of going to oxidizing conditions in the event of a plant transient, e.g. loss of letdown flow.

2.13 Hydrogen influence on PWSCC Propagation

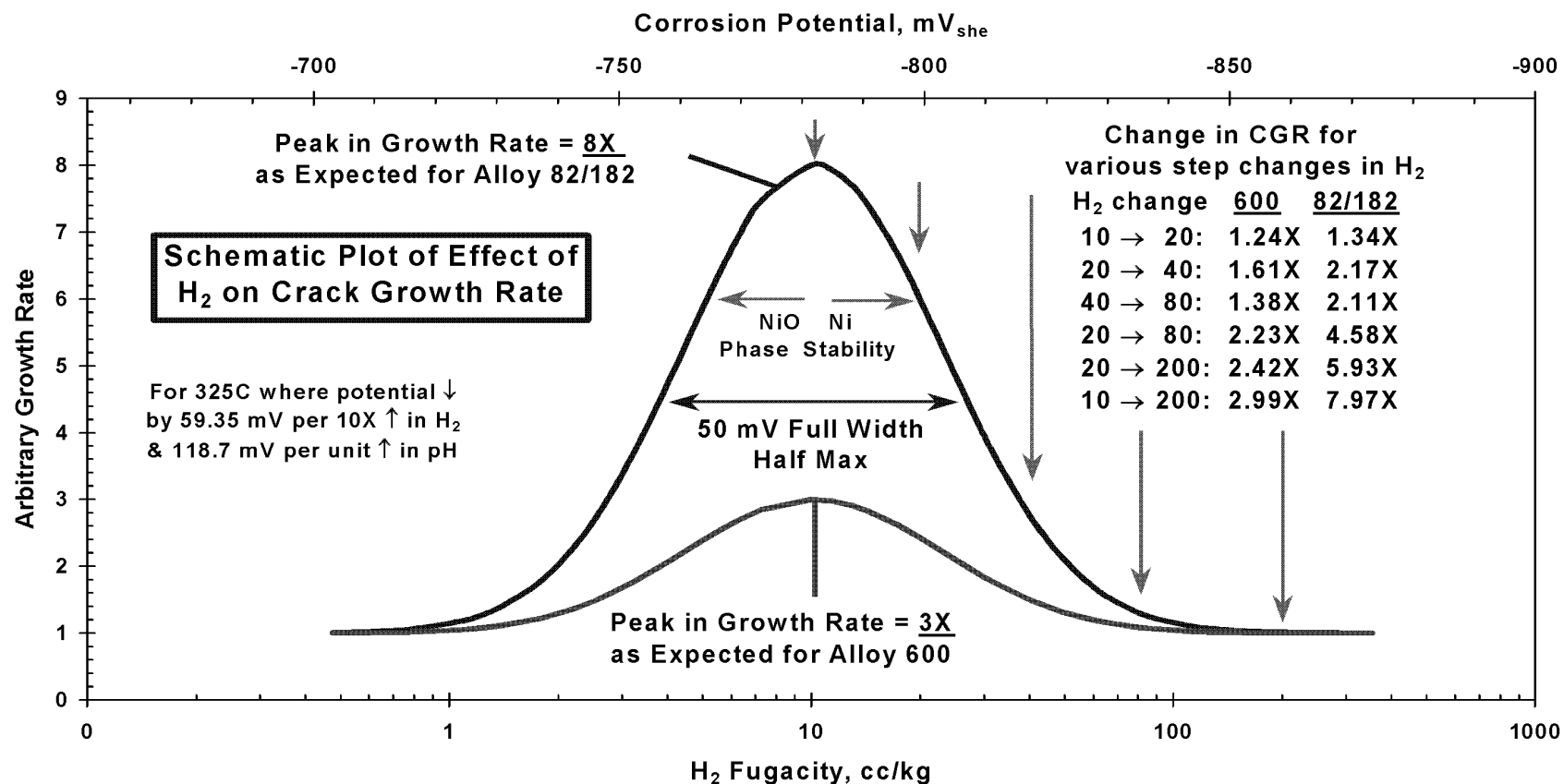


Illustration – position of peak and magnitude depend on temperature and materials

2.14 Primary Water Chemistry - Main remedies

Alloy	Problem	Remedy	Efficiency
600 MA	PWSCC	Low or High H ₂	± Variable
		Limited pH, Li, 40 ppb Zn	± Variable
600, 690	High ⁵⁸ Co	Passivation, Surface state	++ good
All	High Co	Zinc	+ rather good
All	CIPS, AOA	Enriched Boric Acid ¹⁰ B	++ good
		Limited B, Li	+ rather good
		K instead Li	? unknown
18-10Ti	Pitting, SCC	Avoid Cl	++ good
	Resins	H ₂ instead NH ₃	++ good

Remedies will partially depend on the design, materials
 No highly efficient option for inappropriate material IN600
 (600 MA or 600 TT in presence of high stress level)

3.1 Secondary Water Chemistry - Generalities

- Keep long term integrity of components
- Insure operation in good conditions for safety, availability, costs and maintenance

The challenges include

- Avoiding ammoniacal corrosion of Cu alloys
- Minimizing FAC (Erosion/Corrosion) of Carbon Steels
- Mitigating IGA/SCC of Alloy 600 SG tubing
- Lowering fouling of SG tubing, heat transfer, flow
- Decreasing operating and maintenance costs
- Decreasing wastes releases into the environment

These various objectives may be conflicting

3.2 Secondary Water Chemistry - Main concerns

Since the 70's, the main concern has been

- ❑ For PWR of western design: mitigation of **denting** and then **Alloy 600 MA**, very sensitive to **IGA/SCC**, particularly in alkaline conditions;
- ❑ For VVER: mitigation of **corrosion of 18-10 Ti** stainless steel SG tubing, particularly for the newer SG with higher temperature, sensitive areas;
- ❑ For **Canadian** design, important degradation (pitting, etc) on many SG with Monel 400;
- ❑ For German design, improvement of chemistry selection (limited degradation in SG with **Incoloy 800** mainly in the past under PO_4);

For SG that will operate **on the long term** (mainly Inconel 600TT-690/PWR, 18-10 Ti/VVER) the new challenge should focus on:

- **corrosion transport limitation,**
- **environmental and economical (availability, maintenance) issues.**
- **lead pollution and influence on corrosion (IN600 - IN690 in US PWRs).**

FAC of **carbon steel** (less and less used) is also solved by similar remedies.

3.3 Secondary Water Chemistry - Main Options

- Determine the type and concentration of conditioning reagents
- Determine the acceptable limits for impurities

Conditioning Selection

All Volatile Treatment

- Ammonia or amine (morpholine, ethanolamine, amines mixing)

Reducing Environment

- Addition of hydrazine
- Few air Ingress

Impurities Limitation

- High quality demineralized water
- Mitigate condenser leaks
- Avoid other impurities

3.4 Strategy for pH_{25°C} in Feedwater

	Acceptable pH areas		Unacceptable pH areas		
pH at 25°C	6	7	8	9	10
Copper Alloys Condensers Heaters					
Titanium Condensers					
Stainless Steel Condensers Heaters					
Carbon Steel Heater, ...					
Inconel SG Tubes					
Resins (IER), effluents					

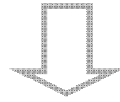
- In presence of copper alloys, limitation of pH_{25°C} ~ 9.2 with NH₃ (or higher with amine)

- Without copper, more open choice, with increased pH (optimum close to 10) and upper limit from economical and environmental constraints

Oranges Areas, acceptable if other constraints

3.5 Conditioning Treatment versus Design

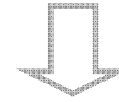
Ammoniacal Corrosion (or similar with amines) of copper alloys



$\text{pH} \leq 9.3$ with ammonia
(potentially slightly more with amines)

Limitation of pH or reagent concentration depending on the operating mode of condensate polishers and SG Blowdown resins

Flow Accelerated Corrosion of Carbon Steel



Necessity of a sufficient pH_T at operating temperature

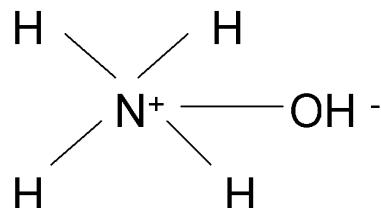
Limitation of reagent concentration due to operating costs and wastes releases into the environment



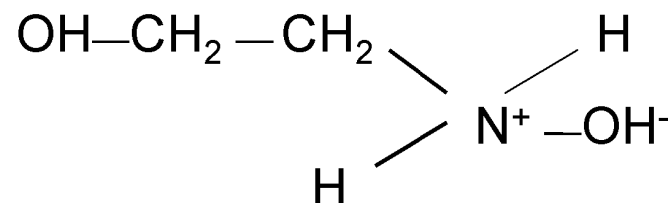
Selection of ammonia, amines or amines mixing able to protect the whole steam-water system, with acceptable costs, operating constraints and liquid effluents or solid wastes releases

3.6 Secondary water conditioning reagents

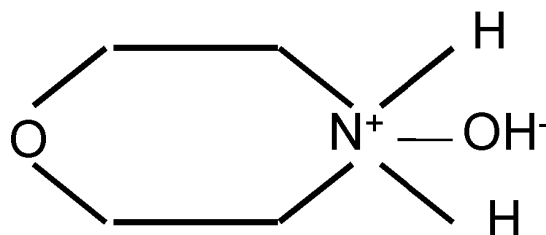
Ammonia $\text{NH}_3, \text{H}_2\text{O}$



Ethanolamine $\text{C}_2\text{H}_7\text{NO}, \text{H}_2\text{O}$



Morpholine $\text{C}_4\text{H}_9\text{NO}, \text{H}_2\text{O}$



Mainly Ammonia (most of German units), morpholine (most of French units), ethanolamine (most of US units)

Few other amines used, frequently mixed with one of the above ones

3.7 Hydrazine Selection N_2H_4

HYDRAZINE : – Reduction of O_2 and oxides



– Thermal Decomposition



Presence of copper alloys

> 10 μg / kg in feedwater

⇒ Obtain a sufficient **reducing effect**

($N_2H_4 > 2$ to $8 \times O_2$)

⇒ Not too high value, for not too high production of NH_3 (ammoniacal corrosion)

Absence of copper alloys

≈ 50 to 100 $\mu g/kg$ in most cases

EPRI > 20 and > $8 \times O_2$

No benefit for values > 100 ppb

Test performed with redox potential: 25 to 200 ppb N_2H_4
 No benefit gained by an increase of hydrazine concentration
 for Suspended Solids mitigation (content and composition)

**International consensus for a target of N_2H_4
 = at least 20 ppb N_2H_4 and $8 \times$ Oxygen**

3.8 AVT Treatment : amine or ammonia

- In the USA, most units use an amine or a mixing of amines for the treatment. The most frequently used is **ethanolamine (ETA)**, with an advantage in presence of condensate polishers and regenerated resins.
- In Japan, half of the units are treated with ammonia at high pH and the other half with ethanolamine.
- In Germany and some other European Countries where the units do not have copper alloys or condensate polisher in permanent use, ammonia at high pH - HAVT (ammonia at pH_{25°C} 9.8 to 10) is satisfactorily used.
- In France, most units with morpholine

Amine mandatory when copper alloys. Amine or HAVT without copper

3.9 Comparison of 2 amines in the presence of copper alloys

	Morpholine	Ethanolamine
Advantages	Distribution coefficient of 1 → constant concentration throughout the secondary system → good protection of many parts of the system against carbon steel FAC .	High alkalinity → lower concentration → more favourable for the environment and good compatibility with the use of condensate polishers
	Good feedback experience for SG fouling and corrosion	Very low concentration of organic acids produced by thermal decomposition
	Compatibility with the operation of blowdown resin beyond breakthrough in its exhausted form (after saturation): ~1 year for the cation resin	Good protection against FAC in some parts of the system, where the pH is higher than with morpholine
Disadvantages	Low alkalinity → high molar content not always compatible with the use of condensate polishers	Partition coefficient <1 → non-homogeneous protection for the various parts of the secondary system
	Limited stability → presence of some organic acids, increasing the cation conductivity in the SG blowdown and decreasing the detection sensitivity of other impurities	Lower possibility of blowdown resin operation beyond breakthrough in the exhausted form, due to the higher affinity of ETA for cation resins compared with morpholine → lower Na elimination. Good results in 1 American unit on condensate polishers

3.10 Comparison of 2 amines + ammonia without copper alloys

	Morpholine	Ethanolamine	Ammonia
Advantages	Coefficient distribution of 1 → constant concentration all over the secondary system.	High alkalinity → lower concentration → more favourable for the environment .	Easy treatment and monitoring, with potentially only hydrazine added if the ammonia is recycled.
	Good protection against FAC and corrosion transport through the system at high pH	Good protection against FAC and corrosion transport through the system	No organic acids produced as by products. Thus, no impact on cation conductivity and impurity detection.
	Compatibility with the operation of blowdown resin in exhausted (saturated) form	Low concentration of organic acids produced by thermal decomposition	
Disadvantages	Low alkalinity → very high molar content hardly compatible with condensate polishers	Partition coefficient < 1 → non-homogeneous protection for the various parts of the secondary system	Requires a high pH _{25°C} (almost 10) to give sufficient protection against FAC and for corrosion product transport. High N release into environment.
	Limited stability → presence of some organic acids, increasing the cation conductivity in the SG blowdown.	Lower possibility of blow down resins operation in exhausted form (relative affinity) → lower Na elimination or more frequent regeneration or replacement.	Limited possibility of blow down resins operation in exhausted form (relative affinity) and high frequency of regeneration required. Hardly compatible with condensate polishers.

3.11 French Feedwater Chemistry Specifications

	pH at 25°C	N₂H₄ µg/Kg	Mo mg/kg	NH₄⁺ mg/kg
Morpholine with copper	9.1 to 9.3 tentatively higher	>10	4 to 6	< 0.3
Morpholine without copper	9.5 to 9.6	50 to 100	≈ 6	1 to 2
Ammonia	9.6 to 9.8	50 to 100		2 to 5

4.1 Vaporisation - Concentration

Vaporisation



Impurities
Concentration

Concentration



Over concentration
of impurities

Partition Coefficient

concentration in steam
concentration in water

Water concentration in SG bulk
is ~ 100 times higher than in
feedwater ($Q_{FW/SGBD}$)

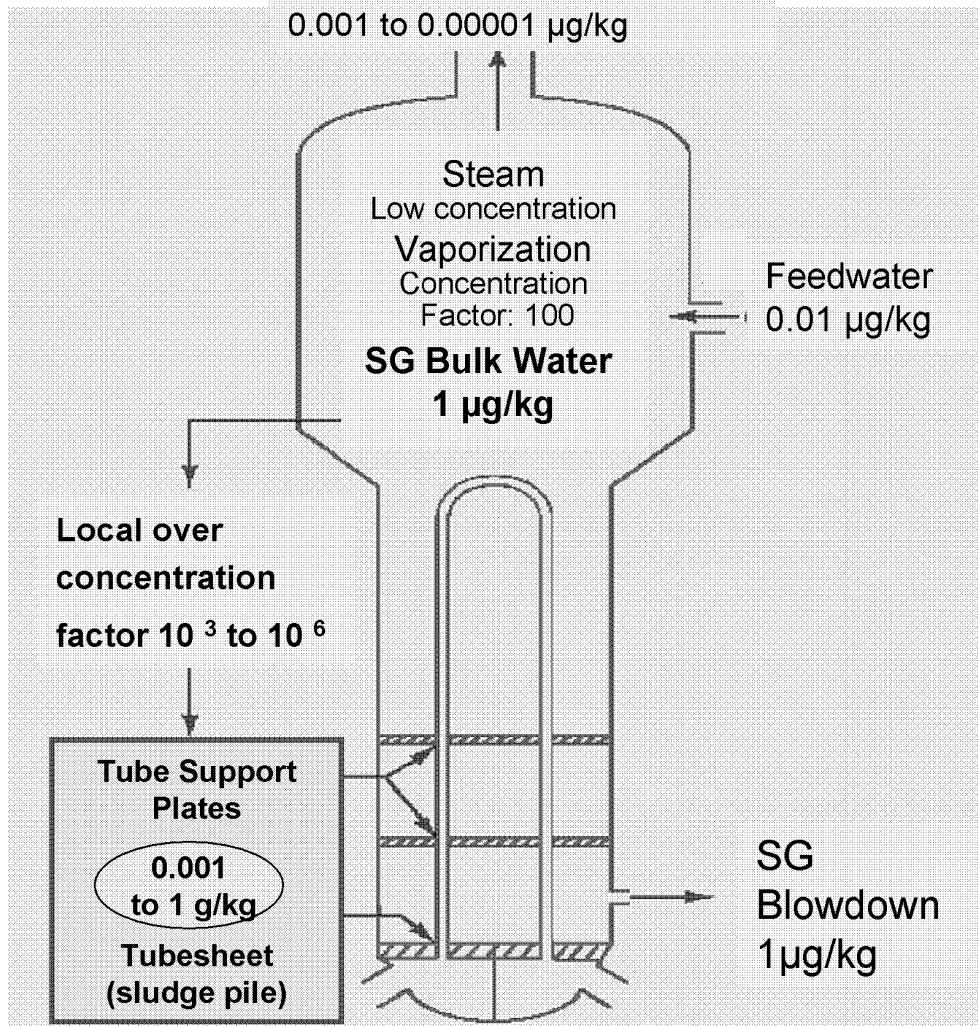
Concentration Factor

concentration near tube wall
concentration at SG blowdown

Concentration factor is:

- ≈ 10 to 10^2 free span ;
- $\approx 10^3$ to 10^6 restricted flow areas.

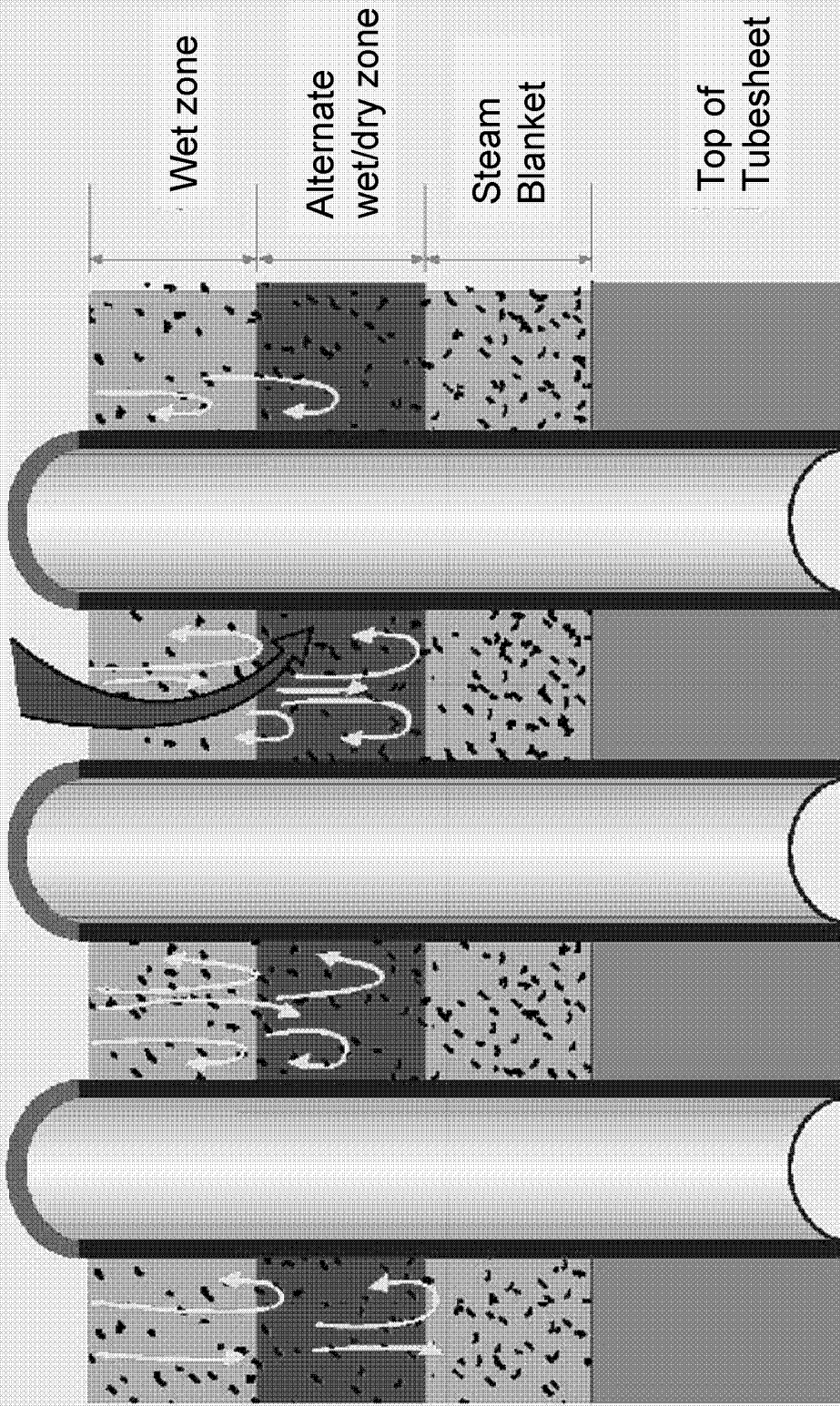
4.2 Concentration in various points of SG



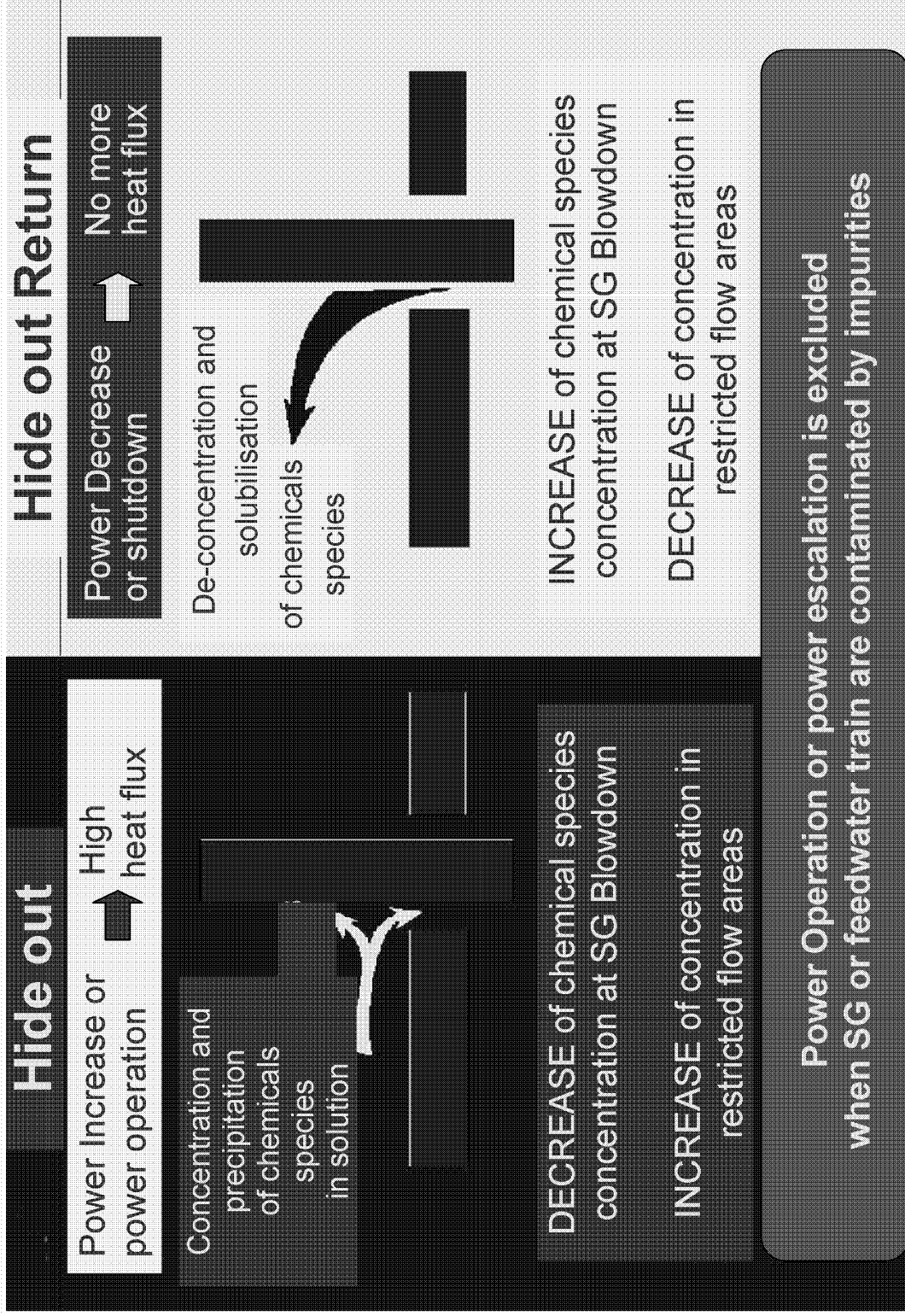
- Very low concentration in feedwater (alimentation)
- Moderated concentration in the bulk water and SG blowdown (purge)
- Much higher concentration of impurities in area with restricted flow
- Constitutes a challenge for the secondary water chemistry, particularly with SG tubing 600 MA

4.3 Sludge pile above tubesheet

Concentration zone



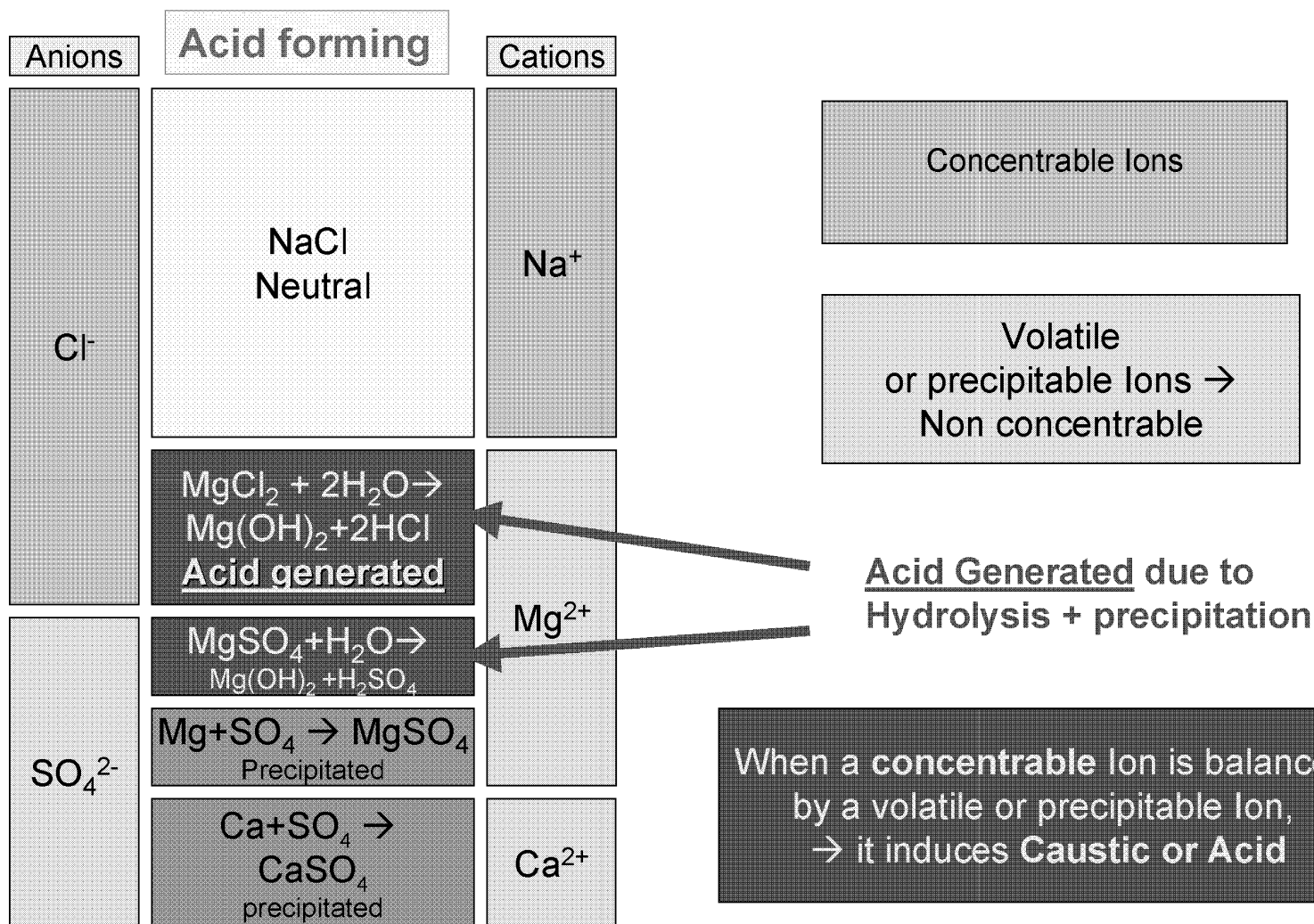
4.4 Hideout - Hideout return



4.5 Chemical Transformation: River Water

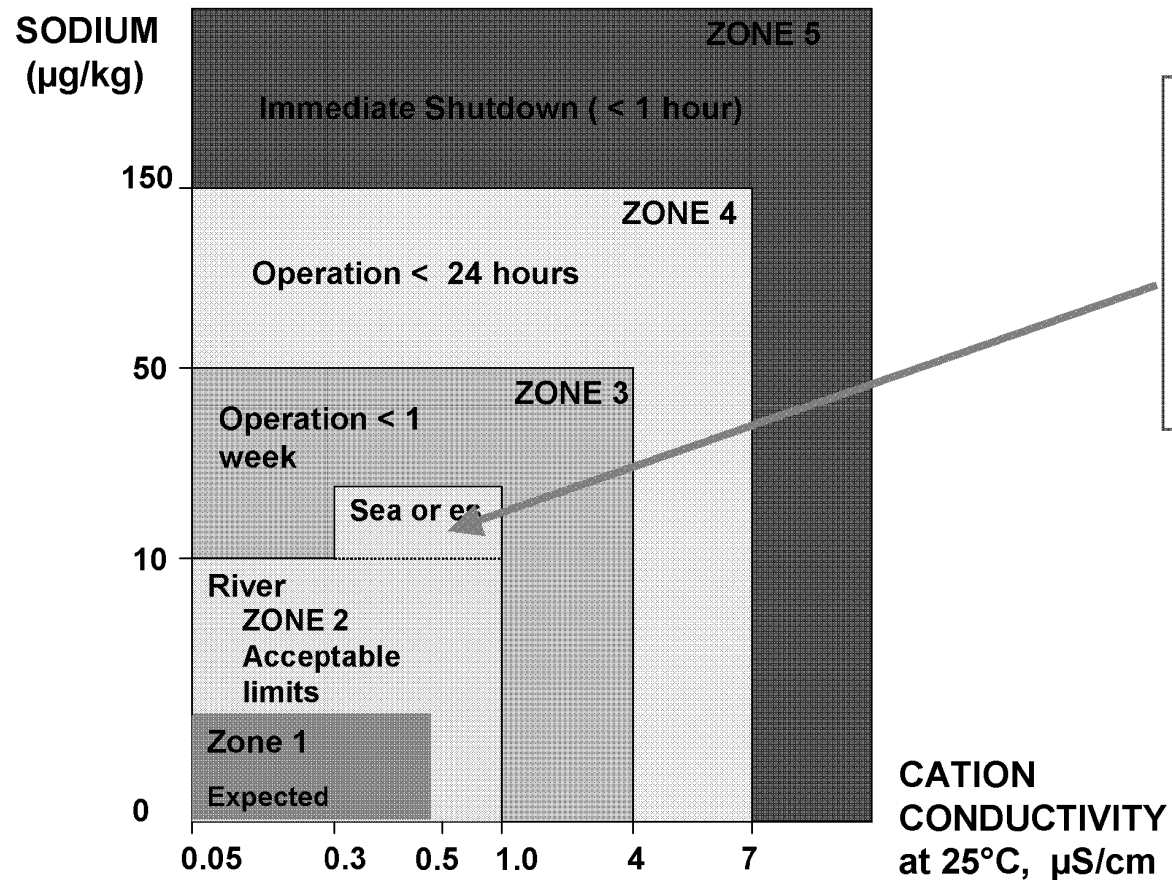
Most Frequent Case Na > Cl			Less Frequent Case Na < Cl		
Anions	Alkaline forming	Cations		Anions	Cations
Cl ⁻	NaCl Neutral	Na ⁺	Concentrable Ions	Cl ⁻	Na ⁺
HCO ₃ ⁻	NaHCO ₃ → CO ₂ +NaOH <u>Caustic generated</u>				CaCl ₂ + 2H ₂ O → Ca(OH) ₂ +HCl Acid generated
	CaHCO ₃ → 2CO ₂ + Ca(OH) ₂ Volatile or precipitate	Ca ²⁺	Volatile or precipitable Ions → Non concentrable	HCO ₃ ⁻	CaHCO ₃ → 2CO ₂ + Ca(OH) ₂ Volatile or precipitate
SO ₄ ²⁻	Ca+SO ₄ → CaSO ₄ precipitated			SO ₄ ²⁻	Ca+SO ₄ → CaSO ₄ precipitated

4.6 Chemical Transformation: Sea Water



4.7 SG Blowdown Specifications – French PWRs

Action Levels when Power > 25%



Sea Water Cooled Units
Tolerance for small sea water ingresses, acidic trend, less detrimental

4.8 VVER 2ry System Specifications - Ukraine

Parameters	Condensate	Feed-water	Blowdown water	Steam
pH at 25°C,	-	9,0 ± 0,2	8,0-9,2	-
Electric conductivity, µS/cm	<0,35	<0,3	<5,0	<0,3
Sodium, mkg/kg	<2,0	-	<300	-
Chloride, mkg/kg	-	-	<100	-
Sulfate, mkg/kg	-	-	<200	-
Iron, mkg/kg	-	<15	-	-
Copper, mkg/kg	-	<5	-	-
Oxygen, mkg/kg	<30	<10	-	-
Hydrazine, mkg/kg	-	> 40 (10)	-	-
Morpholine, mg/kg		3-6		

Specifications at SG Blowdown are also much less restrictive than on PWR of Western countries. Different design, lower temperature and power, less sensitive SG tubing materials as compared to Inconel 600, but also some observed corrosion in some cases.

4.9 Various Cases at SG Blowdown

- In France: Some flexibility in case of specific condenser sea water ingress with none localisable leaks
- In France: Some flexibility for sodium in zone 2 if sodium is coming from sea water and is not present in alkaline condition
- In the USA: more stringent limits due to past history and important degradation of OD SG tubes with Inconel 600MA.

But possibility to continue operation in AL1 Plant specific evaluation.

- Whatever the specification severity: will hardly get rid of 600 MA corrosion
- Alloy 690 does not present the same sensitivity and does not require those unnecessary limits, as shown by laboratory tests and feedback since 1990
- The international feedback with other Alloys Incoloy 800 or stainless steel 18 % Cr-10% Ni on VVER evidenced the absence of corrosion albeit much less stringent specifications and more important impurity levels.

4.10 Impurities: Na, Ca, Mg, Cl, SO₄, F

Species	Origin	Characteristics	Consequence
Sodium	<ul style="list-style-type: none"> - Condenser water - auxiliary circuit - Make up water 	May concentrate Alkaline environment	Very detrimental for SG tubes (mainly A600 MA)
Calcium Magnesium	Condenser water	Non volatile, May precipitate in SG	No corrosion risk since cannot concentrate But risk of heat transfer decrease from deposition in case of important quantities
Chloride, sulphate, fluoride	<ul style="list-style-type: none"> - Condenser water - SG Blowdown resin - F: welding - Sulphur compounds; resin deterioration 	May concentrate Sulphates may also precipitate and adsorb on metal wall	Cl, F: SCC Cl: pitting of SG tubes Cl + oxygen: denting at Tube Support Plate level Sulphur compounds from resins: very detrimental for SG tube corrosion

4.11 Impurities: Organic Anions, Oxygen

Species	Origin	Characteristics	Consequence
Organic Anions	<ul style="list-style-type: none"> - Morpholine Decomposition (mainly in O₂ presence) - Oils and greases 	Partially volatile Weak Acid	Increase of cation conductivity in SG and other parts of the system Low noxiousness for SG Uncertain for turbine
Oxygen	Air ingress (depending on pressure, condenser, ...)	Strong Oxidizer Increases Morpholine Decomposition Reacts with metals ⇒ oxides	SG tubes SCC at high temperature Risk denting, pitting .. At low concentration, beneficial for FAC

5.1 Copper alloys corrosion

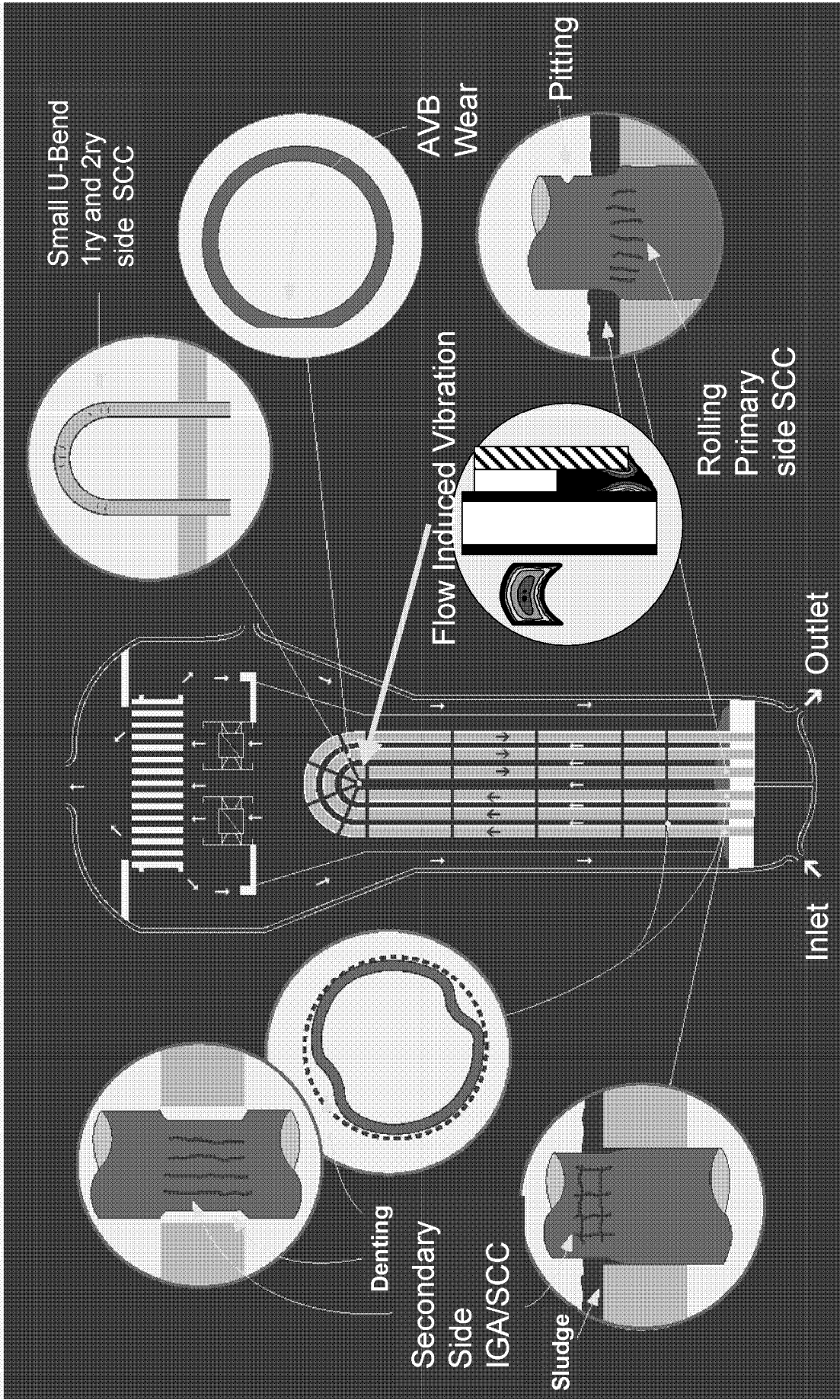
N ₂ H ₄ ppb	NH ₃ ppb	Morpholine ppm	pH 25°C	O ₂ ppb	Cu ppb
7	275	0	9.0	6	0.55
45	855	0	9.35	7	1.75
100	955	0	9.40	9	1.70
7	155	5	9.15	8	0.40
50	605	3.9	9.35	5	0.95
85	1175	6.4	9.50	7	1.90
0	80	4	9.10	4	0.30

Ref. Ph. Berge. The Use, Need, and Desirable Properties of Amines for Use in Steam-Water Circuits.

CEGB - Amine Workshop Proceedings SWR/SSD 0791/N/96. Bristol, England, 29 April - 1 May 1986.

- Copper corrosion depends on pH_{25°C} ⇒ Limited to 9.2 with ammonia
- Lower copper corrosion (~ 1/2) for same pH_{25°C} with morpholine
⇒ possibility of operating at a slightly higher pH with an amine.

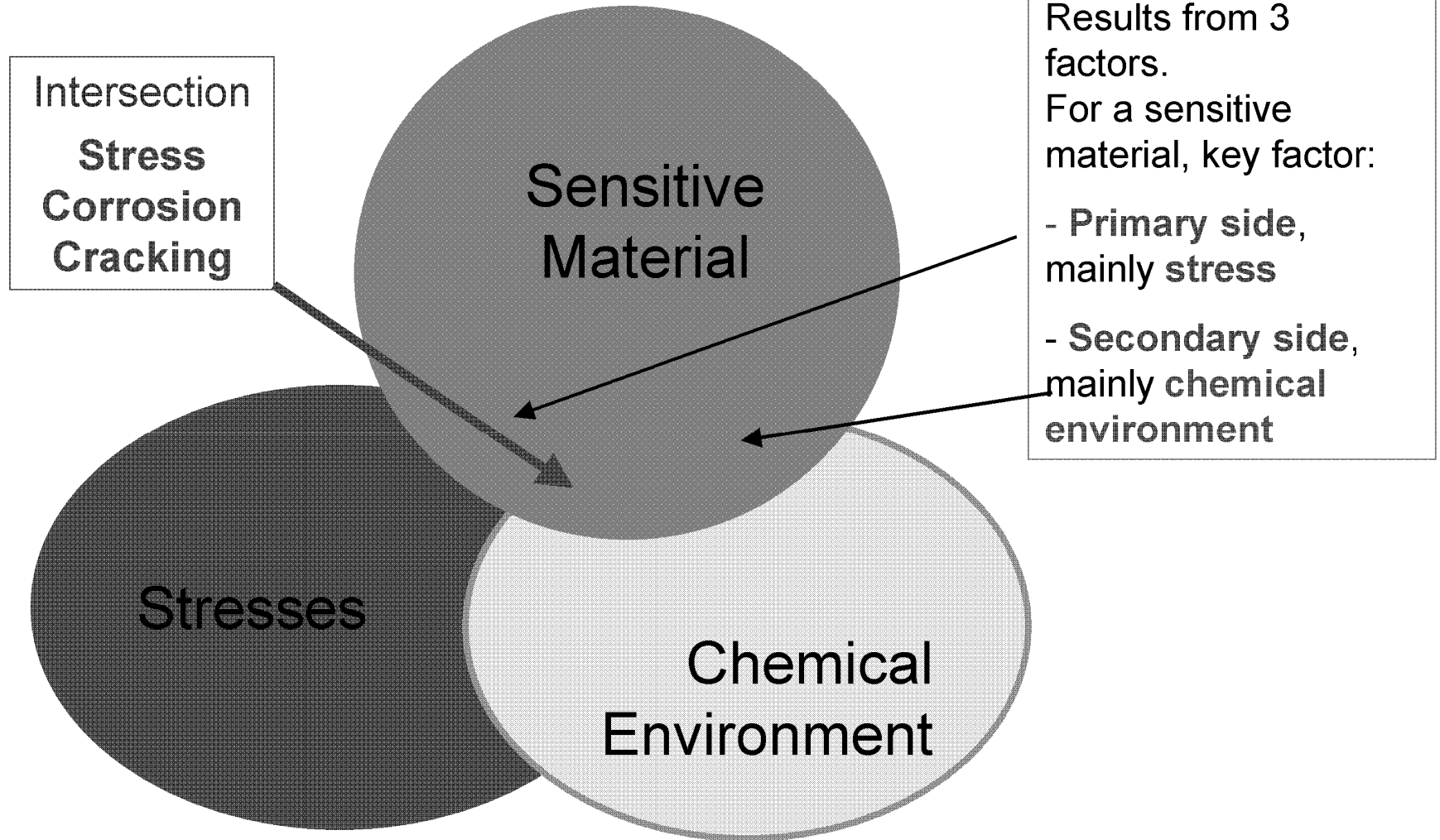
5.2 Degradations in Recirculating SG



5.3 Various Materials of SG tubes

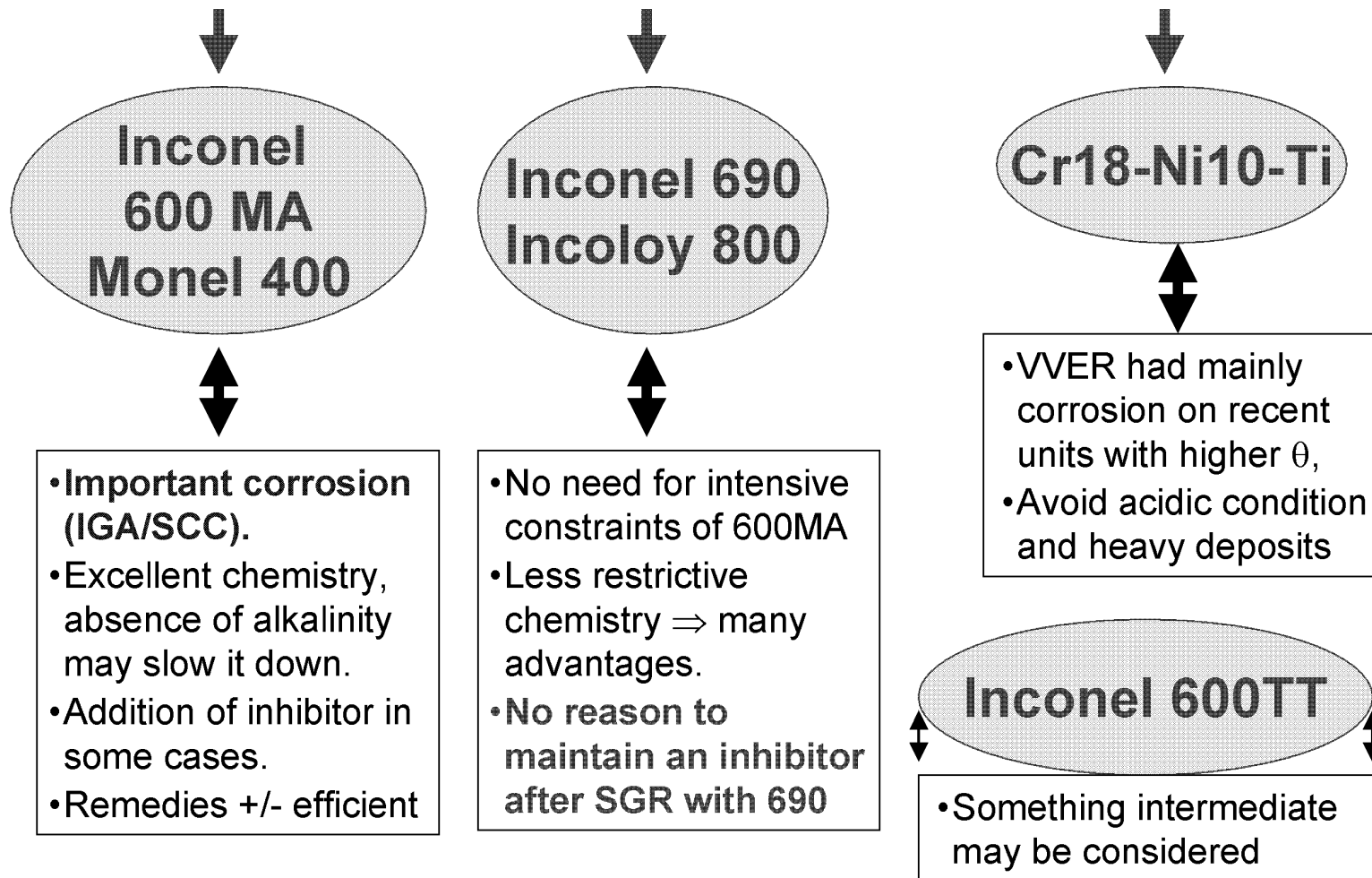
Type <i>Usual Name</i>	C	Cr	Fe	Ni	Co
Stainless Steel (> 13 % Cr)					
13 % Cr	≤ 0.12	12-14	Balance	-	
(AISI) 304L	≤ 0.03	18-20	Balance	8-12	
(AISI) 316L	≤ 0.03	16-18	Balance	10-14	
Nickel base Alloy					
Alloy Inconel 600	≤ 0.05	14-17	6-10	> 72	< 0.1
Alloy Inconel 690	≤ 0.05	27-31	7-11	> 58	< 0.035
Alloy Incoloy 800	≤ 0.10	19-23	Balance	30-35	
Alloy 18-10 Ti (VVER)	≤ 0.08	17-19	Balance	10-11.5	< 0.05

5.4 Stress Corrosion Cracking (SCC)

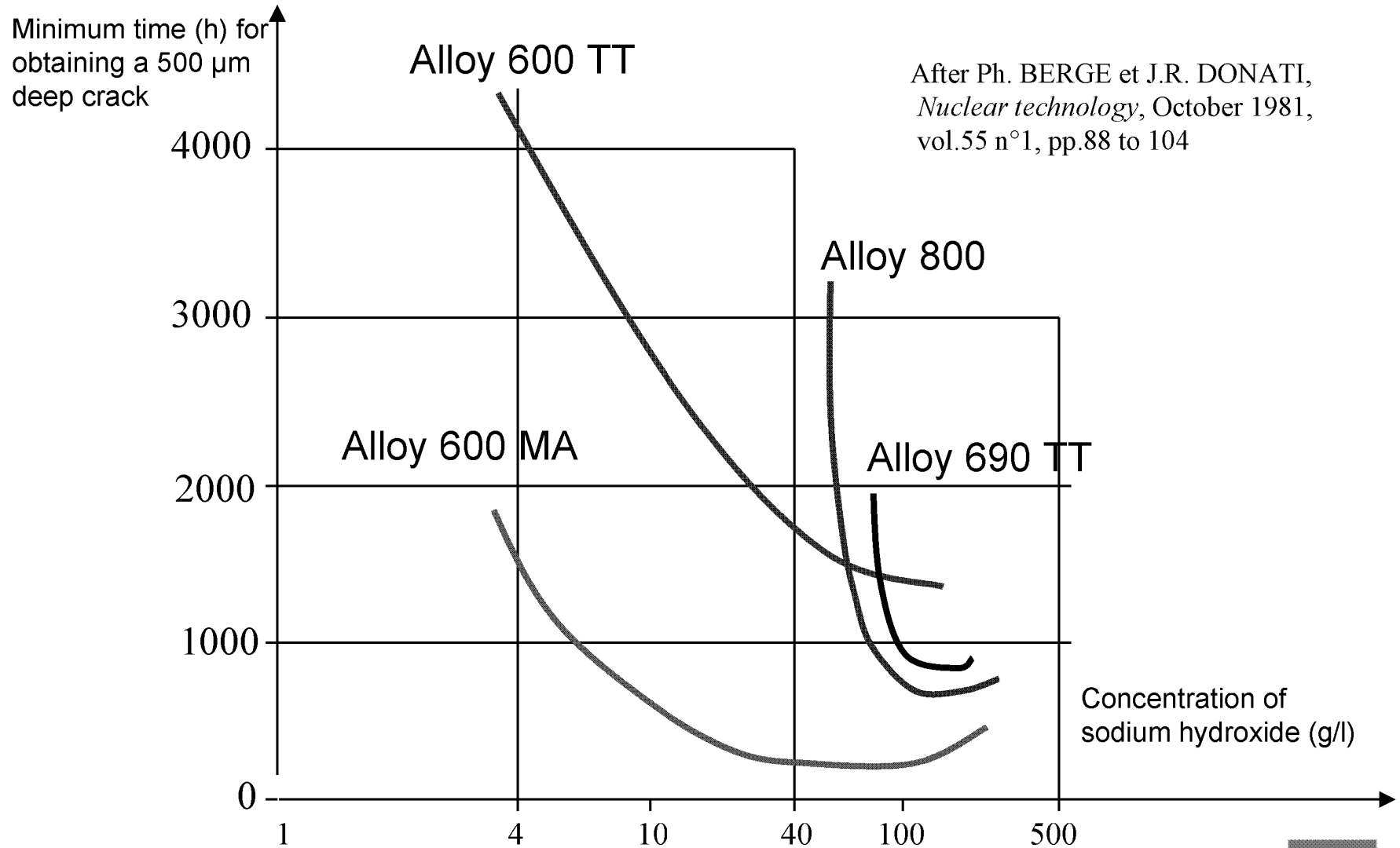


5.5 Secondary Water Chemistry - SG Corrosion

Corrosion and remedies related to tubing sensitivity to various impurities



5.6 Chemistry and Material Influence on SCC



5.7 Detrimental Chemical Species

NaOH for Inconel

- **OH** intergranular generalized corrosion (IGA) in alkaline environment
 - Intergranular stress corrosion cracking (presence of stresses) IGSCC
 - Cracking in oxidizing environment
 - **Sodium Hydroxide is the main causative element for Inconel 600**
 - **Oxidizing species are also detrimental**
- Acidic Chloride for VVER 18-10 Ti

Other impurities:

- **Oxides** (Fe_2O_3 , CuO ...) in alkaline environment. IG SCC
- **Copper**
- **Lead** Cracking of mixed mode type (intergranular and transgranular) when important pollutions
- **CO₂** in OH environment
- **Sulfates** in acidic or alkaline environment
- **Resins** and their **decomposition products (reduced sulfur species)**
- **Complex** environments uncertain
 $\text{PO}_4 + \text{SiO}_2 + \text{Al}_2\text{O}_3 +$ may be organic

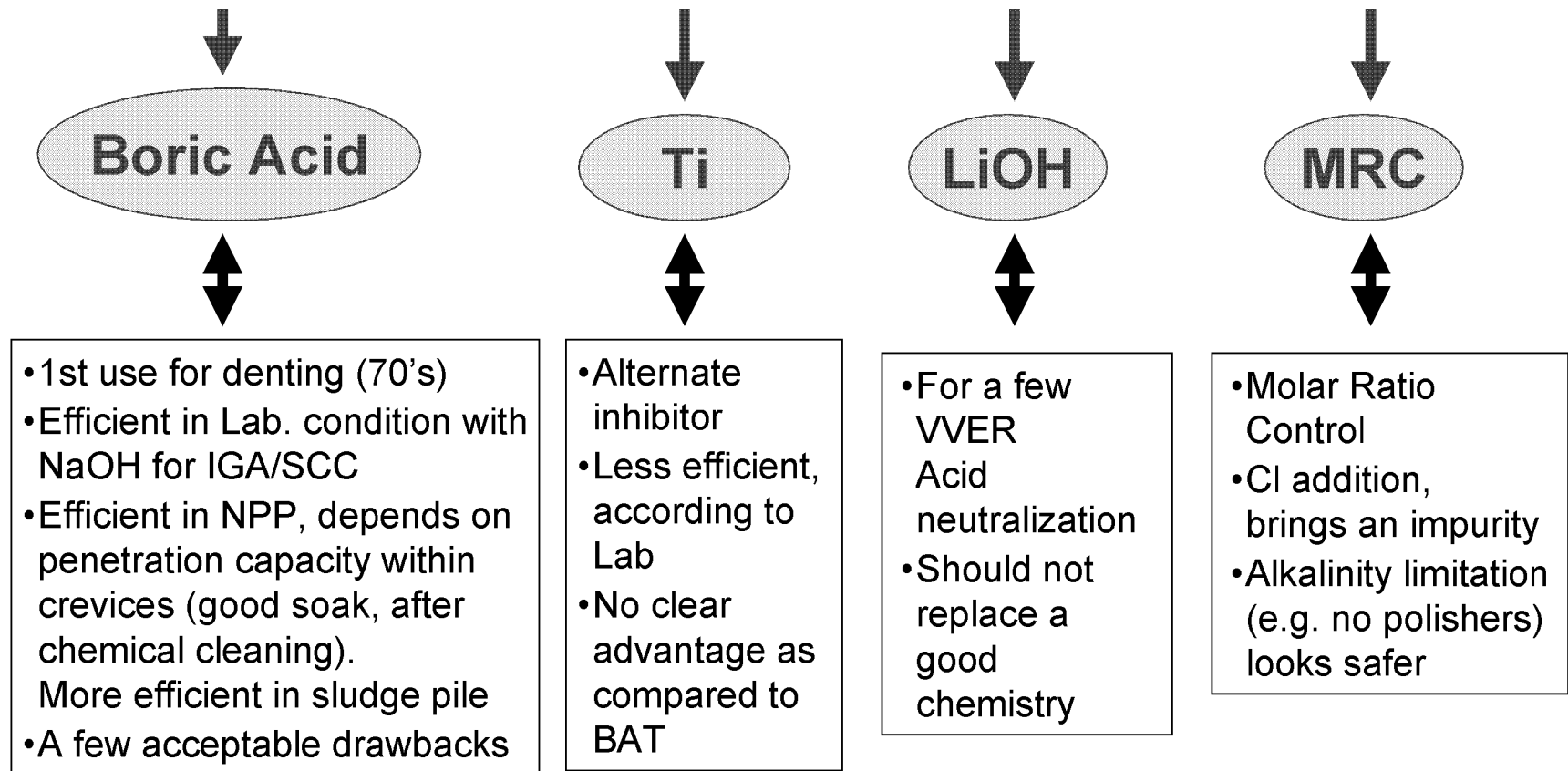
5.8 Lead influence and contribution to IGA/SCC

- ☐ Lead has frequently been considered as the cause of cracking, particularly at the beginning of laboratory tests with cracking on Alloy 600, in 1959.
- ☐ Lead is indubitably a detrimental parameter for SG tube cracking.
- ☐ Lead is found in most of SG tubes and in sludge
- ☐ In most cases, it has not been possible to draw any correlation between presence of lead and an increased risk of cracking (for amount close to typical value or slightly higher, i.e. 1% Pb/deposits and 0.1 %/sludge)
- ☐ Only important lead pollution cases were clearly identified at the origin of specific and quick degradations in a few cases (Belgium, Canada).
- ☐ Several American experts consider that lead is a significant contributor to IGA/SCC
- ☐ According to a French study on many units, lead is not at the origin of most of degradations on Alloy 600MA. Key factors: caustic environment and material sensitivity.
- ☐ Alloy 690 better resists to plausible lead pollution than 600, particularly in environments close to neutrality.
- ☐ Alloy 690 may crack in strongly alkaline environments polluted by lead.
- ☐ Some part of lead will deposit in feedwater train materials
- ☐ SG Blowdown only eliminates a fraction of lead.

**Whatever the respective opinion of various experts,
⇒ it is important to avoid any unnecessary lead contamination**

5.9 SG corrosion remedies: BAT - Ti - LiOH - MRC

Corrosion inhibitors selection depends on material and cooling water



600 MA with sea water -600 TT- 800 - 690: no inhibitor required

5.10 French Feedback on Secondary Side SG Corrosion

Nbr units	Tubing	TSP (Tube Support Plate)		Cooling water	SCC Level
		Design	Material		
6	600MA	Circular	Carb S	River	High
2	600MA	Circular	Carb S	Sea/Estuary	Low
1	600MA	Broached	Carb S	Loire	M/H
2	600MA	Broached	Carb S	Estuary	≈ 0
1	600MA	Broached	13%Cr	Loire	≈ 0
1	600MA	Broached	13%Cr	Estuary	≈ 0
26	600TT	Broached	13%Cr	Any	No
19	690TT	Broached	13%Cr	Any	No

- SG tubes on the secondary side are only affected for 600 MA, and mainly on river water cooled units with an alkaline trend.
- SG tubes 600 MA of sea water cooled units are very slightly affected.
- Only 600 MA tubing with carbon steel Tube Support Plates, easily corroded and creating an environment where impurities may concentrate, are significantly affected.
- No tube with 600 TT or 690 TT is cracked on the secondary side.

6.1 Deposits Origin

INTERNAL ORIGIN

- Corrosion products
- Poor Lay up
- Other (resins, metallic shots)

EXTERNAL ORIGIN

- Cooling water (compounds with low solubility, e.g. Ca, Mg, SO₄)

Carbon steel Corrosion
= main contributor

Deposits

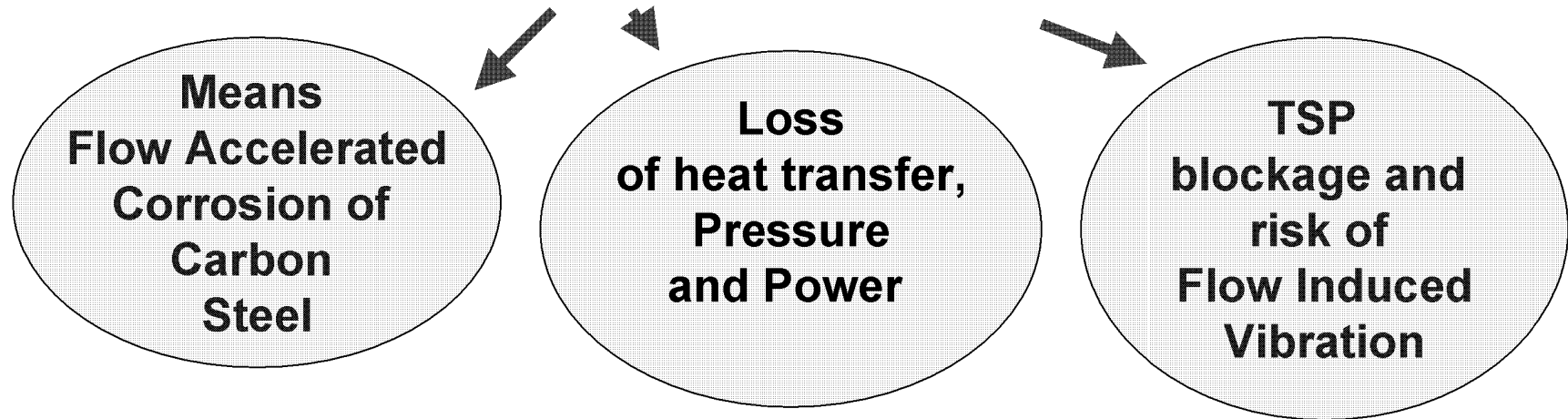
on the TUBE
Decrease of heat transfer

On the TUBESHEET
Sludge = increased risk
of SG tube corrosion

6.2 Corrosion Products: TSP Blockage - FAC - remedies

The most important and challenging issue for many units

Corrosion products from feedwater train and other components



May be limited by selecting adequate chemistry and operation practices:

- **HAVT** (ammonia pH almost 10) **or Amine** (mandatory with copper),
- **Avoid** permanent use of **condensate polishers**,
- **Materials** selection or replacement, **add dispersants**

6.3 Actions for Deposits Limitation

Linked to Corrosion product transport - Deposition



Minimize production

- High pH
- Amine selection
- Same objective as for FAC
- $N_2 H_4$ limited to 50 - 100 ppb



Minimize deposition

- Amine selection
with specific properties
- Dispersant addition PAA

**If preventive ways insufficient
Chemical Cleaning (higher cost and wastes)
or other alternative methods (ASCA, etc.)**

6.4 Flow Induced Vibration at Cruas (FIV)

Fatigue Cracking caused by Flow-Induced Vibration

- ~ 500 l/h on SG2 – R08C47 on cold leg Cruas 4
- On 11 Feb 2006, at night: 12 min. from 11 l/h (0.05 gpm) to ~ 500 l/h
- Early detection by N16 + quick shutdown
- SG isolated, no environmental impact
- Tube non supported by AVB (Design only to Row 11)
- 210 ° circumferential crack at upper face of 8th TSP
- Tube identified by water test
- No Eddy Current bobbin coil indication at Nov. 2005 forced outage
- Central area of tube bundle with specific local thermohydraulical conditions due to :
 - important deposits on broached upper TSP
 - TSP with holes w/o tube in central part

6.5 Other cases of FIV in the world

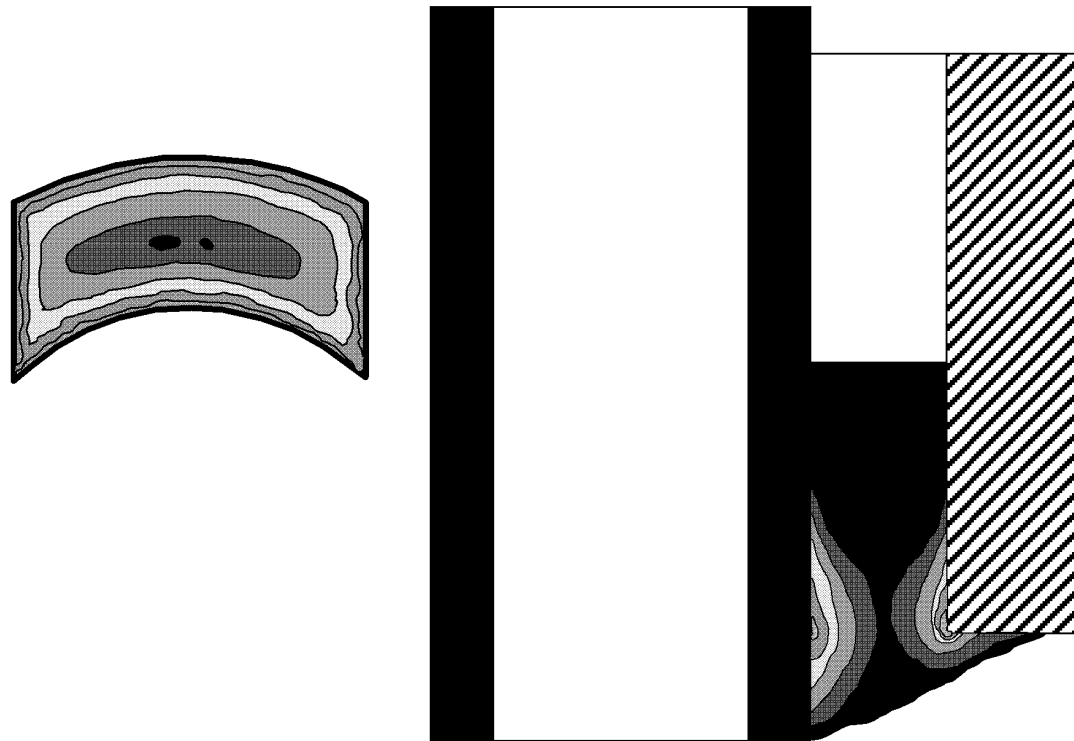
- **North Anna 1:** July 15, 1987: Rupture of R9-C11 - SGC - model 51 A
- AVB misplaced. Design to Row 1, some cases to Row 8. This R9 : no AVB
- Stress level increased by denting + U-Bend deflection = High cycle fatigue.
- Leak increase during 30 hours before rupture.
- **Indian Point 3:** Oct 19, 1988: R44-C50. SG Model 44. Cause = Denting (+ minor IGA/SCC?). Circumferential Crack near the top of the upper TSP (#6).
- **Three Mile Island 1990 (OTSG)**
- **Mihama 2:** Feb 9, 1991. SG 44. AVB misplaced in central area of bundle. Manufacturing anomaly non detected. Fatigue cracking at upper TSP.
- **Cruas 1:** Feb 4, 2004. R08-C49-SG2- 51 B. See details UER of April 2004. Leak of 3.8 l/h (0.017 gpm). Immediate shutdown. Circumferential 90 ° signal. Lack of material at upper TSP (#8). Wrongly attributed to loose part.
- **Cruas 4:** Nov 7, 2005. R08-C48- SG 2 -51 B : See details UER of Dec 2005. Leak of 9 l/h (0.04 gpm). Shutdown before reaching the limit of 20 l/h. Again Circumferential 90 ° signal at upper TSP (#8). Reason not accurately known.

6.6 FIV Cruas : Broached TSP Blockage

TV Inspection at TSP# 8 - Blockage of water pass

Deposits common Characteristics:

- Builds up from bottom part of water pass of quatrefoil area
- On the tube as well as in the quatrefoil area, almost centripetal progression

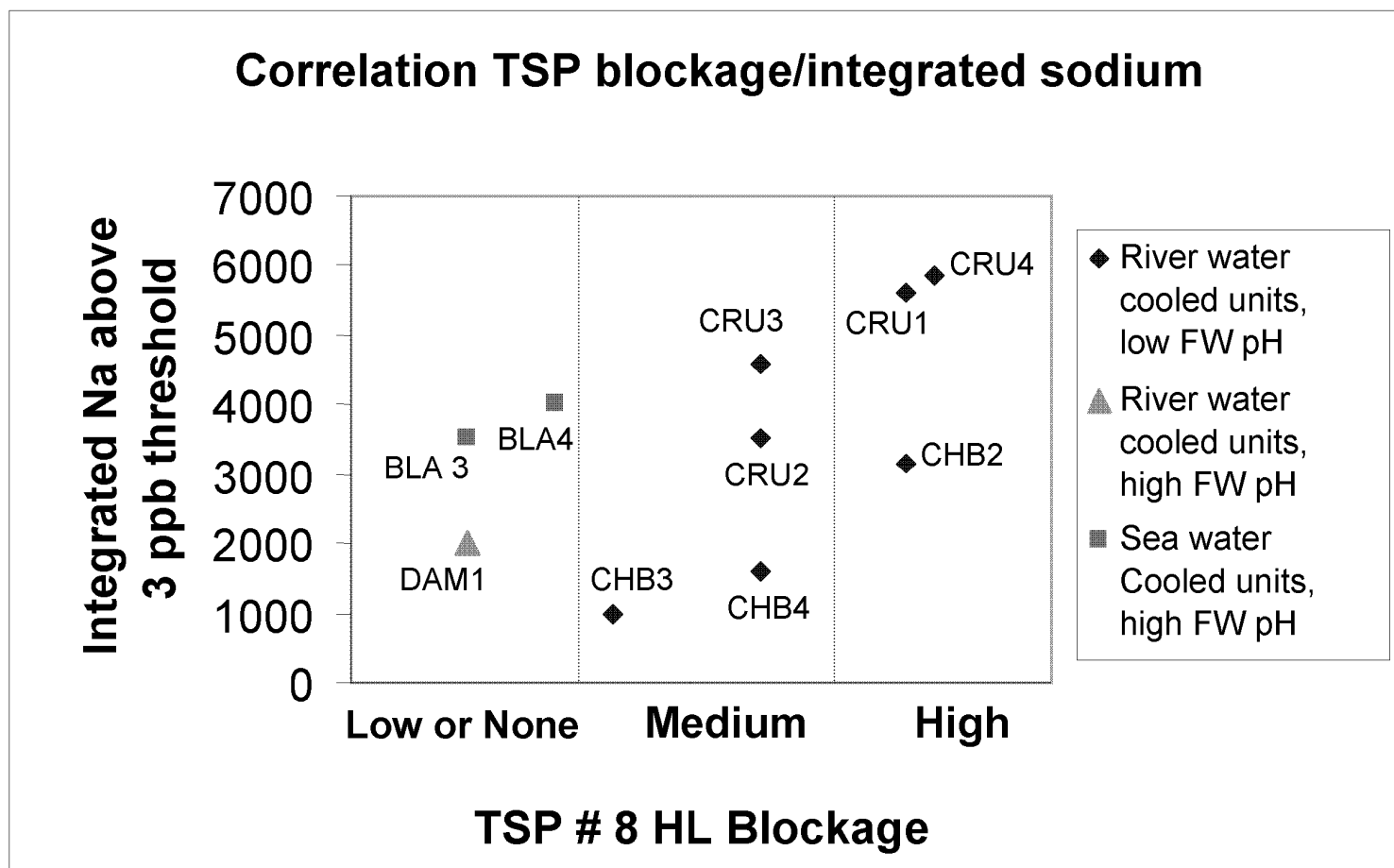


6.7 FIV in French units : Chemistry Influence

The low pH treatment (9.2 due to copper alloys) is a key aggravating factor for TSP blockage.

- ☐ Among all the units with SG 51B, no treatment parameter has a value that may explain a TSP blockage difference, expect potentially lower hydrazine and thus ammonia values.
- ☐ The units of CRUAS 1 and 4 have, as compared to other units with low pH morpholine treatment and SG 51B, a higher average sodium value at SG blowdown.
The river water leaks at the condenser may thus have a deleterious effect on TSP blockage by hardening the magnetite deposits.
- ☐ However, the TSP blockage started before the most important condenser leaks and potential correlation should be further evaluated before firm conclusion.

6.8 FIV: pollution impact



6.9 Dispersants

Principle

- Permanent addition at low concentration of a polyacrylic acid reagent (PAA) in the secondary system during normal power operation

Action

- Prevents iron oxides deposition on SG surfaces by keeping particles as suspended solids;
- Oxides mass entering SG is unchanged but with a higher elimination rate through SG Blowdown.

Expected Advantages of the process

- No corrosion of materials,
- Compatible with SG blowdown treatment on Ion Exchange Resins,
- Low impact on cation conductivity at SG Blowdown,
- Possible release of the chemical product into the environment.

7.1 FAC (Flow Accelerated Corrosion)

- **Metal affected :
CARBON STEEL**

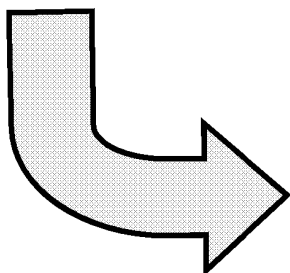
Addition of some chromium slows down the phenomenon starting from 0.01 % Cr with an improvement factor ~ 5 for 0.1% Cr .

- **Chemical Conditions:
Acidic and reducing environment**

If **pH** or O₂ content (few ppb) increases, phenomenon decreases

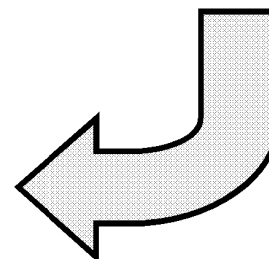
- **Thermodynamic Conditions:**

- Wet steam
- Water at high temperature
- High velocity



- **Location :**

- Separators-reheaters
- HP Heaters
- Drains
- Valves
- Tanks
- SG Internals



7.2 The Remedies on the 3 Factors



CHEMISTRY

- Units with copper alloys: treatment with sufficiently high pHt
- Units without copper alloys: ammonia treatment at $\text{pH}_{25^\circ\text{C}} > 9.8$ (~10) or amine treatment ($\text{pH}_{25^\circ\text{C}} > 9.4$)
- Do not try to excessively lower O_2 (unnecessary with Inconel 690).



MATERIALS

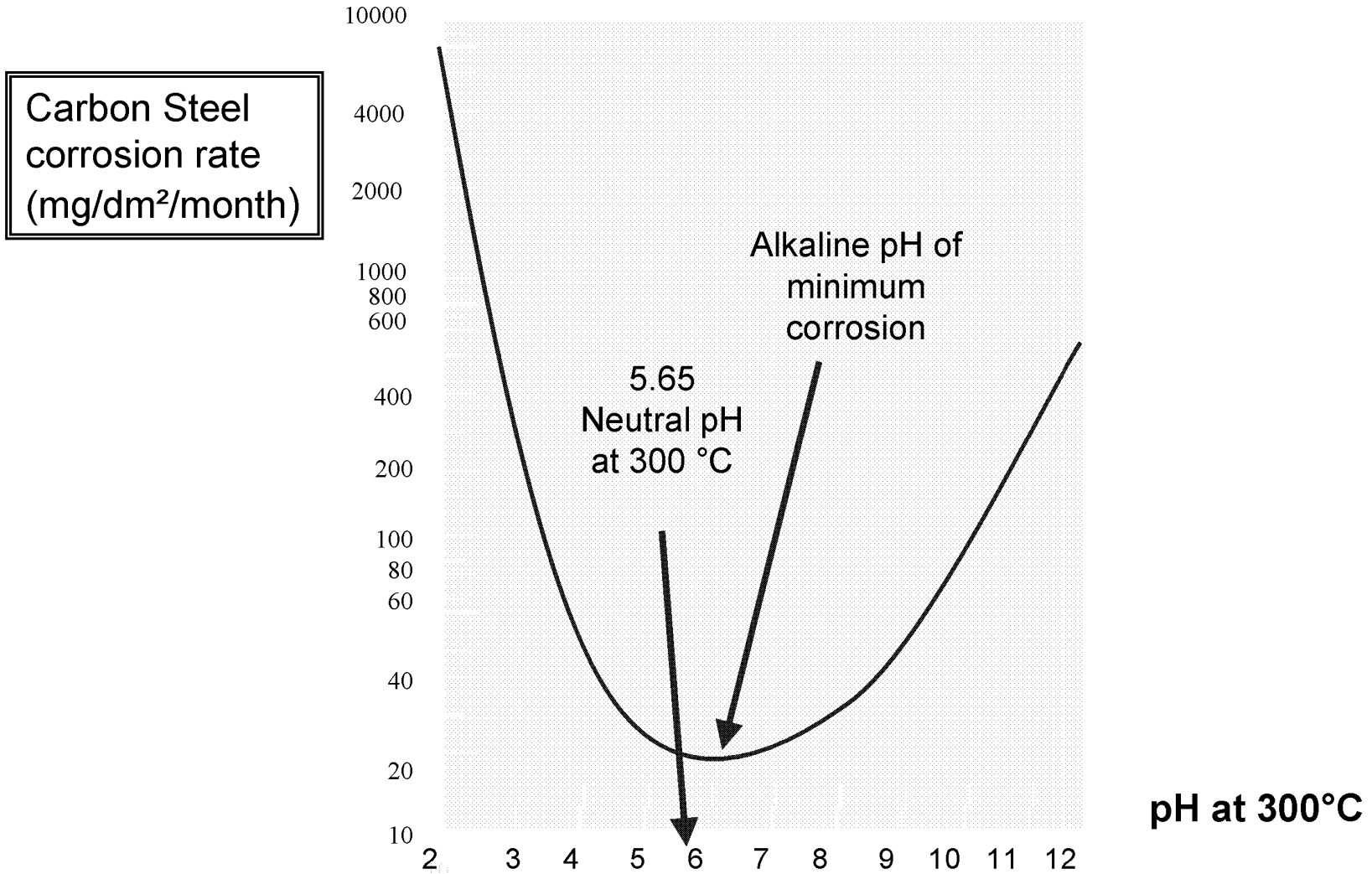
- Selection of stainless or low alloyed steels



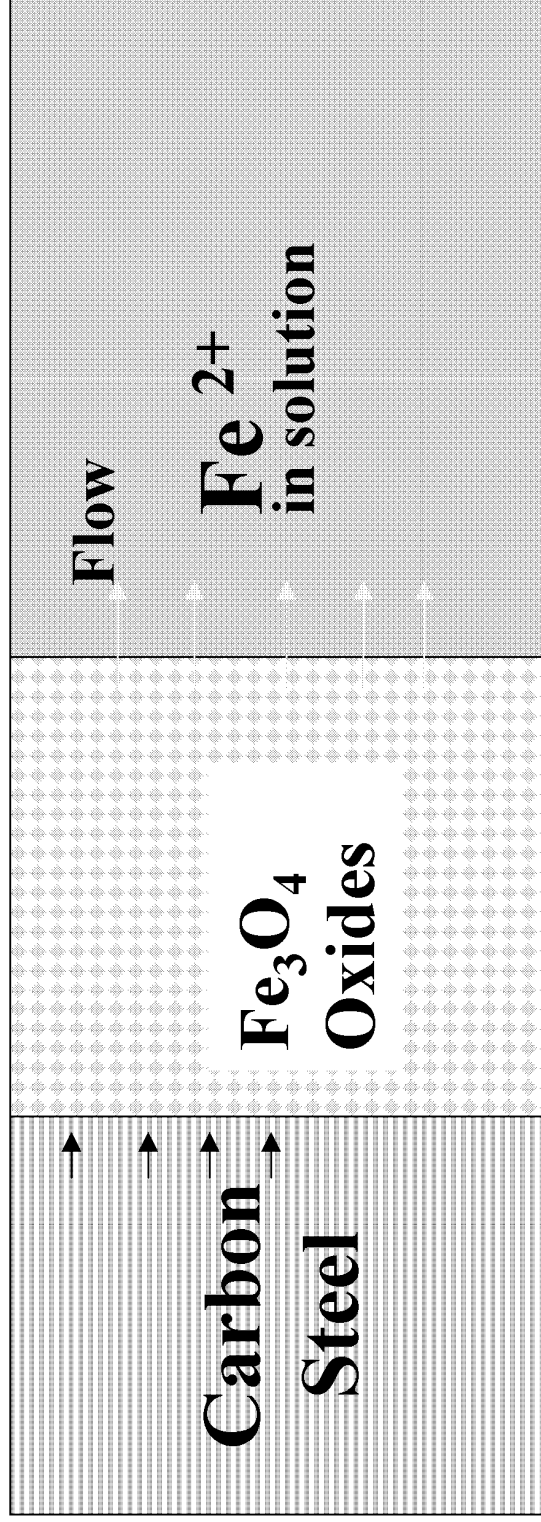
Flow Velocity

- Velocity Limitation.
- Protection against jet impact.
- Reduction of humidity fraction (Separators).

7.3 Corrosion Velocity of Carbon Steel at 300°C

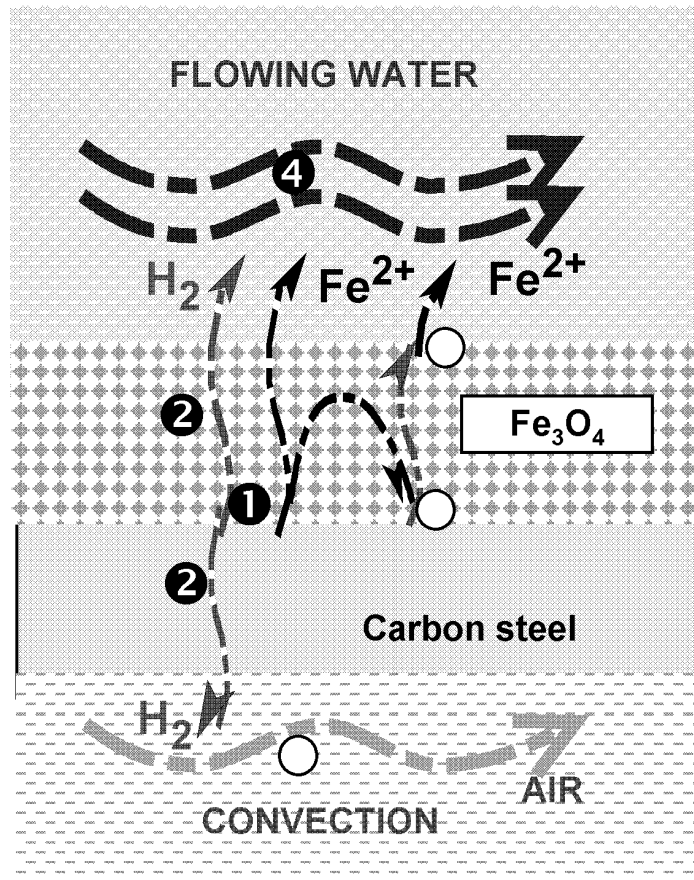


7.4 FAC Simplified Carbon steel corrosion process

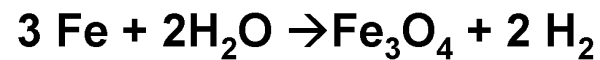
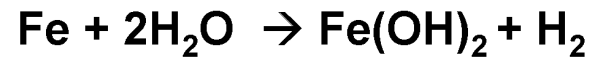


**Solubilization of iron and oxides depends
on chemical and flow conditions**

7.5 FAC Mechanism (Iron Dissolution)

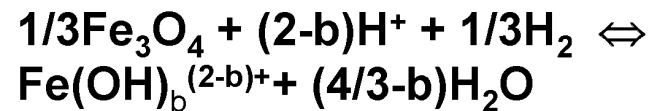


1. Steel oxidation by water at the Steel/Oxide interface, soluble Fe^{++} and magnetite formation



2. Diffusion of soluble species (soluble Fe^{++} and H_2) through the porous oxide layer

3. Reduction of the oxide at water/oxide interface

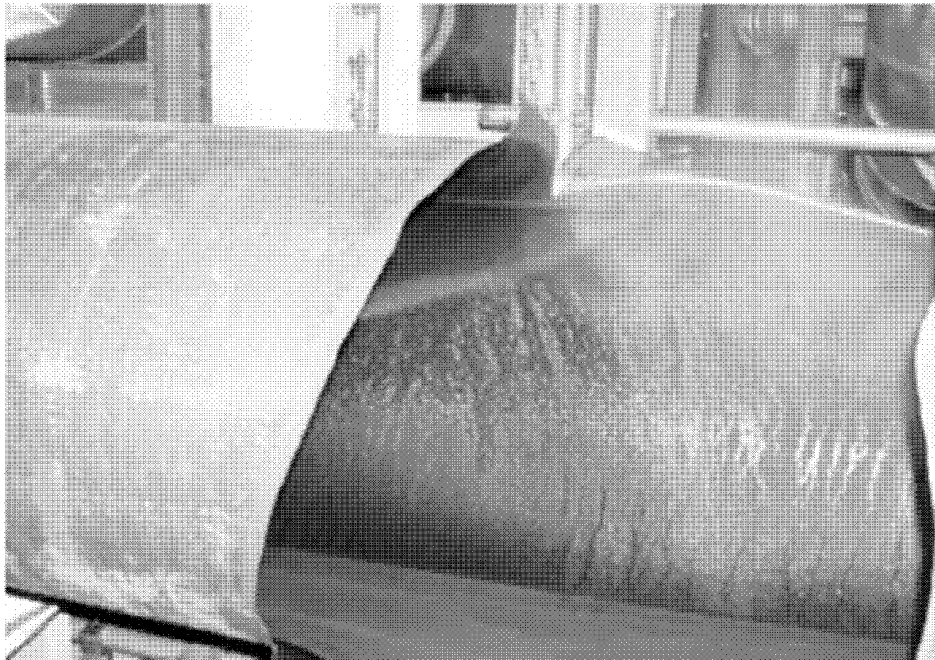


4. Transfer of soluble species in water

7.6 Mihama 3 Accident (Japan- 9 August 2004)

Main Feedwater Piping Rupture

Piping: 560 mm - 150 °C - 21st cycle of operation



9 August 2004.

KEPCO Information

☐ Type of accident

Piping burst in feedwater
between last LP heater and
deaerating tank

Nominal thickness: 100 mm

Residual thickness: 1.4 mm

☐ 18 cycles with ammonia
at low pH due to CP
only 2 cycles in ETA

☐ 5 days before shutdown
with 1st scheduled inspection

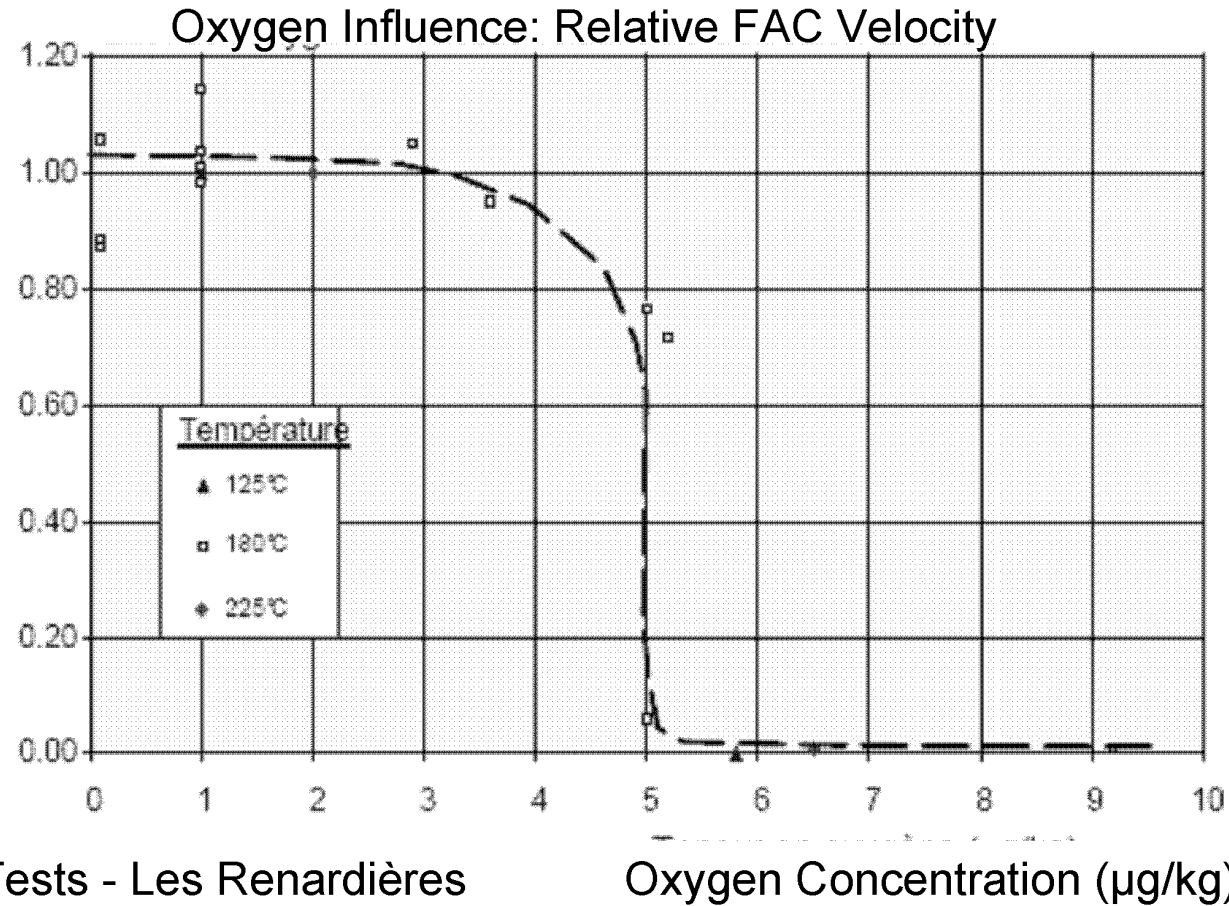
7.7 FAC Ratio with various NH_3 $\text{pH}_{25^\circ\text{C}}$ versus Morpholine $\text{pH}_{25^\circ\text{C}}$ 9.2

Temperature °C	pH NH_3 8.3	pH NH_3 9.2	pH NH_3 9.5	pH NH_3 9.7
140	24	10	4,3	2,1
185	11	6	2,8	1,3
205	7	4	2,3	1,1
225	5	3	2,1	1,0

In two phases environment, with a humidity rate of 10% in steam (weight basis)

The operating temperature pH is important.
A $\text{pH}_{25^\circ\text{C}}$ of at least 9.7 must be selected to be equivalent to Morpholine 9.2. Ammonia at low pH is not acceptable.

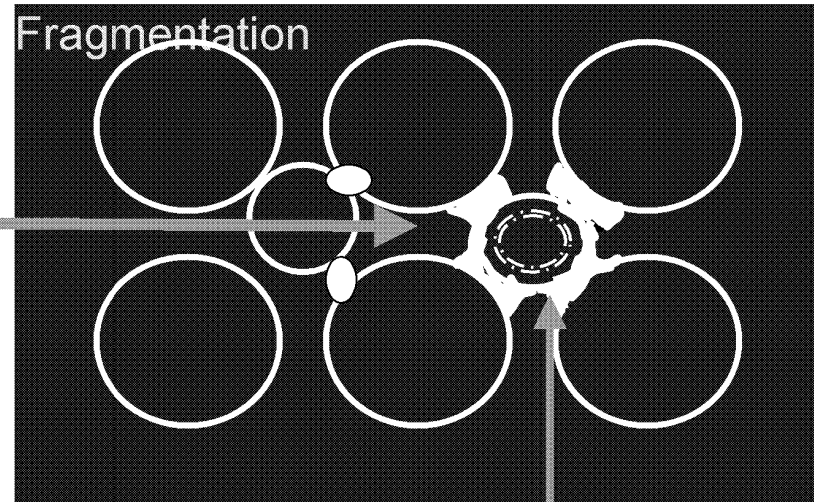
7.8 Oxygen Influence on FAC Rate



Some local oxygen (a few ppb) may be beneficial and kept on purpose. Applied in some cases (MSR, Germany with success)
Oxygen elimination before final feedwater and SG

7.9 Tubes Support Plates Fragmentation

**Portion of
fragmented TSP**
4 corroded zones



Eliminated metal

- FAC :

Dissolution → fragmentation of TSP ligaments Concerning:
external zone, upper TSP, old design (Carbon steel, drilled holes), ammonia
treatment (Gravelines in 96)

- Remedy - switching to morpholine treatment
→ stopped phenomenon

8 Secondary Water Chemistry - Main remedies

Alloy	Problem	Remedy	Efficiency
600 MA	IGA/SCC Condensate polishers or river water cooled	Boric Acid BAT	+ rather good
		Titanium, etc	minor
		Molar Ratio MRC	Plus or minor
600 MA	IGA/SCC Sea water cooled	No permanent use of condensate polishers	+ rather good
All	Pollution	Avoid using polishing plant	+ rather good
		Tight condensers	++ good
All	FAC	High pH _T (High AVT or amine) Keep some O ₂	++ good
All	Corrosion products FIV	High pH _T	++ good
		Dispersant	Promising
		Clean the SG	++ good
18-10Ti	Pitting, SCC	Avoid Cl, acids Add LiOH (+B)	++ good

Remedies can slightly compensate wrong old design (In600, ...)
 Sophisticated, severe chemistry, polishing not necessary for 690, 800
 New challenge is corrosion products deposition

9.1 BWR Treatment - Key questions

One of the main questions: mitigation of Stress Corrosion Cracking (**SCC**)
BWR treatment in Europe is based on various options:

- **NMC** (Normal Water Chemistry) with a good water quality, thus a low concentration of Cl (< 1 ppb), SO_4 , (< 3 ppb) and a low conductivity ($< 0.1 \mu\text{S/cm}$)
- **HWC** (Hydrogen Water Chemistry)
- **NMCA** (Noble Metal Chemical Addition) \Rightarrow minimize SCC
- **DZO** (Depleted Zinc Oxide), zinc addition \Rightarrow reduce dosimetry

These options may be combined.

Years 1970's, the neutral oxygenated treatment was applied.

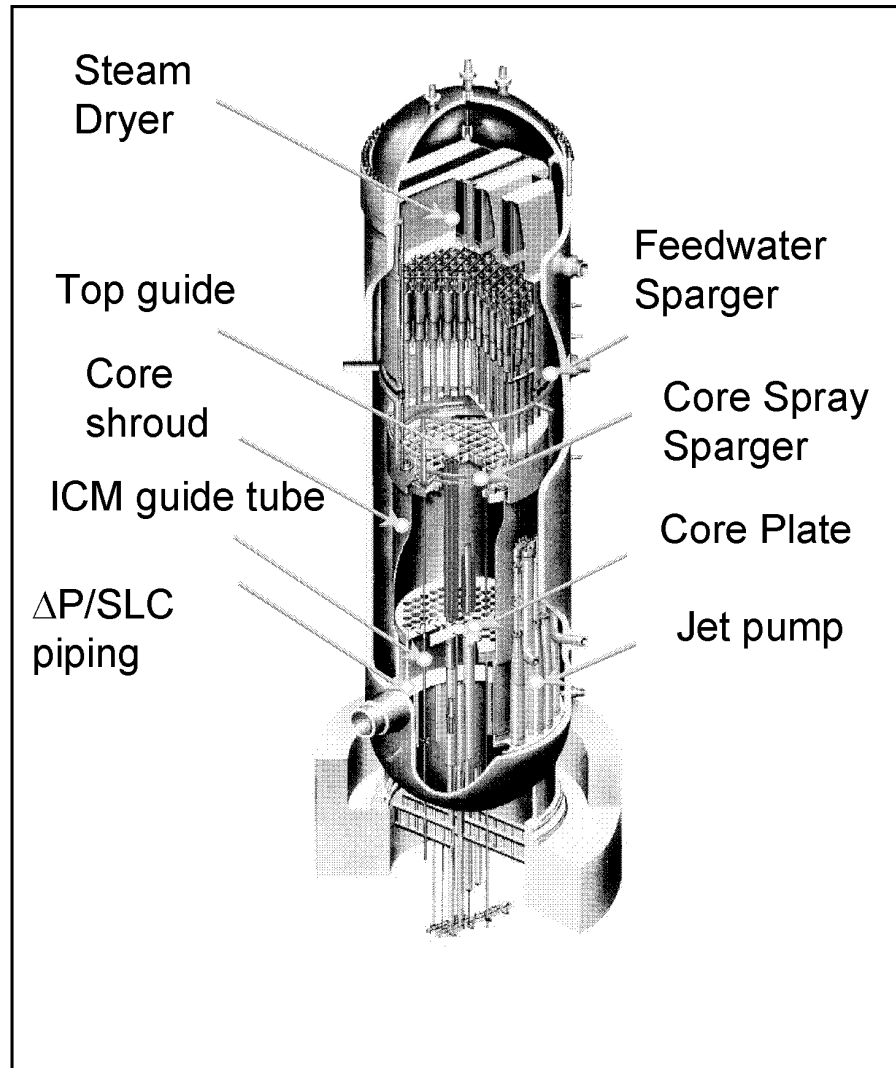
SCC of piping induced replacement of AISI 304 stainless steel components

A chemistry with less impurities has been implemented.

After SCC of core internals in the 1990's, hydrogen has been added to be in a reducing environment.

9.2 BWR Corrosion Products

- Similar corrosion product transport and activation as for PWR, except corrosion products come from the steam cycle
- Deposition occurs in recirculation piping systems and reactor water cleanup system



9.3 BWR Treatment and issues

The main questions remain mitigation of SCC, dose rates, deposits on fuel and FAC

- $H_2 \Rightarrow$ reducing environment \searrow SCC
- But a high hydrogen addition \nearrow ^{16}N radioactive in steam during operation
- It is possible to alternatively keep a reducing environment with less hydrogen with **Noble Metals Chemical Addition (NMCA)**, injected for the first time in 1996 (Duane Arnold) and presently used on 27 American units and 1 in Europe (Muehleberg).
- Zinc and NMCA additions are restricted to avoid adherent deposits on fuel.
- Uncertainties remain on NMCA efficiency toward dosimetry and deposits on fuel. The continuous addition is under development.
- **Iron concentration mitigation** is important to avoid detrimental deposits on fuel. In addition, iron oxides decrease zinc efficiency. Thus, zinc is less in solution to bring its efficiency for dose rate.
- **Copper elimination** applied on BWR allows increasing H_2 efficiency to decrease electro-chemical potential and also allows contributing at decreasing dose rates.
- As for PWR, keeping a sufficient oxygen concentration in the feed water for mitigating carbon steel **FAC**.

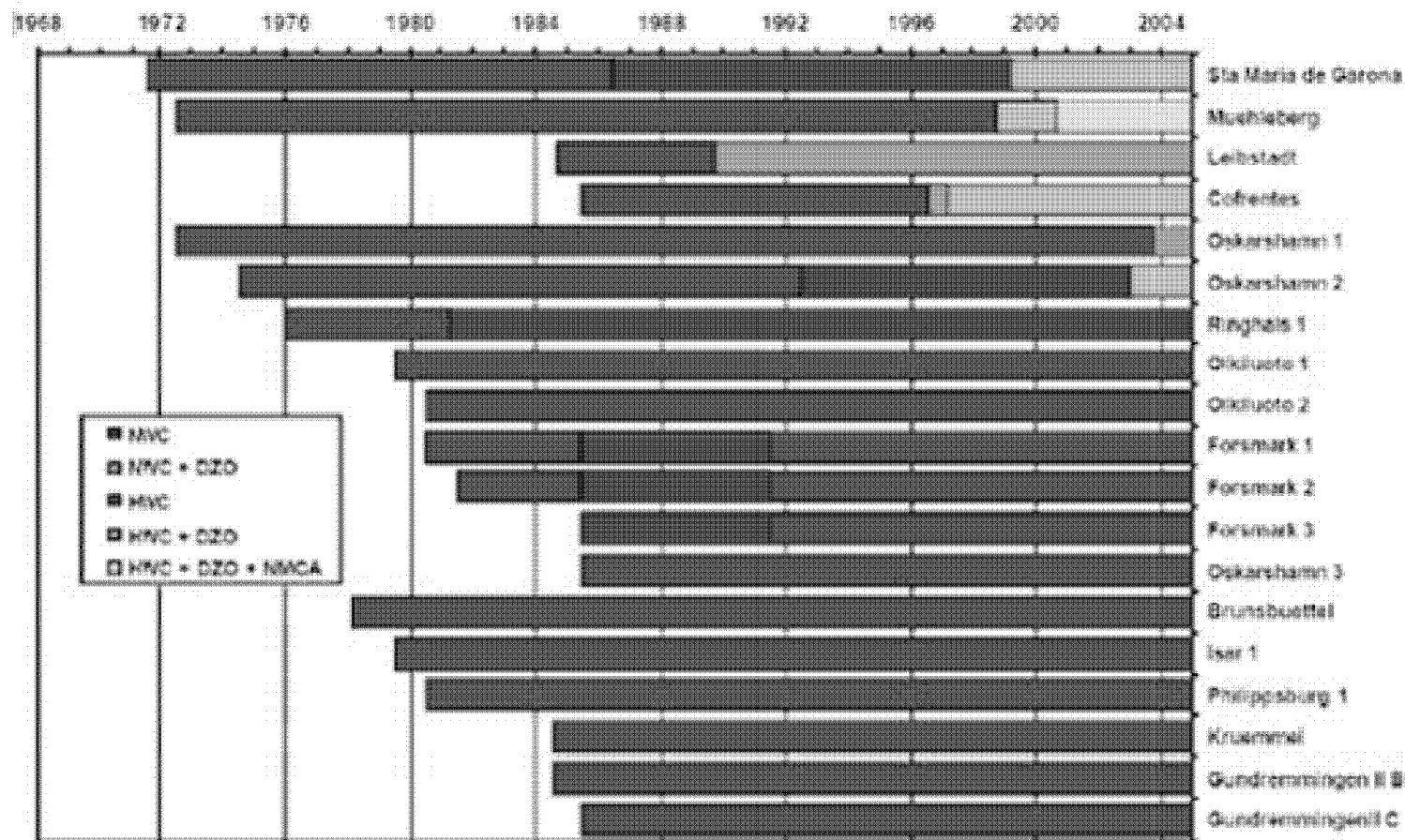
9.4 BWR Treatment in brief

IGSCC Mitigation

- Hydrogen Water Chemistry
 - Noble Metal Application
- Radiation Fields
 - Zinc Injection
- Fuel Concerns
 - Uprating
 - Crud (Iron, zinc, noble metals)
- Balance of Plant
 - Flow-Accelerated Corrosion

9.5 BWR Treatment in Europe

Mainly Normal Water Chemistry in Germany and Scandinavia



International Conference on Water Chemistry of Nuclear Reactors Systems – Jeju Island – Korea, October 2006B. Stellwag, J. Lejon. BWR Water Chemistry Data Survey of European BWR Plants

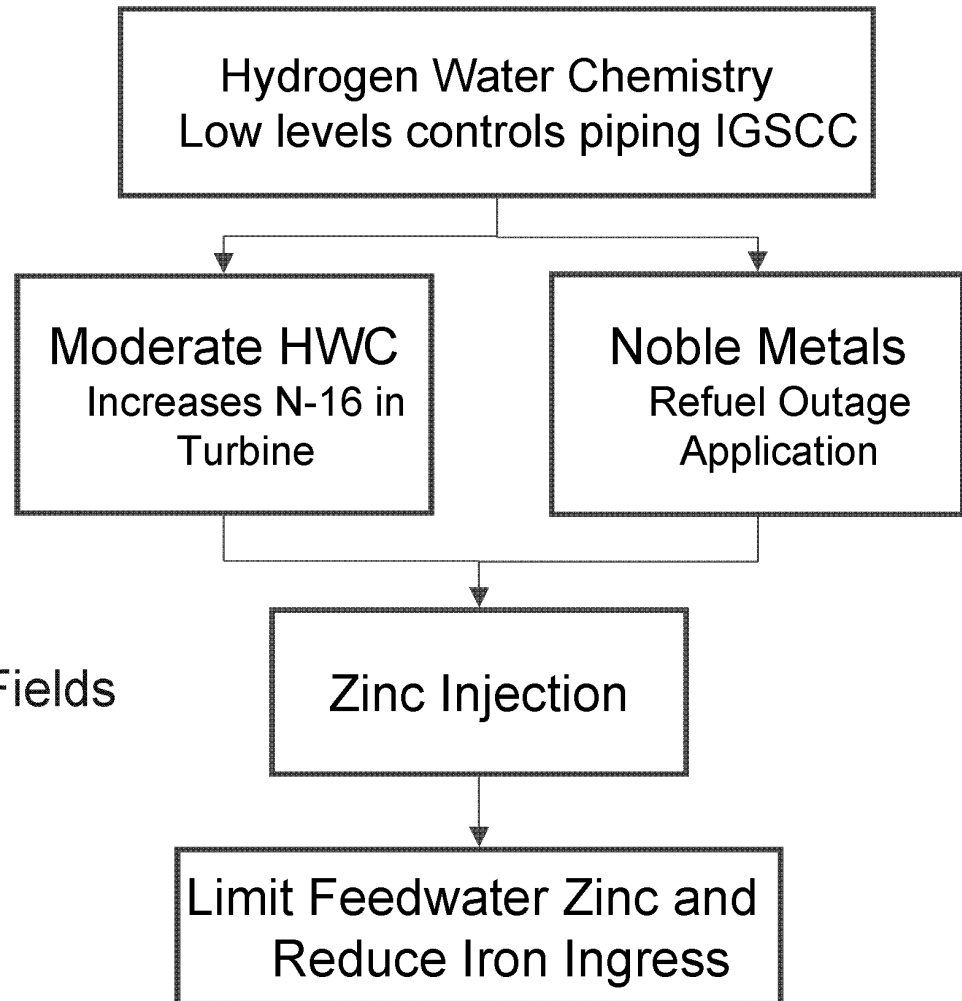
9.6 BWR Chemistry Strategies at US Plants

Objective 1: Control IGSCC
of Piping Systems

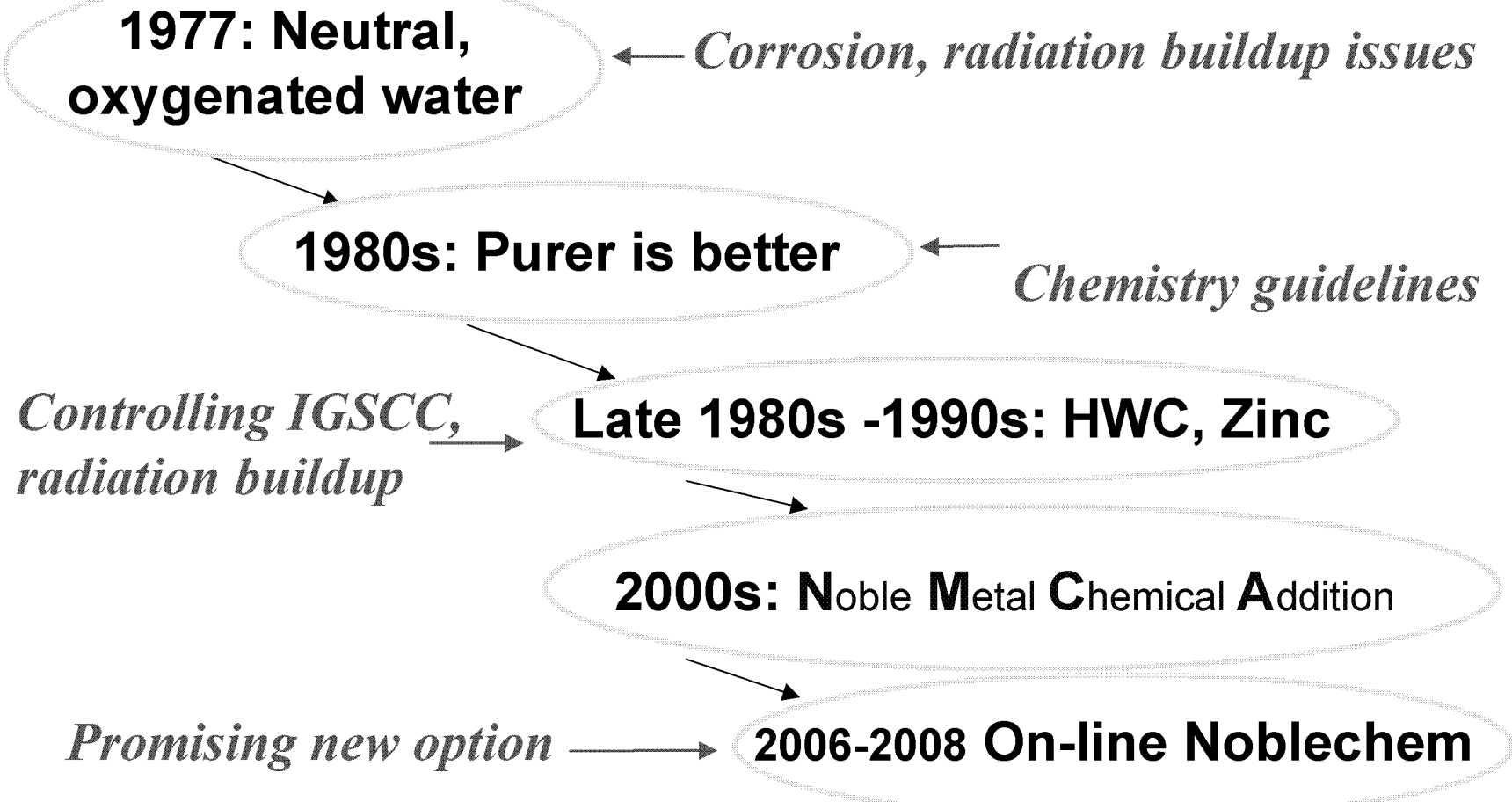
Objective 2: Mitigate IGSCC
of Reactor Internals

Objective 3: Control Radiation Fields

Objective 4: Avoid Fuel Crud
Concerns



9.7 BWR Chemistry in the USA 1977-2008



Increasing Complexity of BWR Chemistry

9.8 NMCA and Zinc

- IGSCC reduced by lowering the electrochemical corrosion potential of the coolant
 - HWC demo started in 1982 at Dresden-2
 - Noble metal demo at Duane Arnold started in 1996
 - Increases the effectiveness of low levels of hydrogen
- Zinc was even more effective for plants initiating HWC
 - Change in structure of crud in the core, and oxide films on out-of-core surfaces, as a result of more reducing conditions
 - Causes big increase in radiation fields, to a large extent mitigated by zinc
 - Even more zinc required to avoid increased fields with noble metals – feedwater zinc limited by fuel concerns

10 Conclusion

- The extensive use of Inconel 600 instead of traditional Stainless Steel (304) for avoiding SCC in presence of Chloride (and/or oxygen) induced extremely important degradation by SCC even in pure water.
- Chemistry optimization for dose rates limitation in Primary coolant of PWR had to avoid any slight increase of such a corrosion, already problematic
- Chemistry severity and complexity have been implemented for secondary water of PWR to mitigate IGA/SCC of Inconel 600 MA with limited efficiency
- Amine treatment or high pH has been widely used in the secondary water of PWR to mitigate FAC of carbon steel
- Chemistry has been permanently upgraded (NMCA) in US BWR to mitigate SCC of core components.

Chemistry must also cope with many other constraints than corrosion