

Basics of Corrosion

P. Combrade

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According to the International Standard ISO 8044
« **Corrosion of metals and alloys — Basic terms and definitions** »

Corrosion =
« *physicochemical interaction between a metal and its environment
that results in changes in the properties of the metal,
and which may lead to significant impairment of the function
of the metal,
the environment,
or the technical system, of which these form a part* »

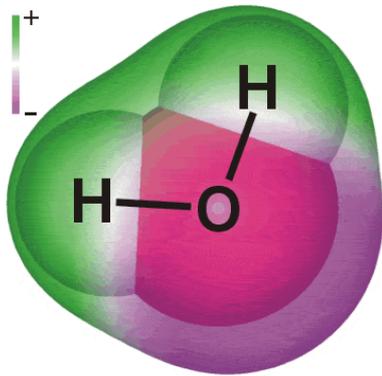
This definition is accompanied by the following note:
« *This interaction is often of an electrochemical nature* »

Why Corrosion of Metals and Alloys ?

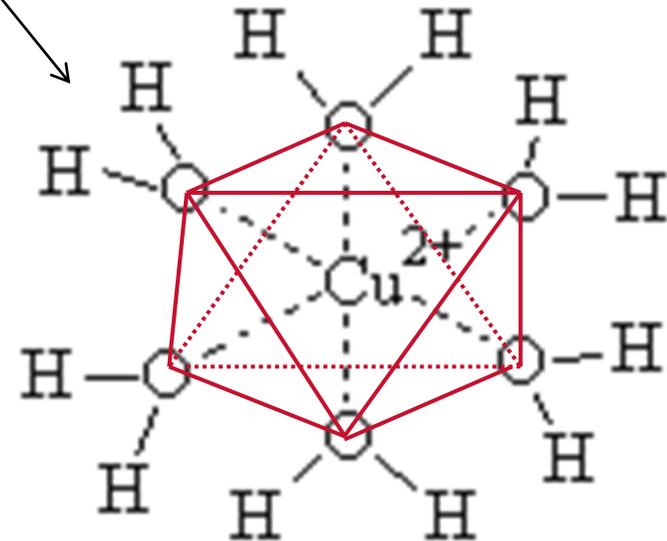
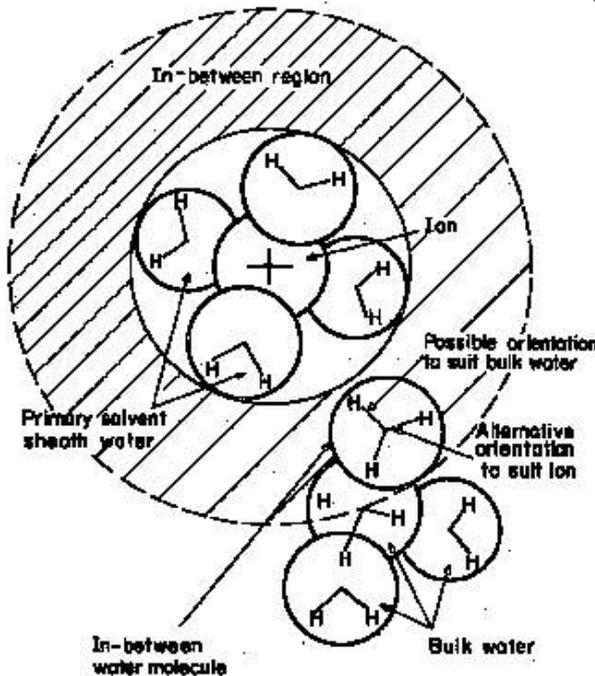
- ▶ Most metallic materials are thermodynamically unstable in aqueous environments, particularly in those containing species more oxidising than water.
- ▶ **Corrosion = metal tends to return to a stable oxidised condition**
 - ◆ Example of corrosion of iron into haematite which is a common form of iron ore
 - oxidation of steel by hot aerated water (> 150/200 °C) :
 - $2 \text{ Fe} + 3 \text{ H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 3 \text{ H}_2$
 - corrosion of steel by hot air
 - $4 \text{ Fe} + 3 \text{ O}_2 \rightarrow 2 \text{ Fe}_2\text{O}_3$
- ▶ Aqueous corrosion = metal degradation in the presence of water
- ▶ Resistance to aqueous corrosion can be due
 - ◆ To very low solubility of the metal (so-called immunity)
 - e.g. Cu in deaerated water
 - ◆ To a low dissolution rate of unprotected metal
 - e.g. C-steel in sea water
 - ◆ To the spontaneous formation of protective surface films
 - Stainless steels, Ni-Cr-Fe Alloys, Al, Ti, Zr alloys in near neutral environments
 - **In LWRs, all materials are thermodynamically unstable but are protected by surface films**
 - ◆ To the application of protective coatings

Electrochemical nature of corrosion

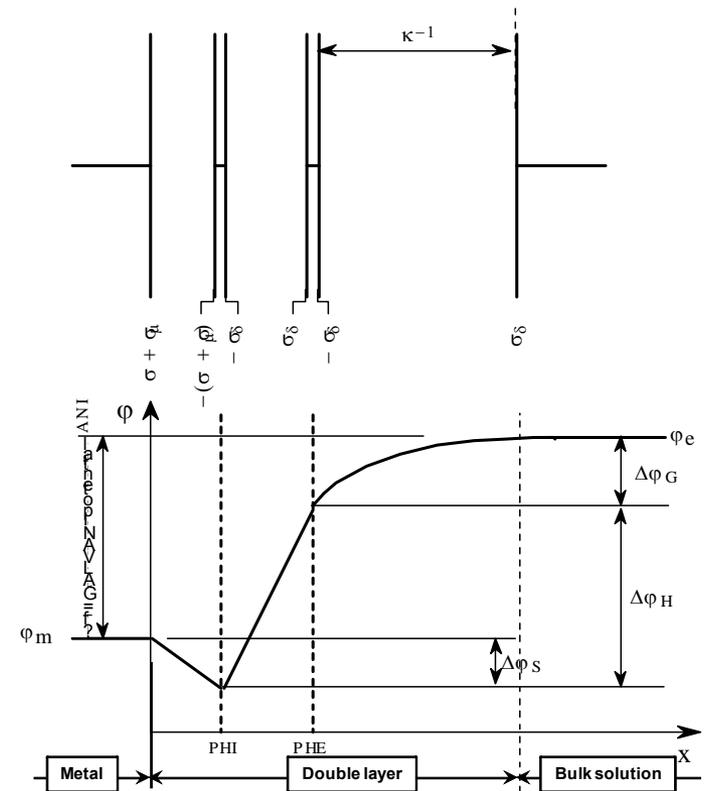
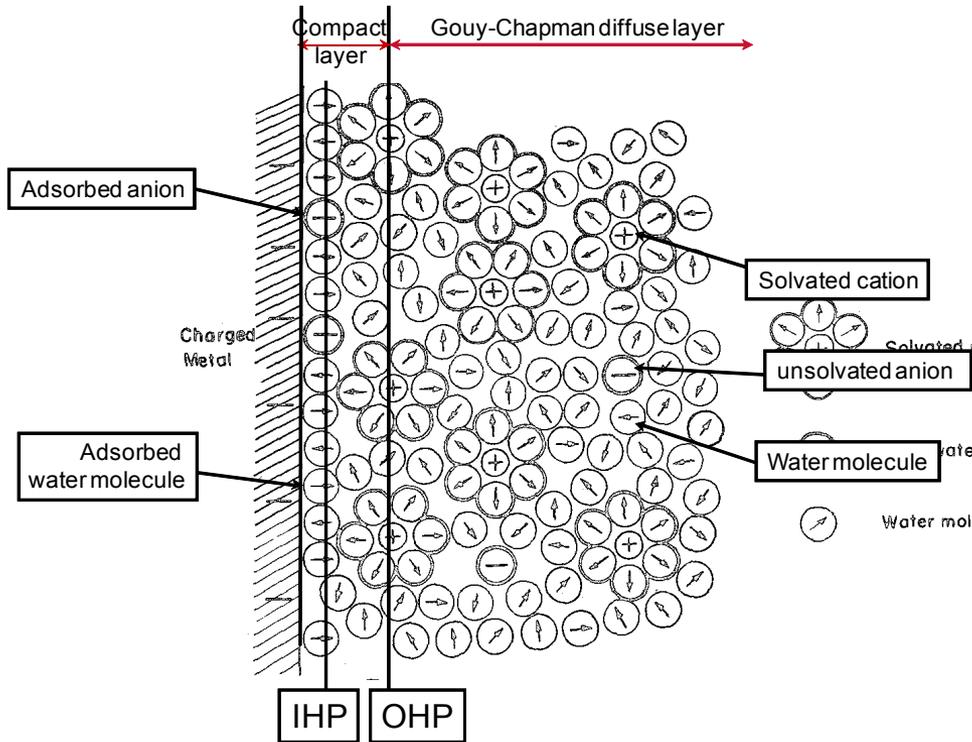
- ▶ In water, most solute are dissociated into anions and cations
- ▶ Due to the dipolar character of the water molecule, positive cations are bound to a sheath of water molecules called the solvation layer
 - Formation of a complex solvated cation $M^{z+}(H_2O)_n$ with $n=6$ in many cases
 - Metallic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



The approximate shape and charge distribution of water



Electrochemical nature of corrosion

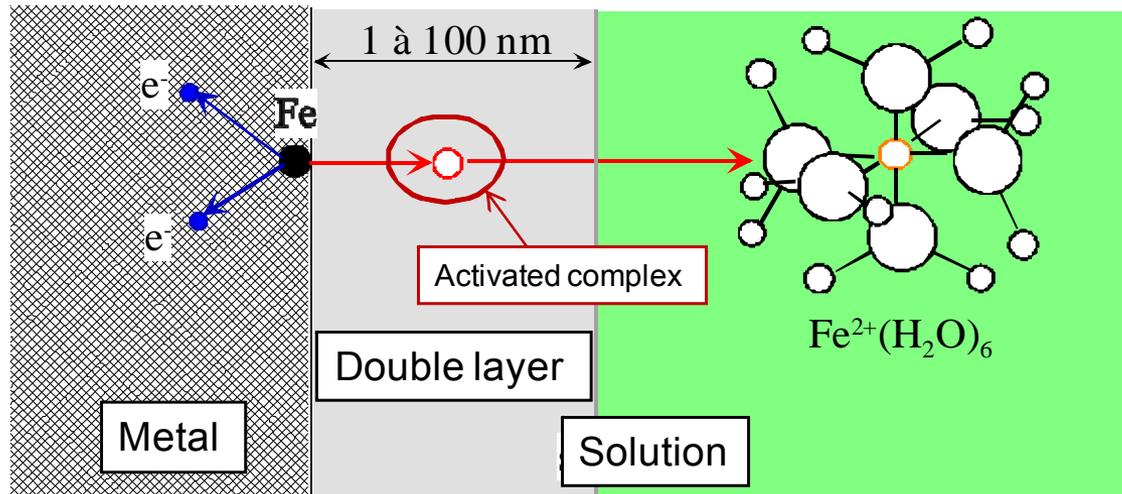
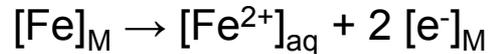


► When a metallic electrode is immersed in an aqueous solution,

- ◆ Electrical charges accumulate at the interface, both in the metal and in the solution creating a so-called "electrical double layer" that can be represented as a series of capacitors
- ◆ A potential difference appears between metal and aqueous solution
 - Metal/solution potential (electrode potential)

$$E = \phi_M - \phi_S$$

- ▶ Reactions involving charge transfer between conductors of different charge carrier nature
 - ◆ E.g. : dissolution of iron into ferrous ions = reaction of oxidation = anodic reaction



- Circulation of an electric current from the metal towards the solution
 - Anodic current $I_{\text{ox}} = I_{\text{a}} > 0$
- ◆ E.g. : reduction of proton from water = reaction of reduction = cathodic reaction
 - $[\text{H}^+]_{\text{aq}} + 2 [\text{e}^{-}]_{\text{M}} \rightarrow [\text{H}_2]_{\text{g}}$
 - Circulation of an electric current from the solution towards the metal
 - Cathodic current $I_{\text{red}} = I_{\text{c}} < 0$

- ▶ During electrochemical corrosion reactions, charges are exchanged between the metal and solution i.e.
 - ◆ an electronic current flows in the metal
 - ◆ an ionic current flows in the solution
- ▶ Faraday's law gives the reaction rate in terms of a current intensity through M/S interface

$$I = zF V_{\text{react}} \text{ in } \text{A.m}^{-2}$$

where z is the number of electrons exchanged in the electrochemical reaction

F is the Faraday, i.e. the electric charge per electrochemical equivalent weight (i.e. the charge of N electrons where N is the Avogadro number)

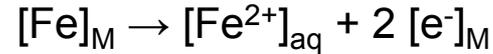
V_{react} is the reaction rate expressed in $\text{mole.s}^{-1}.\text{m}^{-2}$

- ▶ Thus, current measurements are the main tool to characterize corrosion rates even though it is generally impossible to isolate the dissolution or oxidation current from all other electrochemical reactions occurring at the metal surface

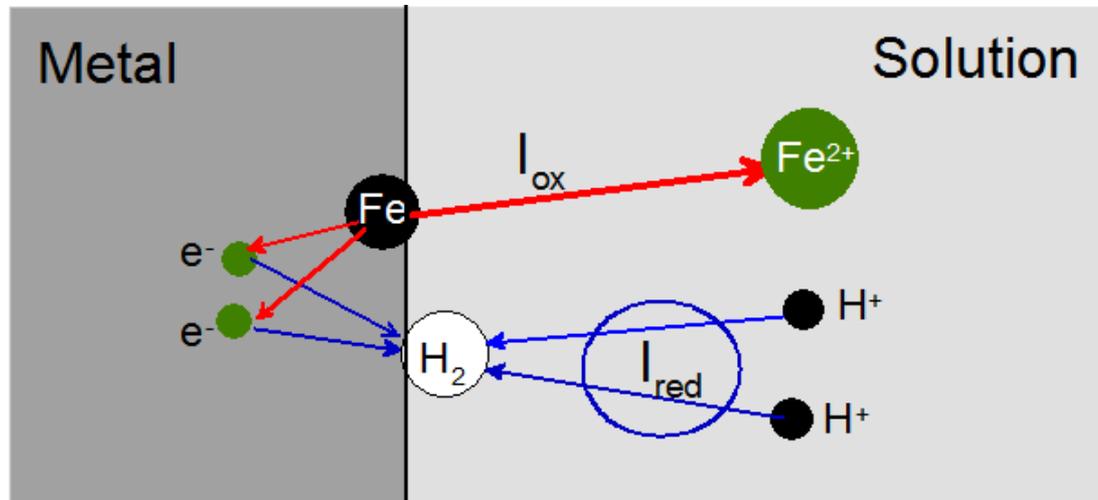
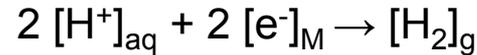
► Corrosion = anodic reaction (oxidation) + cathodic reaction (reduction)

◆ e.g. corrosion of iron in deaerated environment

- Anodic reaction



- Cathodic reaction



◆ Electrical neutrality of each phase requires (for an electrically isolated electrode)

$$i_{\text{ox}} = -i_{\text{red}} \quad \text{i.e.} \quad i_{\text{a}} = -i_{\text{c}}$$

Main electrochemical and chemical reactions involved in aqueous corrosion

- Electrochemical reactions

- Anodic

- Dissolution

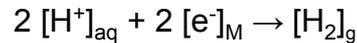


- Oxidation

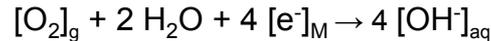


- Cathodic

- Reduction of protons (or water)



- Reduction of dissolved oxygen

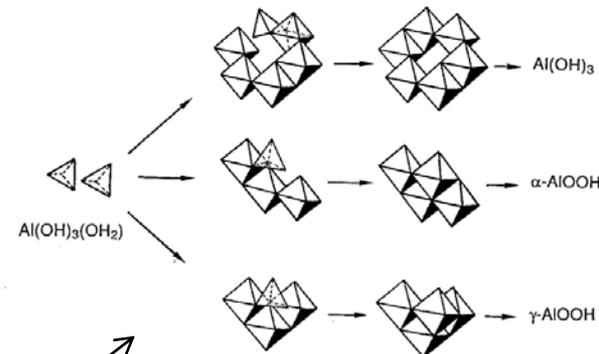
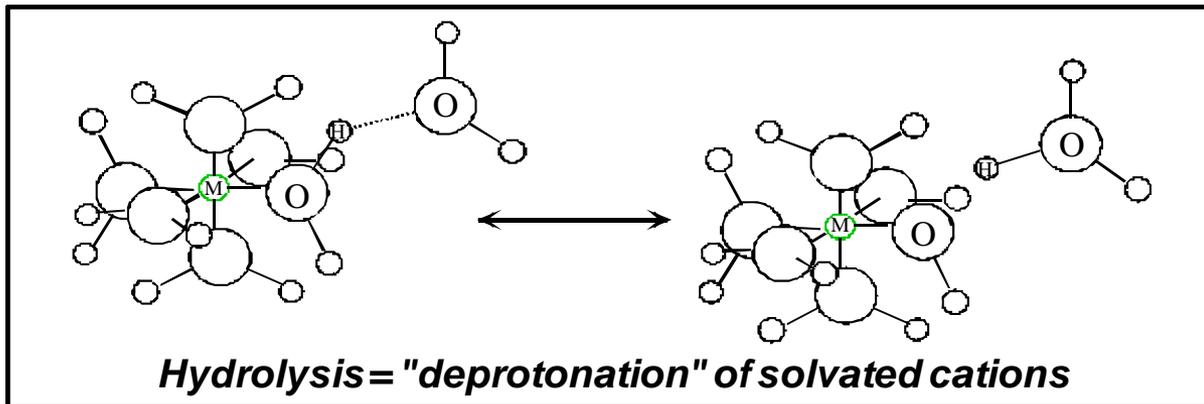


- Chemical reactions

- Cation hydrolysis



Or more realistically



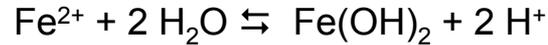
Cation hydrolysis reactions are responsible for the precipitation or the dissolution of solid oxides and/or hydroxides from solution

Thermodynamics of aqueous corrosion

Chemical and electrochemical equilibria

► Chemical reactions

- ♦ e.g. Hydrolysis of ferrous cations



- ♦ Under constant p and T conditions, Gibbs free energy change for this reaction is

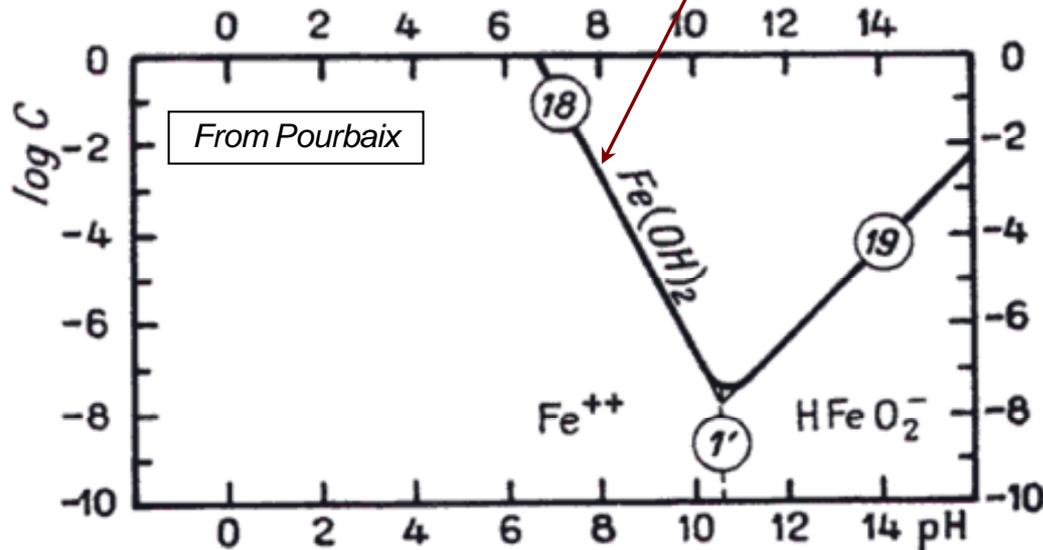
$$\Delta G_r = \mu_{\text{Fe}(\text{OH})_2} + 2 \mu_{\text{H}^+} - \mu_{\text{Fe}} - 2 \mu_{\text{H}_2\text{O}}$$

where μ_i is the chemical potential of the species $i \rightarrow \mu_i = \mu_0 + RT \text{Log } a_i$

- ♦ Equilibrium occurs when there is no change in Gibbs free energy i.e. $\Delta G_r = 0$

which for the solubility of ferrous hydroxide, for example, can be written as a function of pH:

$$\text{pH} = 6,65 - 1/2 \text{Log} [\text{Fe}^{2+}] \text{ or } \text{Log} [\text{Fe}^{2+}] = 13,29 - 2 \text{pH}$$



Chemical and electrochemical equilibria

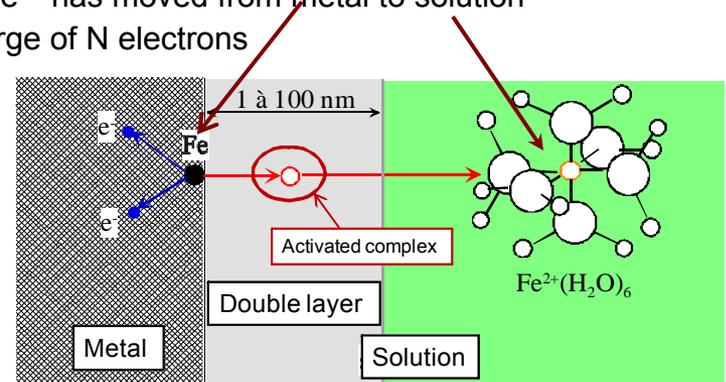
► Electrochemical reactions

- ◆ e.g. $[\text{Fe}]_{\text{M}} \rightarrow [\text{Fe}^{2+}]_{\text{aq}} + 2 [\text{e}^-]_{\text{M}}$
- ◆ Under constant p and T conditions, Gibbs free energy change includes
 - **a chemical term** similar to that of a chemical reaction $-\Delta G_r = \mu_{\text{Fe}^{2+}} - \mu_{\text{Fe}} - 2 \mu_{\text{e}}$
Note that in this formulation the convention is to calculate ΔG_r for reduction and not for oxidation
 - **an electrical term** due to the fact that a charged species Fe^{2+} has moved from metal to solution
i.e. $2 F (\varphi_{\text{S}} - \varphi_{\text{M}}) = 2 FE$ where F is the Faraday i.e. the charge of N electrons
where N is the Avogadro number

$$\text{i.e. } \Delta G_r = \Delta \tilde{G}_r + 2FE$$

Or more generally $\Delta \tilde{G}_r = \Delta G_r + zFE$
where z is the number of charges exchanged during the reaction

Equilibrium occurs when there is no change
in Gibbs free energy i.e. $\Delta \tilde{G}_r = 0$



**At equilibrium, change of chemical energy
is balanced by change of electrical energy**

$$\Delta G_r = -zF \cdot E_{\text{eq}}$$

$$\text{Equilibrium potential } E_{\text{eq}} = - \Delta G_r / zF$$

where z is the number of charges exchanged during the reaction

- A practical way to write equilibrium of electrochemical reactions is via the **Nernst's law**

Assuming the electrochemical reaction $a.Ox_1 + b.Ox_2 + ze^- \rightleftharpoons c.Red$

$$E_{eq} = E_0 + RT/zF \text{ Log}_{10} ([Ox_1]^a \cdot [Ox_2]^b / [Red]^c)$$

where $E_0 = -\Delta G_r^0/zF$ is the standard potential of the reaction

	<i>Equilibria</i>	<i>E₀ (Volt)</i>	
↑ more noble	$Au \rightleftharpoons Au^{3+} + 3e^-$	+ 1,5	
	$Pt \rightleftharpoons Pt^{2+} + 2e^-$	+ 1,188	
	$Ag \rightleftharpoons Ag^+ + e^-$	+ 0,799	
	$Hg \rightleftharpoons Hg^{2+} + 2e^-$	+ 0,796	
	$Cu \rightleftharpoons Cu^{2+} + 2e^-$	+ 0,337	
	$H_2 \rightleftharpoons 2 H^+ + 2e^-$	0	
	$Pb \rightleftharpoons Pb^{2+} + 2e^-$	- 0,126	
	$Sn \rightleftharpoons Sn^{2+} + 2e^-$	- 0,136	
	↓ less noble	$Mo \rightleftharpoons Mo^{3+} + 3e^-$	- 0,20
		$Ni \rightleftharpoons Ni^{2+} + 2e^-$	- 0,257
$Fe \rightleftharpoons Fe^{2+} + 2e^-$		- 0,440	
$Cr \rightleftharpoons Cr^{3+} + 3e^-$		- 0,74	
$Zn \rightleftharpoons Zn^{2+} + 2e^-$		- 0,763	
	$Al \rightleftharpoons Al^{3+} + 3e^-$	- 1,66	

Nernst's law of reactions useful in corrosion

► Oxidation reactions

- ◆ Dissolution of iron into ferrous ions at 25 °C



Equilibrium potential

$$E = E_0 + RT/2F \text{Log}_{10} [\text{Fe}^{2+}] \quad \text{with } E_0 = -0,44 \text{ V}_{\text{SHE}}$$

- ◆ Oxidation of ferrous into ferric ions at 25 °C



Equilibrium potential

$$E = E_0 + RT/F \text{Log}_{10} [\text{Fe}^{3+}]/[\text{Fe}^{2+}] \quad \text{with } E_0 = 0,77 \text{ V}_{\text{SHE}}$$

Nernst's law of reactions useful in corrosion

► Reduction reactions:

◆ Proton reduction



Equilibrium potential

$$E = E_0 + \frac{RT}{2F} \cdot \text{Log}_{10} \frac{[\text{H}^+]^2}{p_{\text{H}_2}} \quad \text{with } E_0 = 0 \text{ (see definition of Standard Hydrogen Electrode, SHE)}$$

$$\text{i.e. } E = -0,06 \text{ pH} - 0,03 \text{ Log}_{10} p_{\text{H}_2} \quad \text{at } 25 \text{ }^\circ\text{C}$$

$$E = -0,114 \text{ pH} - 0,057 \text{ Log}_{10} p_{\text{H}_2} \quad \text{at } 300 \text{ }^\circ\text{C}$$

◆ Reduction of dissolved oxygen



Equilibrium potential

$$E = E_0 + \frac{RT}{4F} \cdot \text{Log}_{10} ([\text{H}^+]^4 \cdot p_{\text{O}_2}) \quad \text{with } E_0 = 1,23 \text{ V}_{\text{SHE}}$$

$$\text{i.e. } E = 1.23 - 0,06 \text{ pH} + 0,015 \text{ Log}_{10} p_{\text{O}_2} \quad \text{at } 25 \text{ }^\circ\text{C}$$

$$E = \approx 1.0 - 0,114 \text{ pH} + 0,028 \text{ Log}_{10} p_{\text{O}_2} \quad \text{at } 300 \text{ }^\circ\text{C}$$

Thermodynamics of Aqueous Corrosion

Pourbaix Diagrams

Pourbaix diagrams M-H₂O

► Graphical representations of equilibria between a metal and water in a pH-potential diagram → Indicate the dominant stable species for each E-pH couple

- ◆ Includes equilibria involving at least one solid phase
 - Solubility of metal and (hydr)oxides
 - Solid/solid equilibria

Electrochemical reaction involving H⁺:
 $\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{H}^+ + 3\text{e}^-$
 $E = 1.057 - 0.177 \text{ pH} - 0.06 \text{ Log}_{10} [\text{Fe}^{2+}]$ at 25 \text{ }^\circ\text{C}

Oblique lines depend on ion concentration

Cation hydrolysis = solubility of (hydr)oxides:
 $\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + 2\text{H}^+$
 $\text{Log} [\text{Fe}^{2+}] = 13,29 - 2 \text{ pH}$ at 25 \text{ }^\circ\text{C}

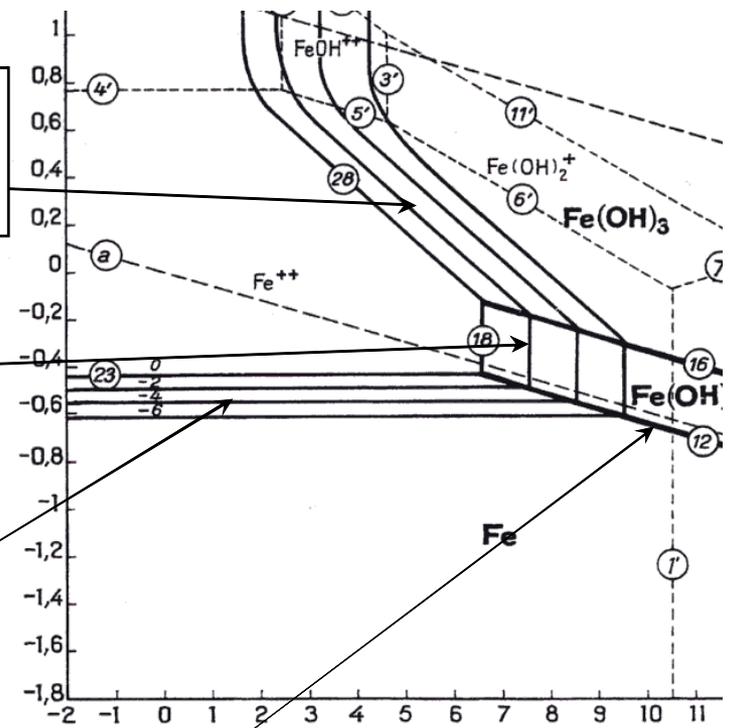
Vertical lines depend on ion concentration

Electrochemical reaction not involving H⁺:
 $\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{e}^-$
 $E = -0.44 + 0.06 \text{ Log}_{10} [\text{Fe}^{2+}]$ at 25 \text{ }^\circ\text{C}

Horizontal lines depend on ion concentration

Electrochemical reaction involving 2 solids and H⁺:
 $\text{Fe} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + 2\text{H}^+ + 2\text{e}^-$
 $E = -0.047 - 0.06 \text{ pH}$ at 25 \text{ }^\circ\text{C}

Oblique single line

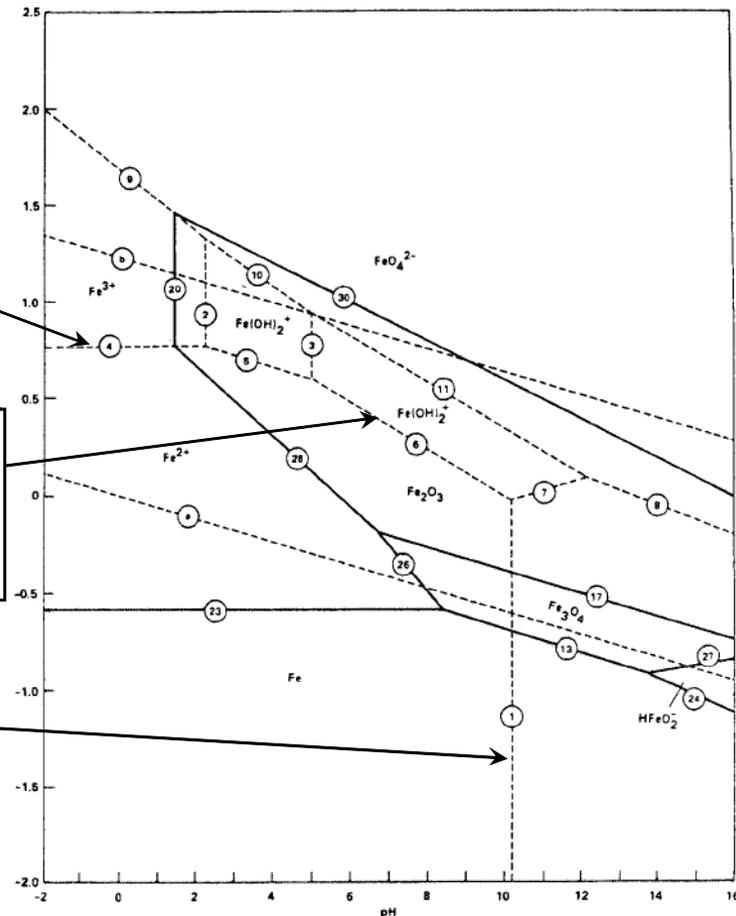


- ▶ Graphical representations of equilibria between a metal and water in a pH-potential diagram → Indicate the dominant stable species for each E-pH couple
 - ◆ Include equilibria between dissolved species
 - Domain of predominant dissolved species

Electrochemical reaction: oxidation of Fe²⁺ into Fe³⁺:
 $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + 3 e^-$
 Horizontal line drawn for equal concentrations of both ions

Electrochemical reaction involving H⁺:
 $\text{Fe}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2^+ + 2 \text{H}^+ + e^-$
 Oblique line drawn for equal concentrations of both ions

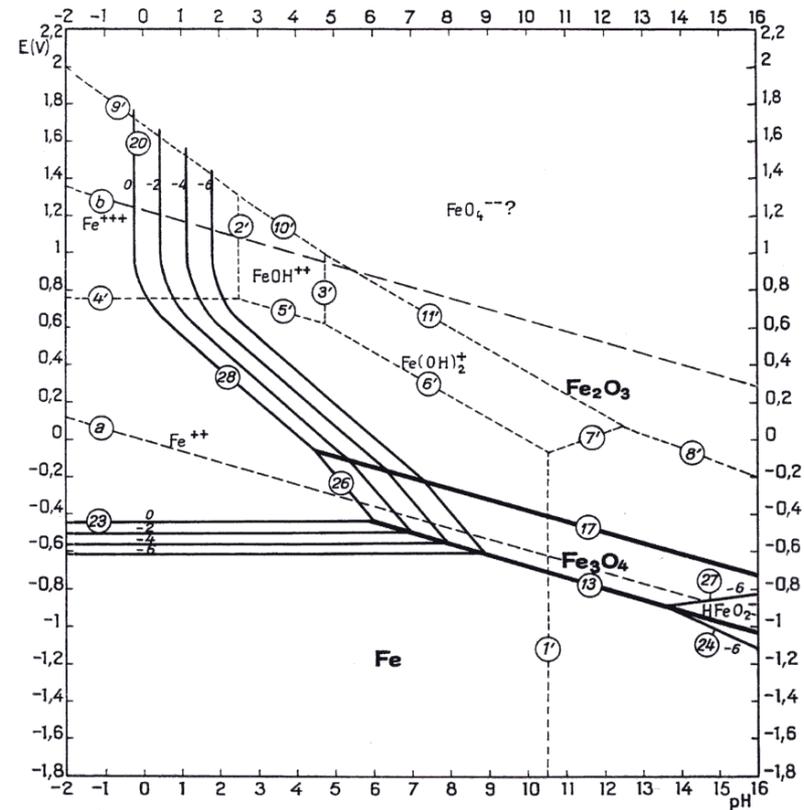
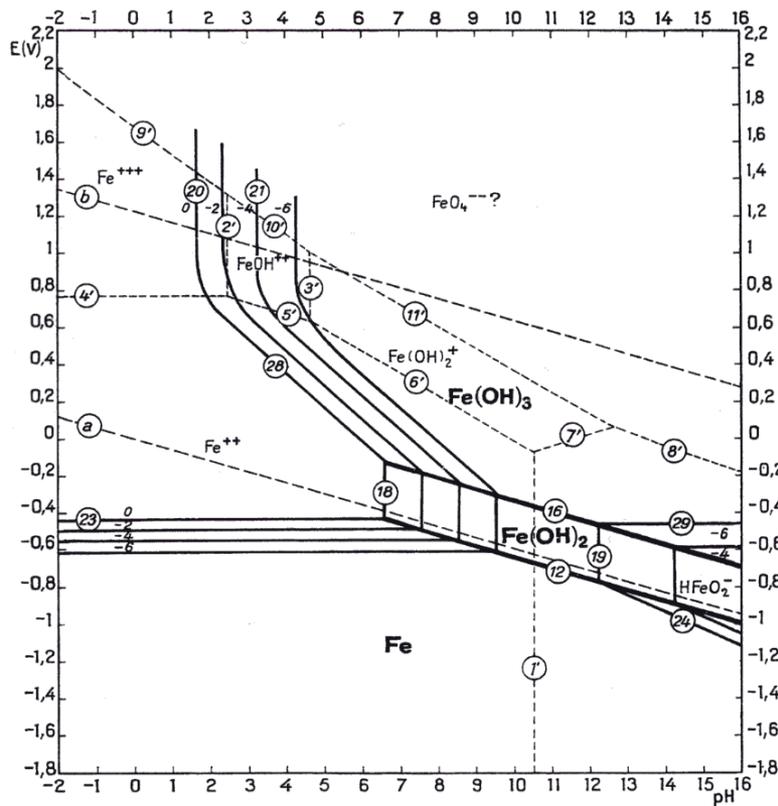
Cation hydrolysis:
 $\text{Fe}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{HFeO}_2^- + 3 \text{H}^+$
 Vertical line drawn for equal concentrations of both ions



Pourbaix diagrams depend on hypotheses of the species that are formed

► For example: Fe-H₂O

- ◆ Ferrous and ferric Hydroxides (left) versus oxides i.e. magnetite and haematite (right)



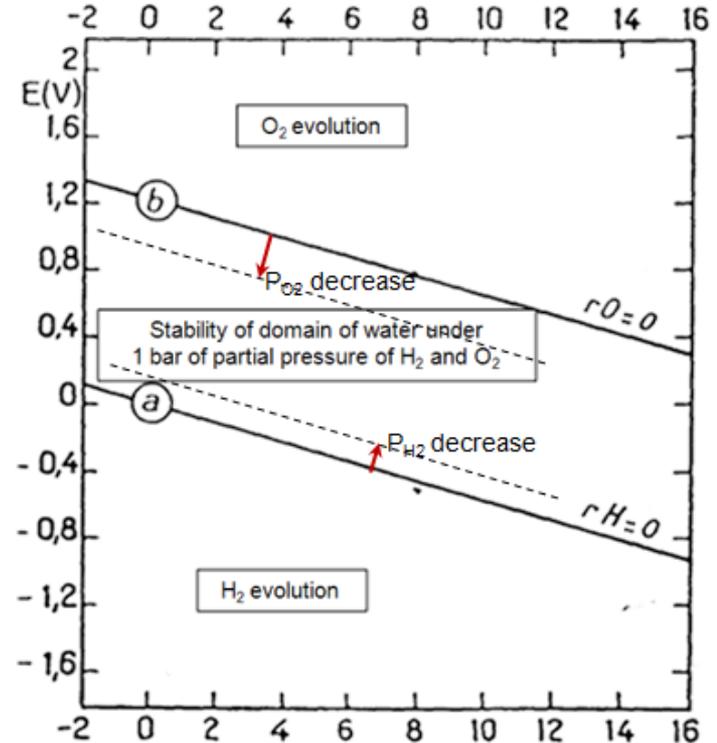
Pourbaix diagram for water – stability of water

► Under 1 bar of H_2 and O_2 partial pressure

- ◆ Water is stable between lines **a** and **b**
- ◆ Above line **b** water is oxidised to oxygen
- ◆ **Below line a**: water is reduced to H_2 and, therefore, is an oxidiser that can cause metal oxidation in the absence of any other oxidising species
 - Deaerated environments
- ◆ **Below line b**, dissolved oxygen can oxidise metal
 - Aerated environments

► Changing H_2 and O_2 partial pressures move the a and b lines vertically

- ◆ At room temperature:
 - line a is displaced by 30 mV when P_{H_2} is changed by a factor 10
 - In normal atmosphere $p_{H_2} \ll 1$ bar
 - Protons or water can be reduced slightly above line b
 - line b is displaced by only 15 mV when P_{O_2} is changed by a factor 10



What can Pourbaix diagrams
(i.e. equilibrium diagrams)
reveal and not reveal
about corrosion?

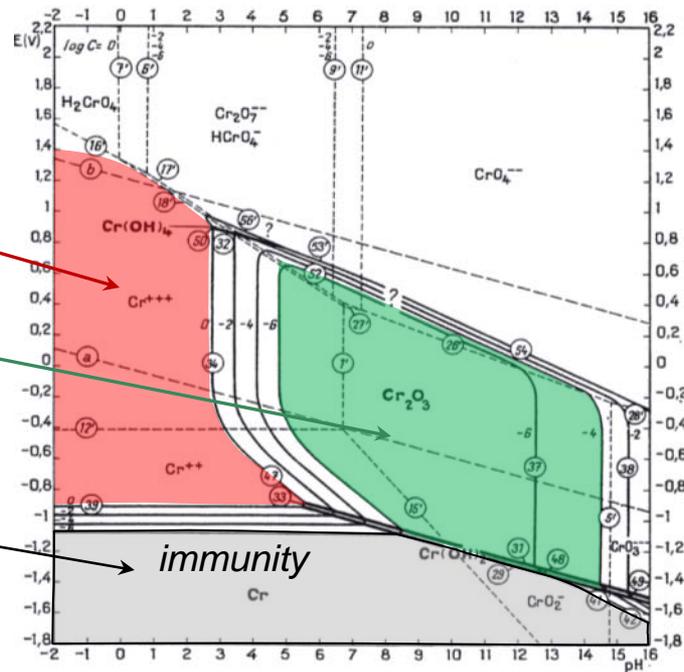
What can Pourbaix diagrams reveal and not reveal about corrosion?

► Pourbaix diagrams indicate

- ◆ regions where corrosion is likely
 - No solid oxide can be formed
- ◆ regions where protection (passivity) may be possible
 - Solid oxide or hydroxide is stable
- ◆ Regions where no significant corrosion is possible - immunity

► However, Pourbaix diagrams do not reliably indicate regions of protection by surface oxides

- ◆ The existence of a stable solid oxide does not prove that it will form nor that it will be protective
 - e.g. Fe is rarely protected by $\text{Fe}(\text{OH})_2$
- ◆ The nature of protective passive films is often different to that of bulk oxide phases
 - e.g. passive films on stainless steels are much more stable in acidic environments than suggested by Pourbaix diagrams

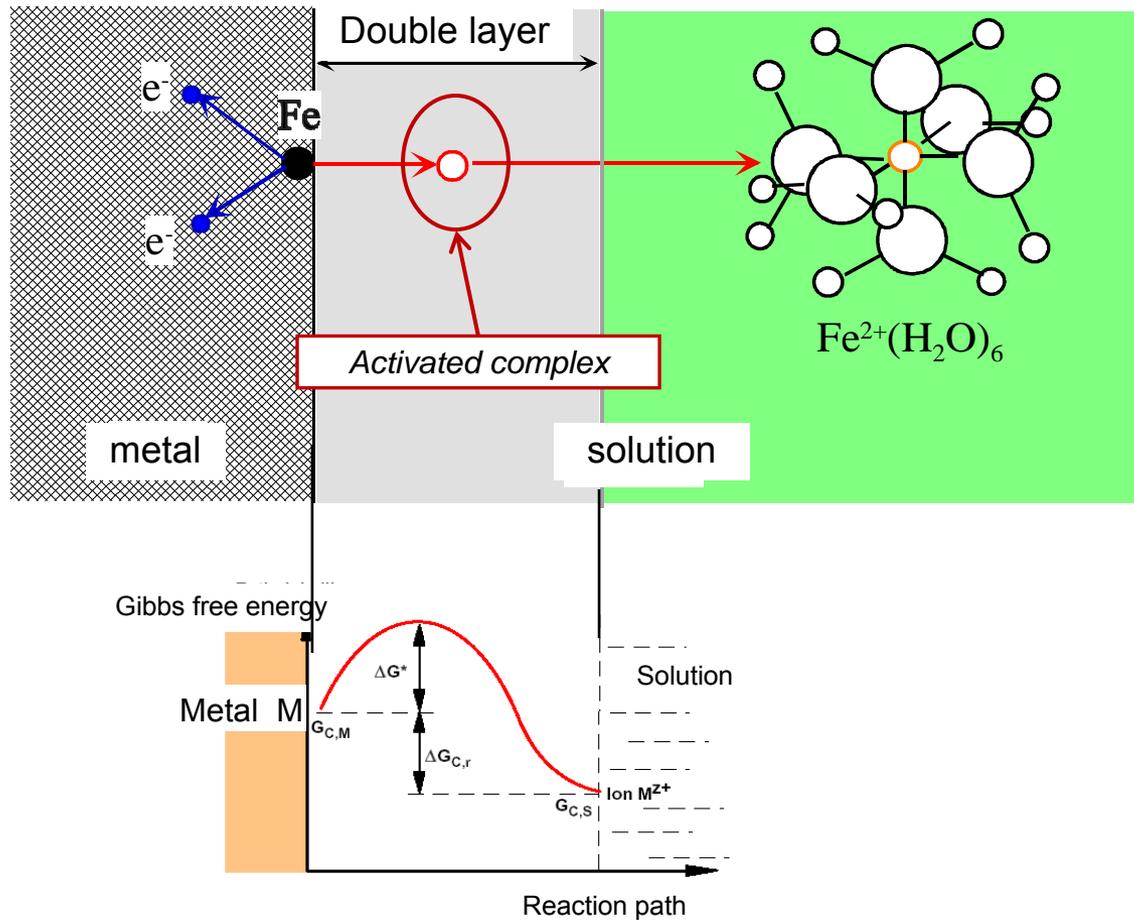


**Pourbaix diagrams are equilibrium diagrams,
they never give indications about corrosion rates**

Kinetics of Aqueous Corrosion

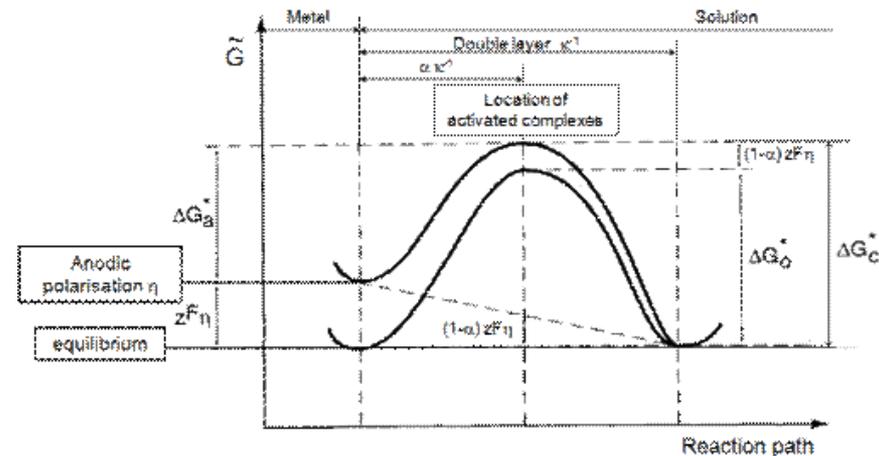
Double layer and activation energy

► Reaction path and activation barrier



- ▶ Overpotential $\eta = E - E_{eq}$
 - ◆ At equilibrium, $E = E_{eq}$, i.e. overpotential $\eta = 0$
 - ◆ When $E \neq E_{eq}$, i.e. $\eta \neq 0$, the reaction is said to be polarised
 - $E > E_{eq} \Rightarrow \eta > 0$
 - $E < E_{eq} \Rightarrow \eta < 0$

- ▶ Direction of the reaction is determined by the sign of η
 - ◆ $\eta > 0 \Rightarrow i > 0 = \text{oxidation}$
 - ◆ $\eta < 0 \Rightarrow i < 0 = \text{reduction}$



► Global kinetics

$$V = V_{\text{ox}} + V_{\text{red}} \text{ (Mole.s}^{-1}\text{.m}^{-2}\text{)}$$

- ◆ Faraday's law allows the reaction rate to be expressed by a current density through the M/S interface

$$I = I_a + I_c = zF(V_{\text{ox}} + V_{\text{red}}) \text{ in A.m}^{-2}$$

- where
- z is the number of electrons exchanged in the electrochemical reaction, and
 - F is the Faraday, i.e. the charge passed for one electrochemical equivalent
 - V_{ox} and V_{red} are the oxidation and reduction reaction rates expressed in $\text{mole.s}^{-1}\text{.m}^{-2}$

► Processes controlling electrochemical reactions:

- ◆ Transfer through an activation barrier (activation polarisation)

- $I = I_0 \cdot \exp(\alpha z F \eta / RT) - I_0 \cdot \exp(- (1-\alpha) z F \eta / RT)$

- ◆ Mass transport in the liquid (concentration polarisation)

- Limiting current $I_{\text{diff}} = zFD_i \cdot |\text{grad } C_i|_0 = z F (C_{\text{Interface}} - C_{\text{bulk}}) / \delta$

- ◆ Ion/charge transfers through a protective film (passivity)

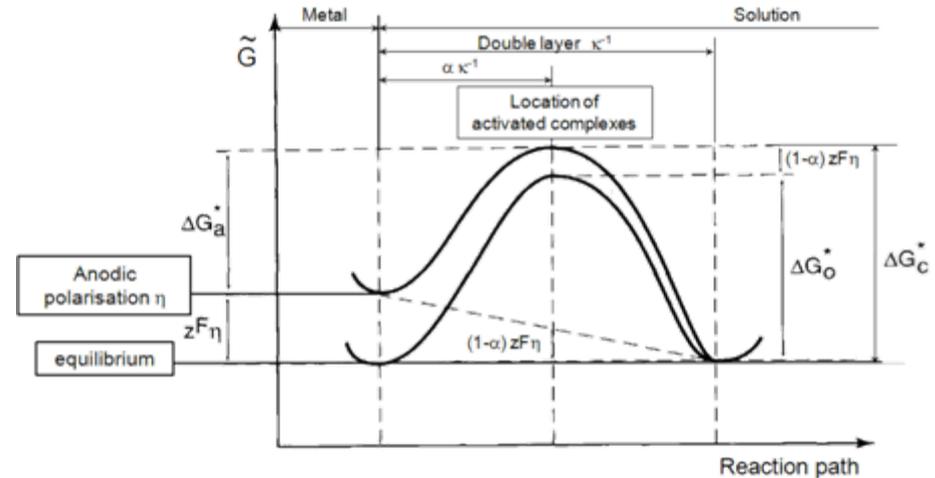
- Dissolution currents are often almost independent of potential in the passive range

► Reaction rate is controlled by the probability of jumping the activation barrier

- ◆ Reaction kinetics obey an exponential law

$$V = V_0 \exp(-\Delta G/RT)$$

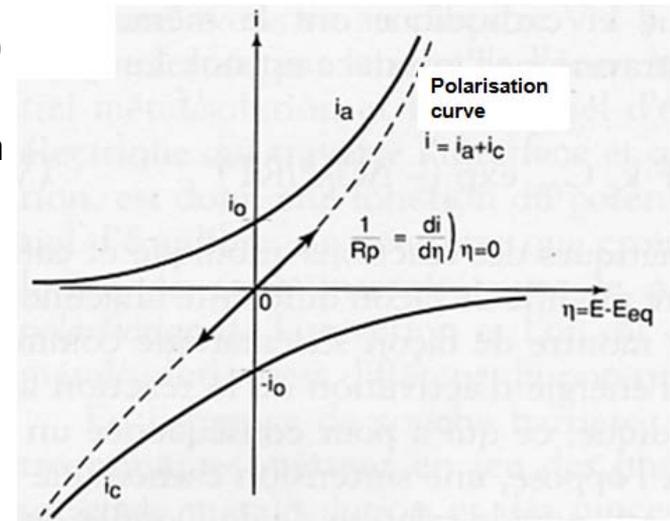
- ◆ The simplest model is that the variation of activation energy is proportional to the extent of departure from equilibrium i.e. the overpotential



► Butler-Volmer law:

- ◆ $I = I_a - I_c = I_0 \cdot \exp(\alpha zF\eta/RT) - I_0 \cdot \exp(- (1-\alpha) zF\eta/RT)$
 - I_0 = the exchange current density of the reaction i.e. anodic and cathodic reaction rates at equilibrium
 - α is a parameter that can be interpreted as the position of activated complexes

— $\alpha < 1$

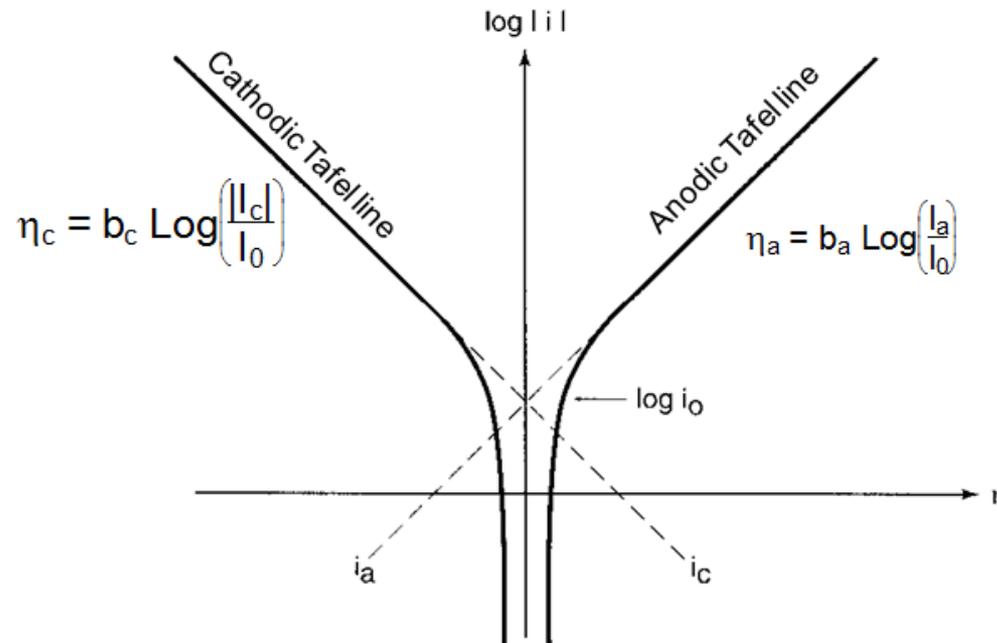


► Tafel law:

◆ Another form of the Butler-Volmer law

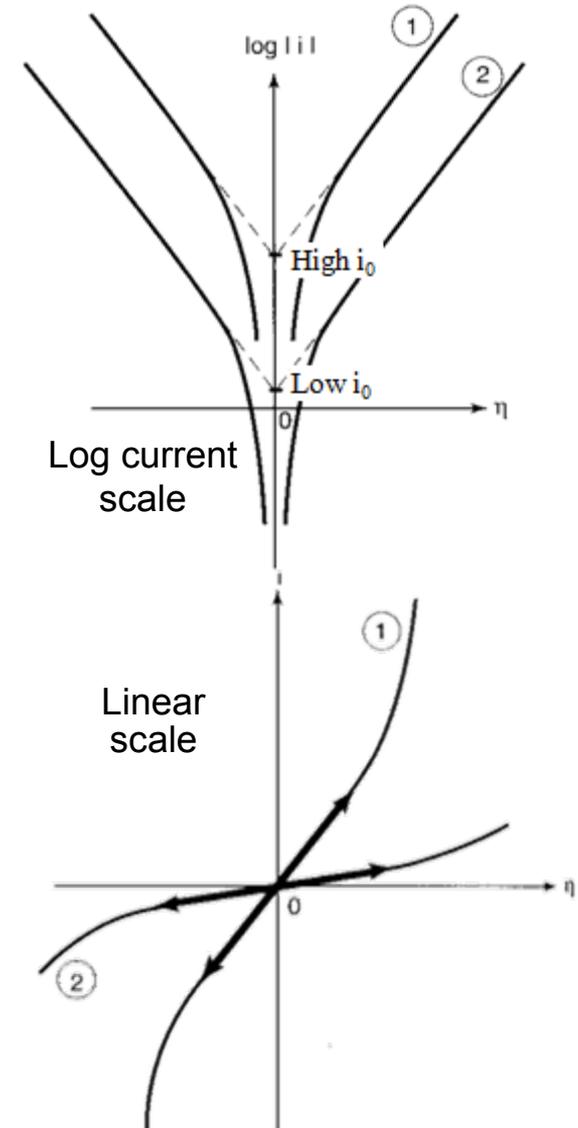
• Tafel coefficients (or slopes):

- Anodic slope $b_a = RT/\alpha zF$
- Cathodic slope $b_c = RT/(1-\alpha)zF$



► Exchange current density controls the reaction rate:

- ◆ Reaction rate is proportional to I_0
 - High $I_0 \rightarrow$ fast reaction rate (1)
 - Low $I_0 \rightarrow$ slow reaction (2)
- ◆ Example of reduction of protons:
 - I_0 and, thus, the reaction rate can vary over 9 orders of magnitude depending on the metal (at RT)
 - Pt $I_0 \sim 10^{-2} \text{ A/cm}^2$
 - Pd, Rh $I_0 \sim 10^{-4} \text{ A/cm}^2$
 - Fe, Au $I_0 \sim 10^{-6} \text{ A/cm}^2$
 - Ni, Ag, Cu, Cd $I_0 \sim 10^{-7} \text{ A/cm}^2$
 - Al, Sn $I_0 \sim 10^{-10} \text{ A/cm}^2$
 - Zn, Pb $I_0 \sim 10^{-11} \text{ A/cm}^2$



- ▶ Limitation of reaction rate by transport of reactants towards the M/S interface or reaction products from M/S interface towards the bulk solution

- ◆ Nernst approximation in a turbulent solution with a diffusion layer near the M/S interface
 - Diffusion assumed through thickness δ
 - Homogeneity beyond the diffuse layer δ

- ◆ Maximum reaction rate determined by maximum mass flux from or to the M/S interface

$$J = D \frac{|C_0 - C_{\text{bulk}}|}{\delta} \quad \text{i.e.} \quad I = zF D \frac{|C_0 - C_{\text{bulk}}|}{\delta}$$

where

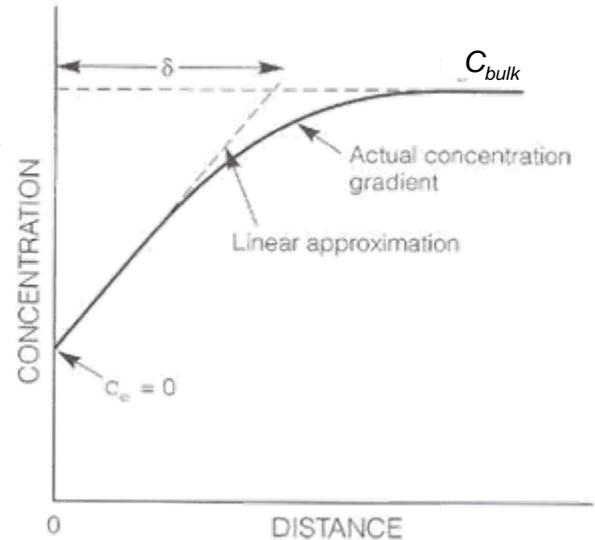
D is the diffusion coefficient of the species and

C_{bulk} is its concentration in the bulk solution

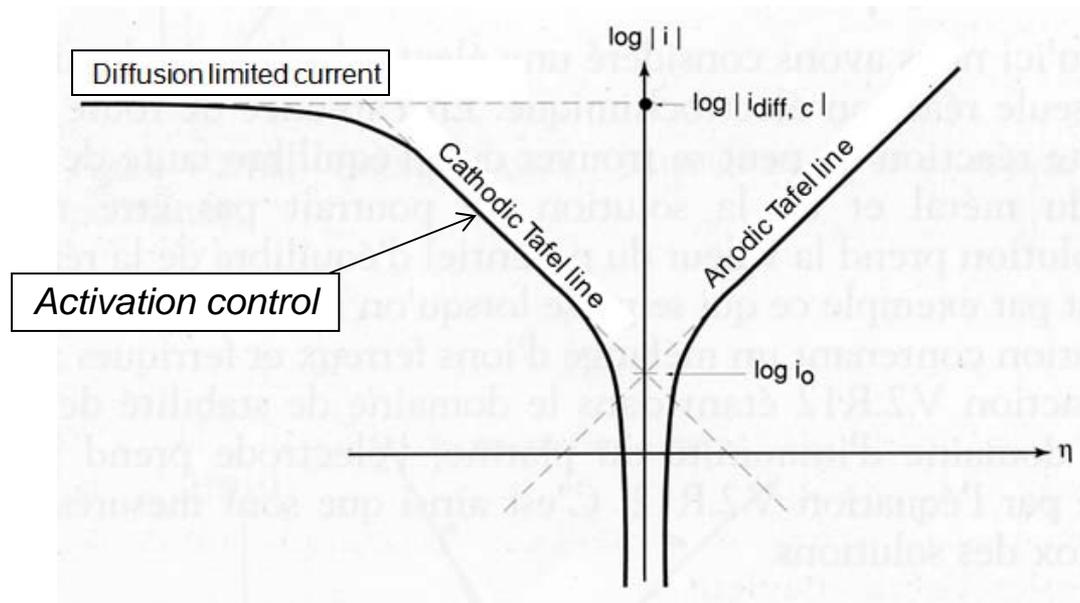
C_0 is the concentration at the M/S interface

- ◆ Assuming diffusion of a reactant is rate controlling, the maximum current corresponds to complete depletion at the interface

$$I = zF D \frac{C_{\text{bulk}}}{\delta}$$



► Example of diffusion control of the cathodic reaction



► Examples

◆ Oxygen reduction

- Available maximum current increases with
 - Concentration of dissolved O_2
 - Flow rate, which decreases the thickness of the diffusion layer δ

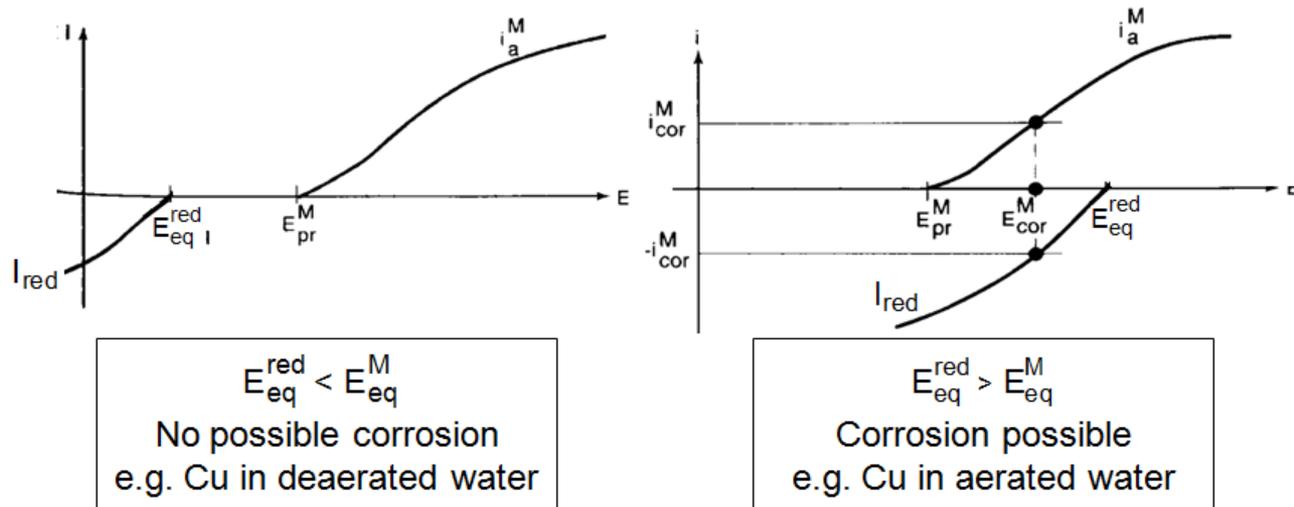
◆ Corrosion under deposits

- Corrosion limited by diffusion of corrosion products through deposit pores

Aqueous corrosion

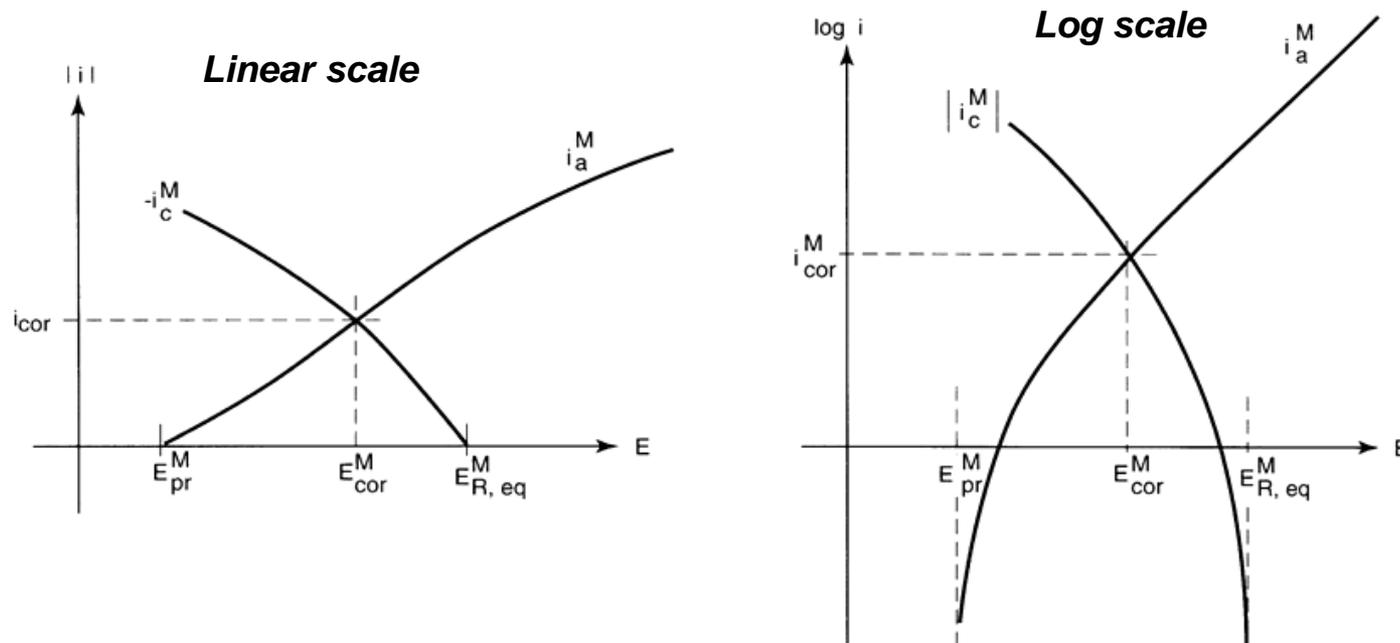
Corrosion = oxidation + reduction

- ▶ Corrosion is possible only if a solution contains an oxidising species that is able to oxidise a metallic material;
i.e. whose equilibrium potential is higher than the protection potential



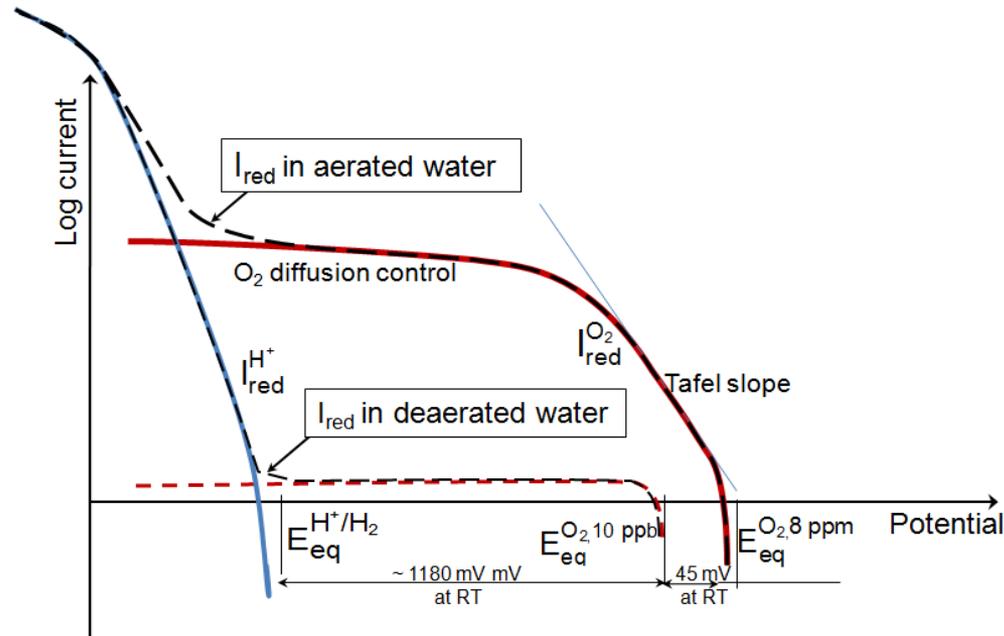
- ▶ If corrosion is possible, the metal/solution potential becomes a mixed potential such that $i_a = i_c$
 - ◆ This potential E_{cor} is called the “corrosion” or “free corrosion” potential
 - ◆ It has no thermodynamic significance

- ▶ Graphical representation of the absolute values of anodic and cathodic currents on linear or log axes that allows immediate visualisation of the corrosion potential



Main cathodic reactions in aqueous corrosion

- ▶ Reduction of protons (or water) and of dissolved oxygen



- ▶ Deaeration:

- ◆ Water with less than 10 ppb of oxygen can generally be considered as deaerated
- ◆ However, compared to aerated water (8 ppm O₂), the equilibrium potential for O₂ reduction decreases by only ~ 45 mV at RT
- ◆ The effect of deaeration of water on corrosion potential
« is not thermodynamic » but « kinetic »
 - In deaerated water, O₂ redox is still very high but the available cathodic current is negligible due to diffusion control

- ▶ In low temperature water,
 - ◆ Protons or water can be reduced relatively easily although the exchange current density can vary by several orders of magnitude depending on the nature of metal surface
 - ◆ However, oxidation of dissolved H₂ rarely occurs at a significant rate

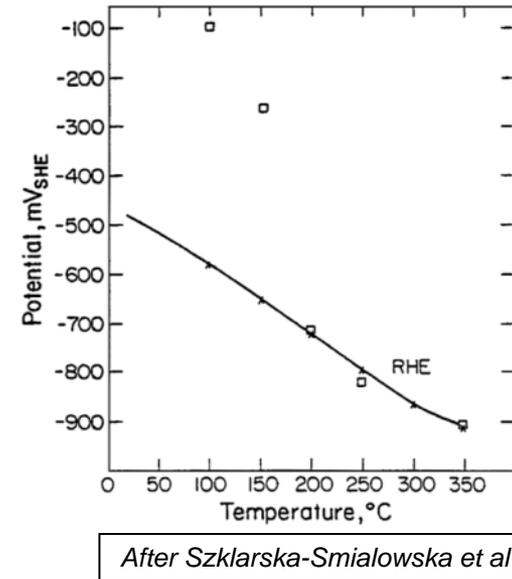
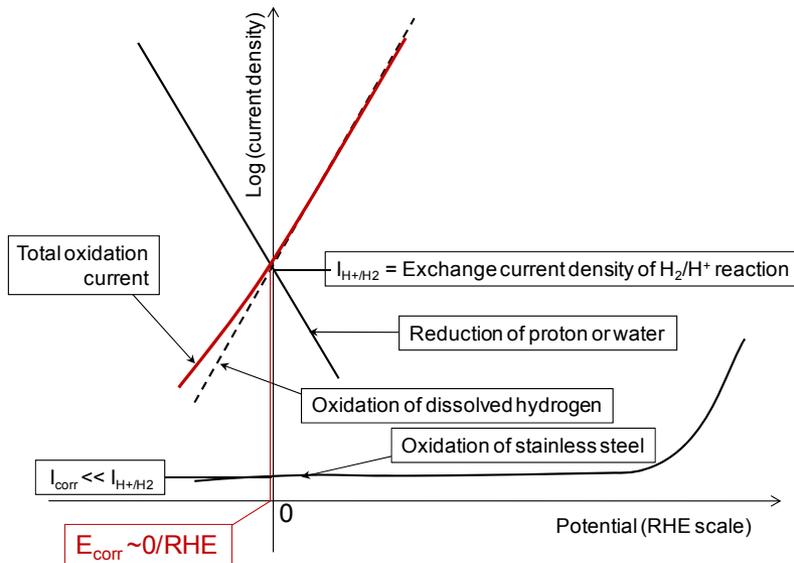
- ▶ In HT water,
 - ◆ The exchange current densities for proton reduction or water reduction on Fe-Cr-Ni alloys are much larger than at room temperature, $i_0 > 10^{-6} \text{ A/cm}^2$, and much larger than the oxidation currents of Fe and Ni base alloys
 - ◆ Oxidation of dissolved H₂ occurs at significant rate
 - ◆ This has several important consequences

Proton or water reduction in HT water

► In HT water (cont'd)

◆ This has several important consequences

- The corrosion potential of Fe-Cr-Ni alloys in deaerated water
 - is always very close to the equilibrium potential of the reduction reactions of protons or water and it can be easily calculated by using the Nernst equation applied to this equilibrium provided $[H_2]$ and pH are known (see PWR primary water)

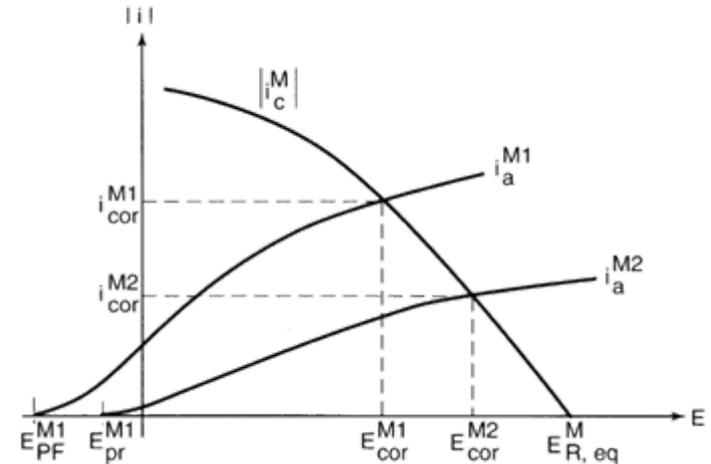


- Added H_2 to BWR coolant effectively combines with any dissolved O_2 to form water and leads to a lower corrosion potential.
This is the basis of the BWR Hydrogen Water Chemistry

Active corrosion and passivity

► Depends both on the anodic characteristic of the material and on the availability of cathodic current

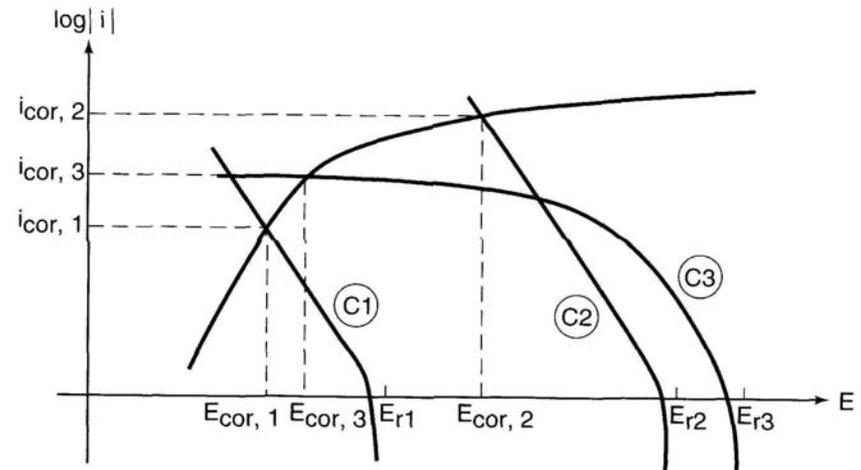
- ◆ For a given cathodic reaction, the higher the corrosion rate, the lower the corrosion potential



- ◆ For a given anodic dissolution characteristic, the corrosion rate depends on the cathodic reaction rate and the higher the corrosion rate, the higher the corrosion potential

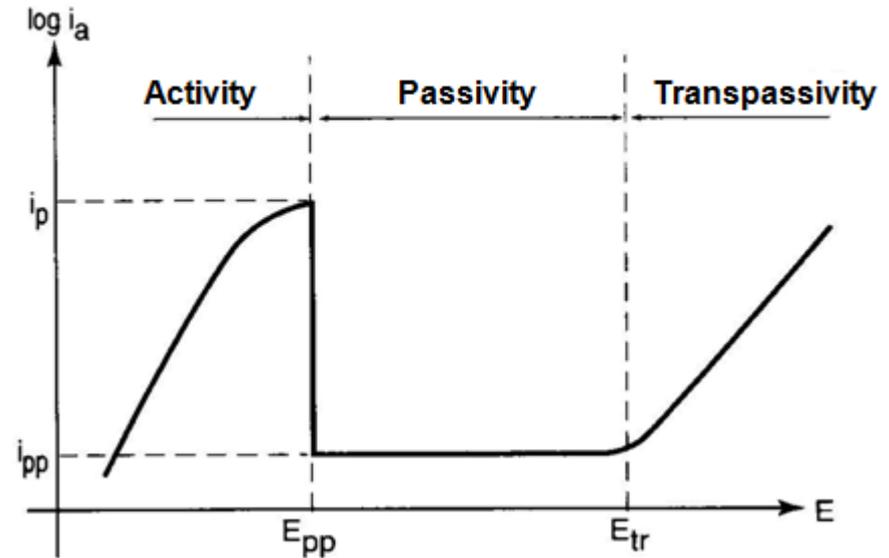
Warning – the efficiency of a cathodic reaction is not necessarily related to a high redox potential but rather to

- High exchange current density
- High mass transport rate

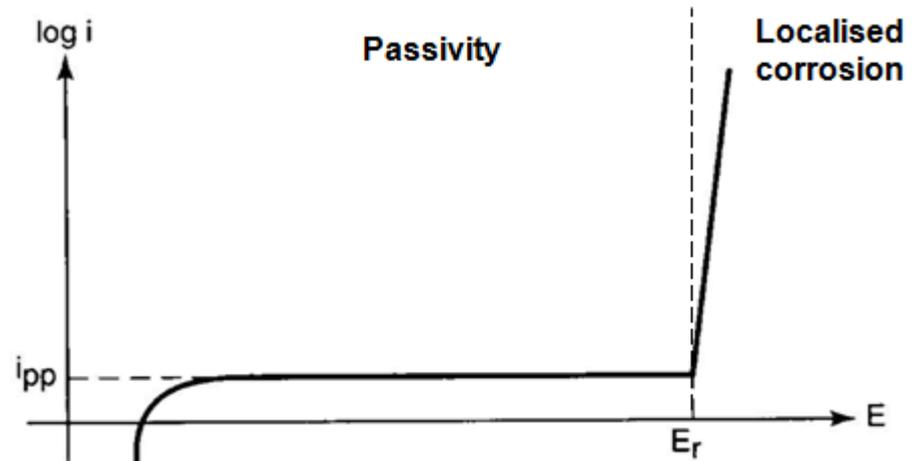


► Anodic characteristic of a passivating material

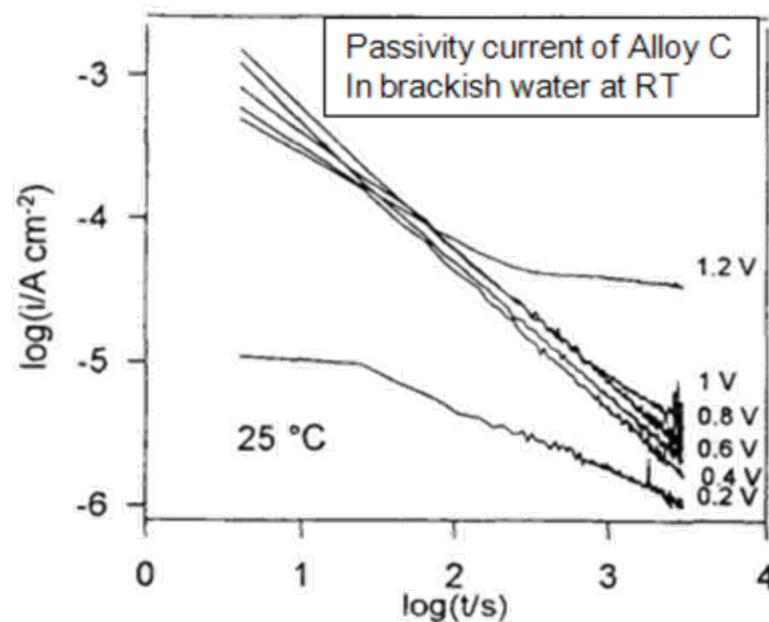
- ◆ Acidic environment – no localised corrosion



- ◆ Neutral environment localised corrosion

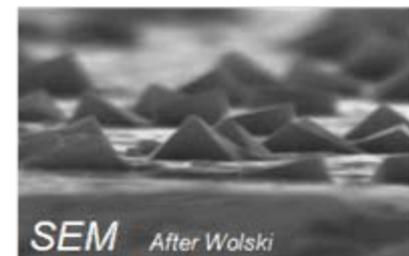
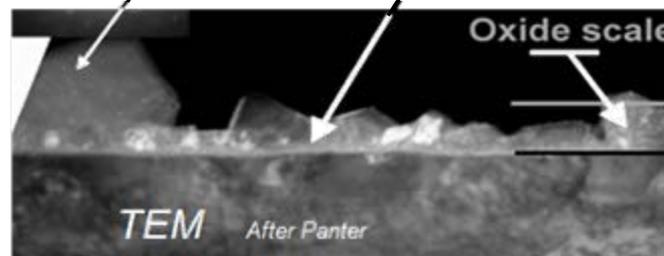
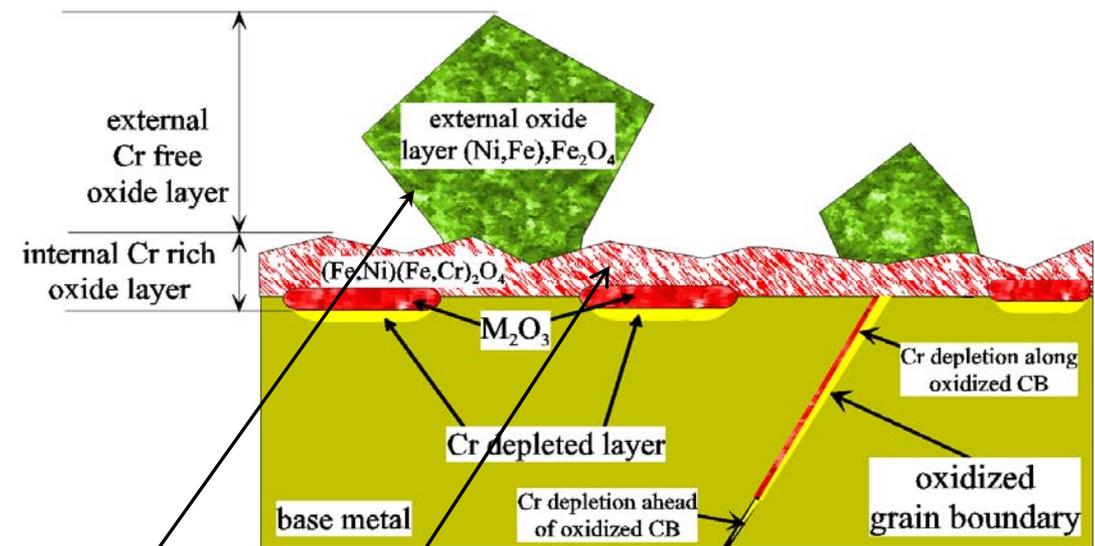


- ▶ Passivity = the spontaneous formation of a compact, protective surface oxide film that strongly limits the oxidation rate of a metallic material
 - ◆ In low temperature environments, passive films are generally very thin, i.e. few nm to tens of nm
 - ◆ e.g. on stainless alloys in room temperature water
 - Duplex films ~ 3 nm
 - Cr rich inner layer, probably crystallised
 - Fe-Cr rich hydrated outer layer
 - almost no Nickel in passive films
 - Film formation in a few ms
 - Log current often decreases as $\sim -\log t$



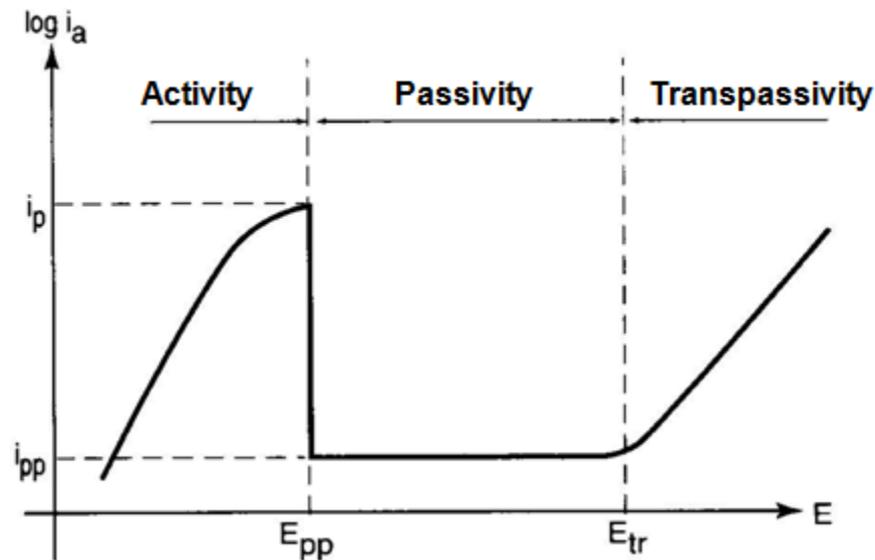
Passivity in high temperature water

- ▶ Nature of protective films changes between 150 and 200 °C
- ▶ In HT water, oxide films are
 - ◆ Thicker
 - Mass transport controlled by chemical gradients rather than by potential gradients
 - No electron tunnelling
 - ◆ Well crystallised
 - ◆ Less (or not) hydrated
 - ◆ Film repair much slower
- ▶ E.g. Ni alloys and SSs in PWR primary water
 - ◆ Duplex oxide film
 - Inner Cr-rich oxide
 - Grown by solid state reactions and transport
 - Outer Cr-free oxide
 - Re-deposited



► Good « quality » of passivity implies:

- ◆ Low passivation current I_{pp}
 - Equivalent to tens of nm/y in near neutral environments to hundreds of $\mu\text{m}/\text{y}$ in acidic environments
- ◆ Low passivation current density, I_p :
 - Easier passivation
- ◆ Large passivity domain ($E_{tr} - E_{pp}$) or ($E_{tr} - E_r$)
- ◆ **Easy and fast film repair**
 - Very important for resistance to SCC and also to localised corrosion

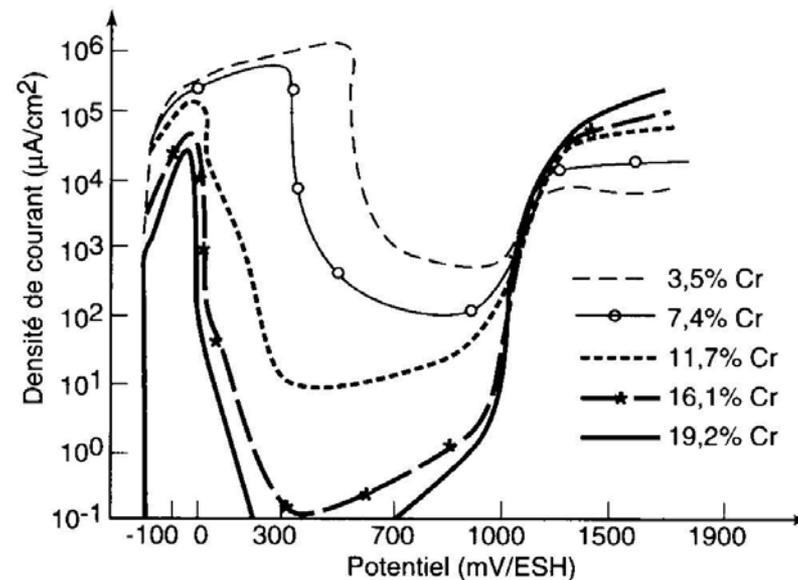
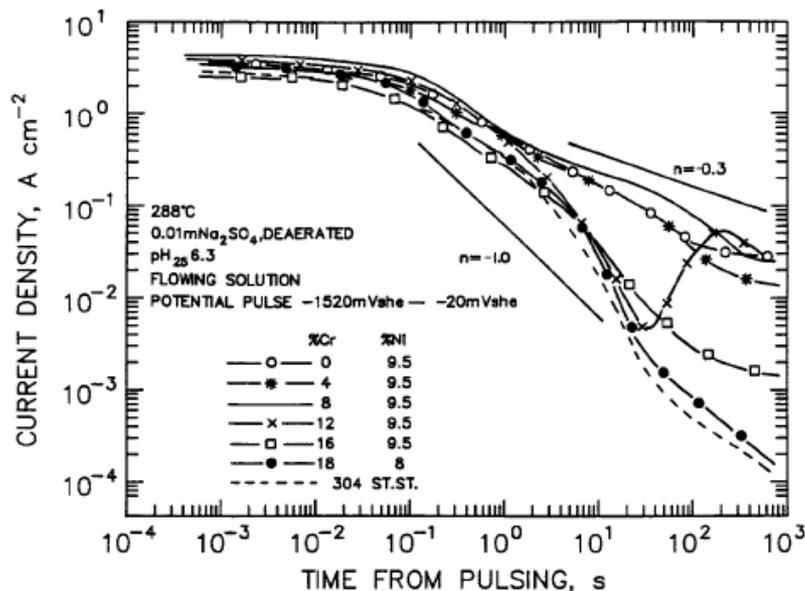


► Example of stainless steels:

◆ Effect of Cr content on « quality » of passivity

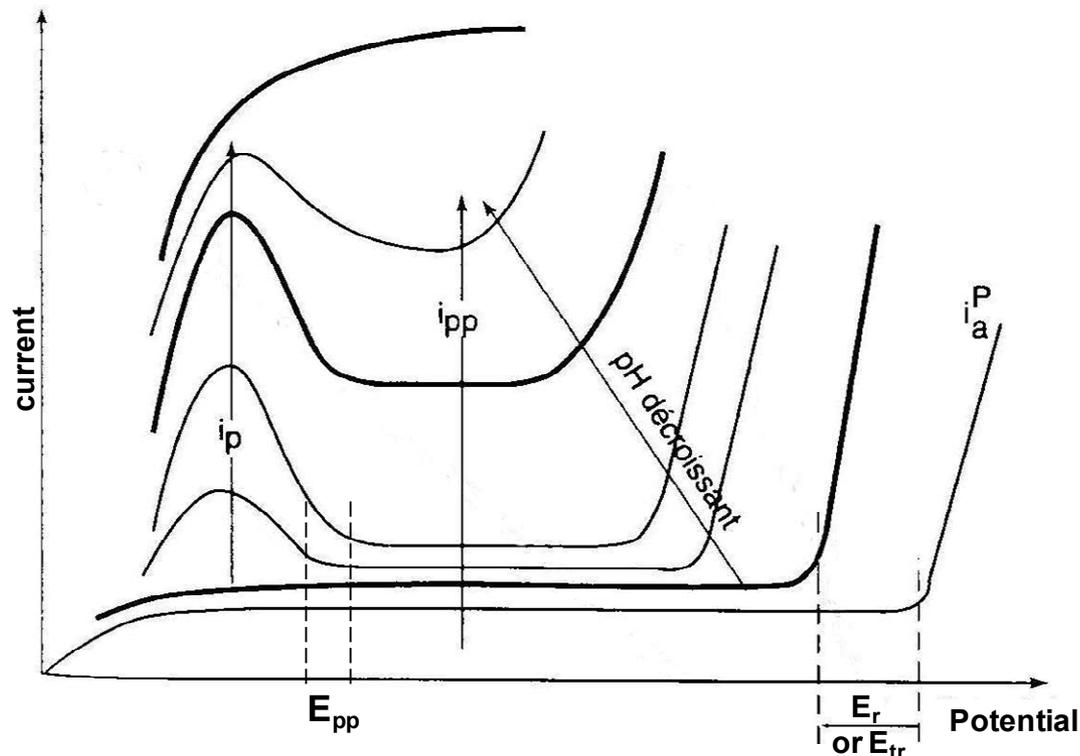
- Polarisation curves in sulphuric acid solution at ambient temperature

- Film repair transients in HT water (from Ford)



Effect of environment on passivity

- ▶ In general, a drop in pH and an increase in temperature lead to degradation of passivity:
 - ♦ increase of passivation current
 - ♦ appearance of an activity peak and increase of passivation current, i_p
 - ♦ decrease of the critical potential for localised corrosion E_r
 - ♦ decrease of the passivity domain ($E_{tr} - E_{pp}$) or ($E_r - E_{pp}$)
 - ♦ for very acidic pH, no stable passivity

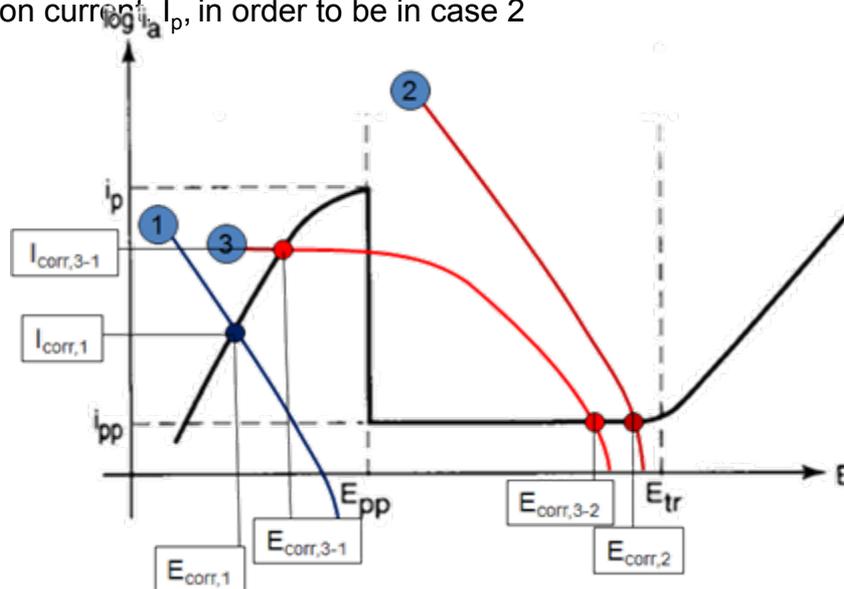


► Behaviour of passivating materials in acidic environment depends on the cathodic reaction:

1. poorly oxidising environment → active corrosion
2. highly oxidising environment → passivity
3. oxidising environment with mass transport limitation
 - 3.1. Pre-passivated surfaces → passivity
 - 3.2. Non pre-passivated surfaces → active corrosion
 - However, local destruction of passivity may cause activation

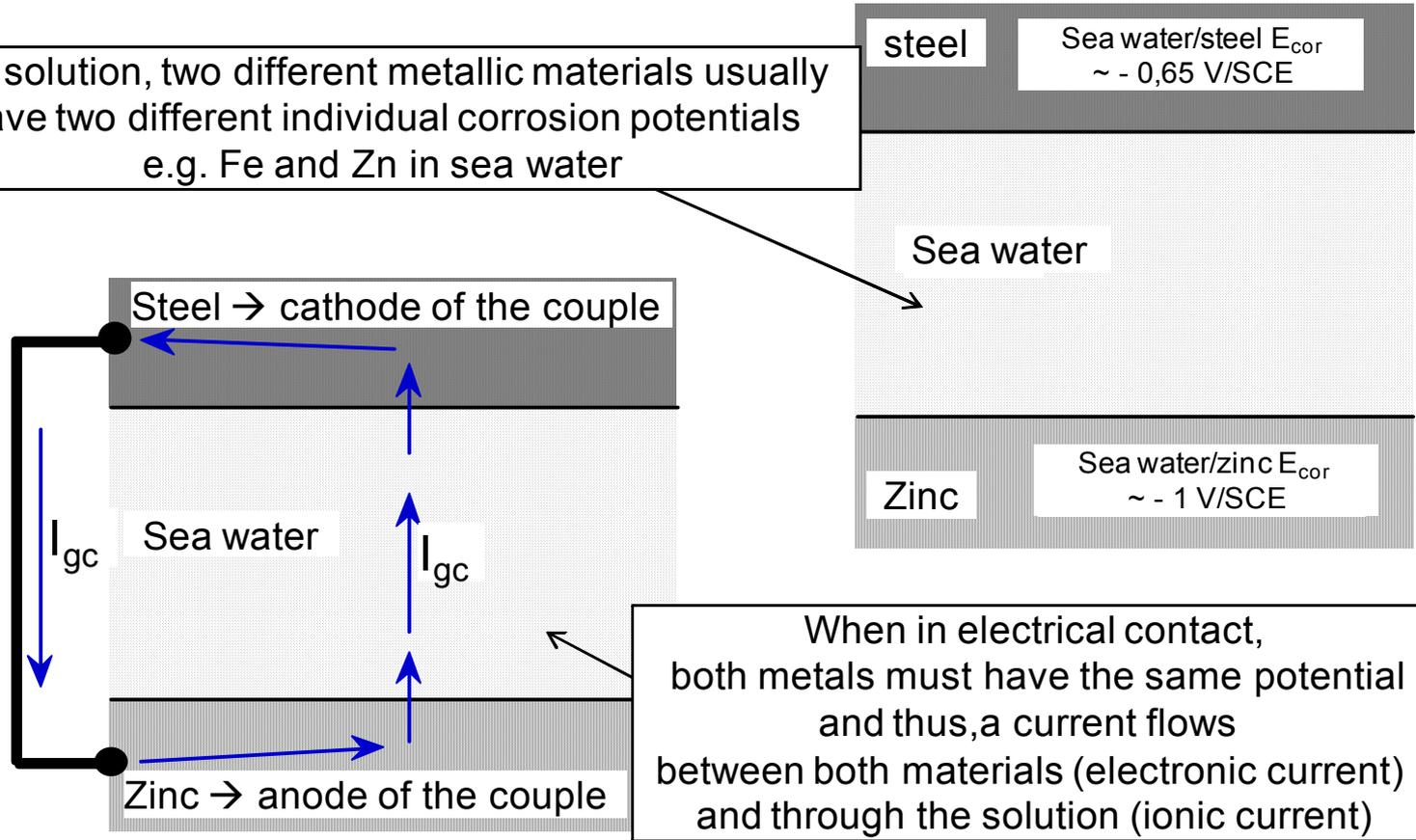
◆ Typical example: transport of sulphuric acid in SS tanks

- Deaerated solution → activity (case 1) → forbidden
- Aerated solution → passivity but risks of activation (case 3) → limitation of temperature to decrease passivation current i_p , in order to be in case 2



Galvanic coupling

In a solution, two different metallic materials usually have two different individual corrosion potentials e.g. Fe and Zn in sea water



- The more noble material has a global cathodic current and becomes the cathode of the galvanic couple
- The less noble material has a global anodic current and becomes the anode of the galvanic couple

Consequences of galvanic coupling

Galvanic coupling implies:

1. Partial “dissociation” of anodic and cathodic reactions

- Excess of anodic current on anode (A) $I_a^A > I_c^A$
- Excess cathodic current on cathode (C) $I_a^C < I_c^C$
- Cathode supplies cathodic current that can « feed » corrosion of the anode

2. Increase in anode potential → increased corrosion rate of active anode

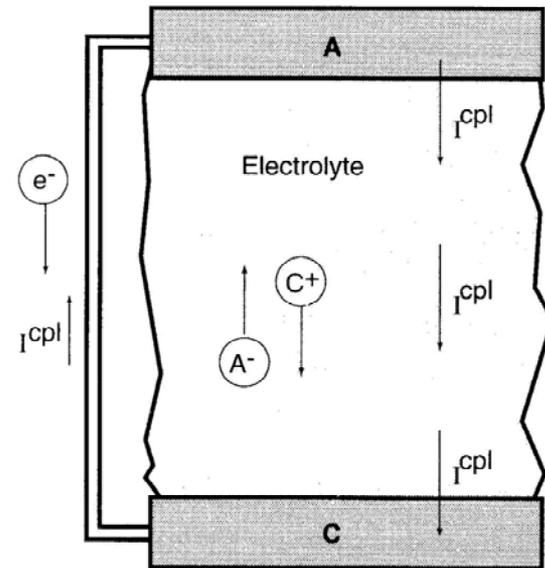
3. Decrease in cathode potential → decreased corrosion rate of active cathode

- See cathodic protection

4. Galvanic current in the liquid →

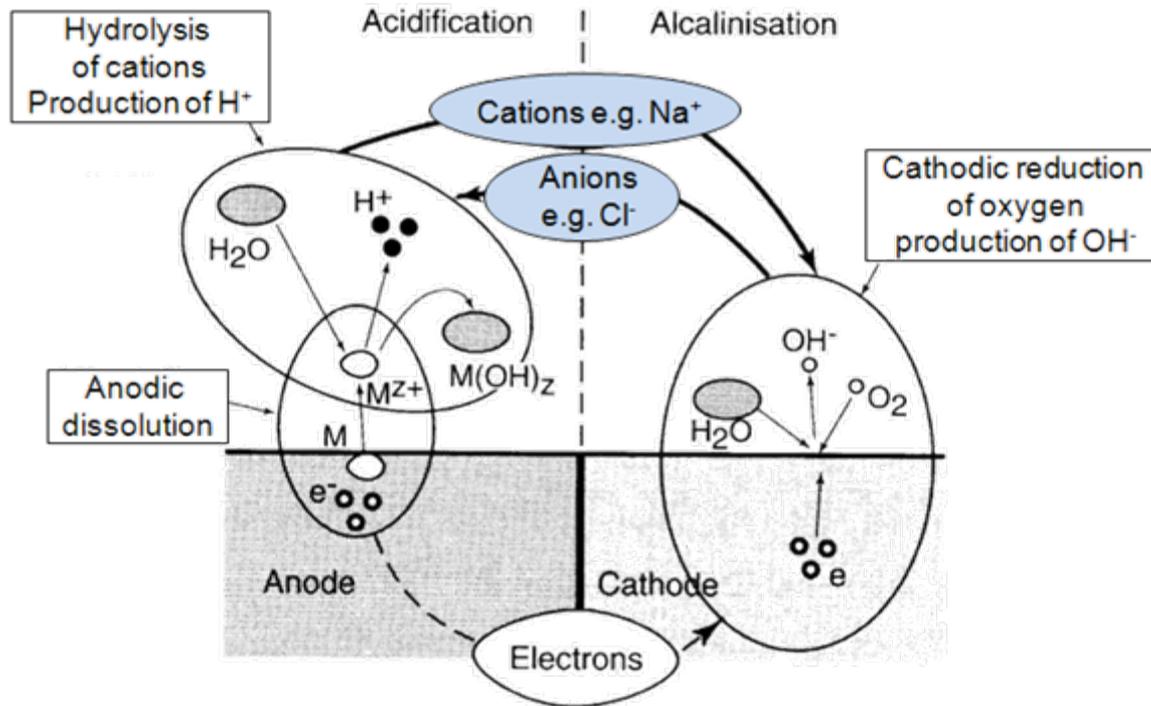
Mass transport in the solution

- Cations migrates towards cathode
- Anions migrates towards anode



Mass transport due to galvanic coupling

- ▶ Partial « dissociation » of anodic and cathodic reactions and consequent galvanic current → **modification of local environments**
 - ◆ **pH drop near the anode**
 - e.g. Very low pH in occluded cells of localised corrosion
 - ◆ **pH increase near the cathode**
 - → precipitation of Ca-Mg based deposits on cathodically protected components in sea water



Localized corrosion

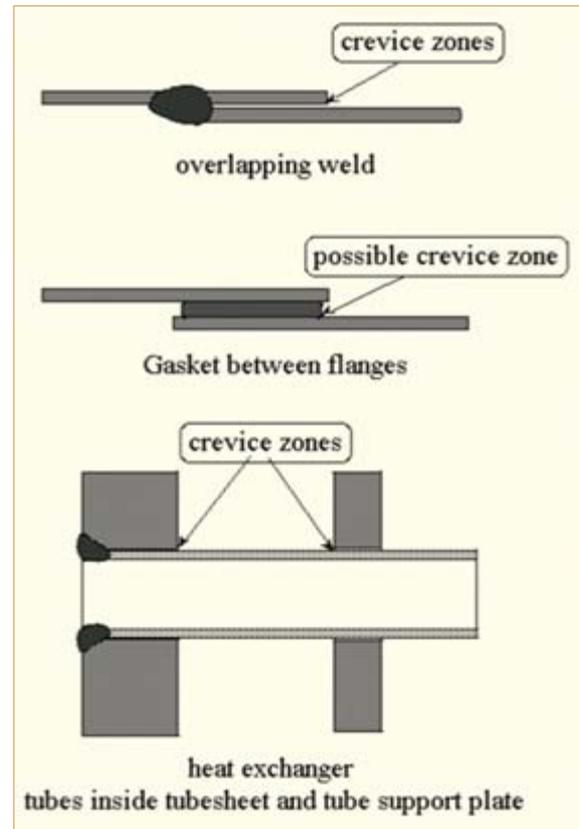
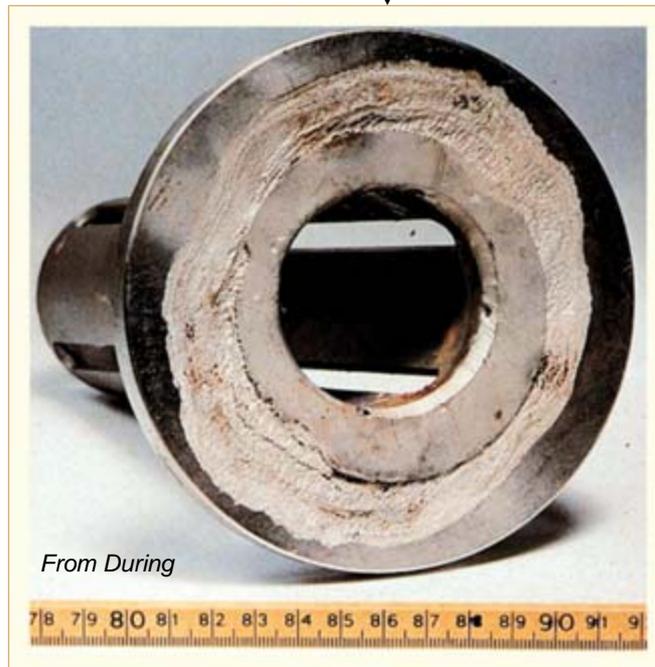
► Pitting

- ◆ Localised dissolution on free surfaces
- ◆ Example : type 304 L SS in water containing ~100 ppm Cl⁻ and unidentified sulphur species



► Crevice corrosion

- ◆ Localised dissolution in confined zones or under deposits
- ◆ Example – type 316 SS under a gasket seal in brackish water

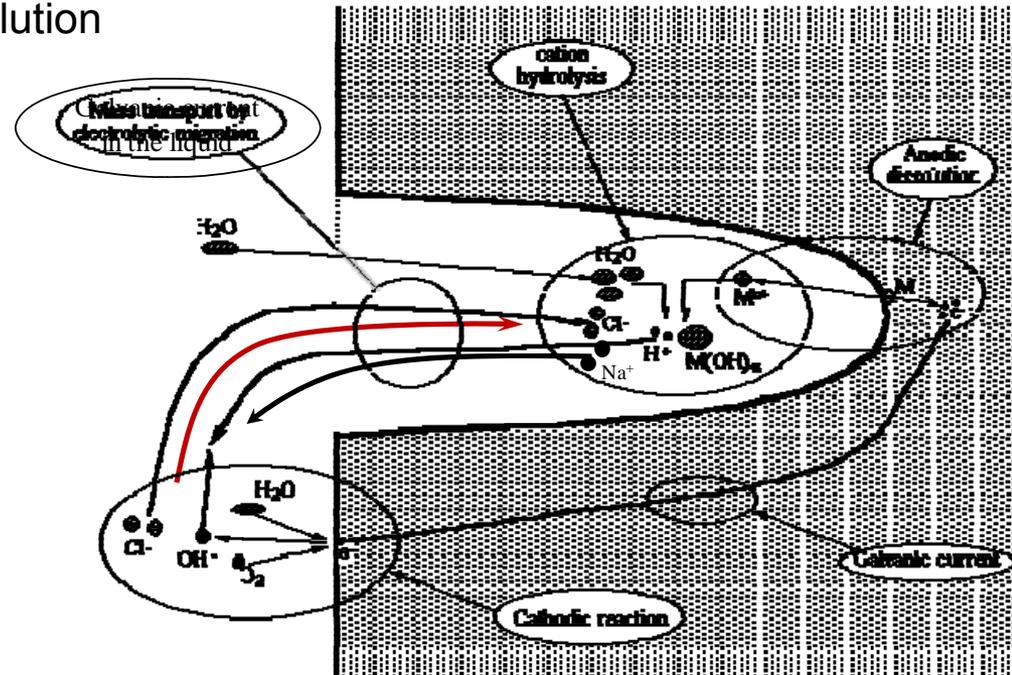


Basic mechanism of localised corrosion

► Galvanic coupling between an **occluded cell with** no oxidising species other than water (i.e. no dissolved O_2) and an external passive surface where reduction of an oxidising species is possible to « drive » anodic dissolution inside occluded cell

- ◆ Galvanic current flows in the liquid from the outside surface towards the occluded cell
 - Cations diffuse out of the occluded cell (mostly Na in Na Cl solutions)
 - Anions diffuse towards the occluded cell (mostly Cl^- in NaCl solutions)
- ◆ In the occluded cell
 - Anodic dissolution \rightarrow Hydrolysis of cations \rightarrow production of H^+
 - No or slow reduction of protons \rightarrow no or low consumption of H^+

\rightarrow formation of concentrated, low pH solution that impair or inhibits passivation in the occluded cell



Environmentally Assisted Cracking (EAC)

▶ Stress Corrosion Cracking

- ◆ Cracking resulting from simultaneous action of a corrosive environment and a static stress field with at least one tensile component

▶ Corrosion-fatigue

- ◆ Decrease of fatigue strength in the presence of an environment
 - Decreased or no endurance limit
 - Increased crack propagation rates

▶ Hydrogen embrittlement

- ◆ Degradation of mechanical properties of the material due to dissolved hydrogen
 - Rupture under static or dynamic loading
 - Possibility of rupture without applied stress → HIC (blistering)
 - Material can be damaged by hydrogen before loading

▶ Liquid Embrittlement (LME)

- ◆ Fast cracking, generally intergranular, of some metal or some alloys exposed to molten metals.
 - Ex SS embrittled by Zn or Cu

▶ Oxidation-fatigue or creep oxidation

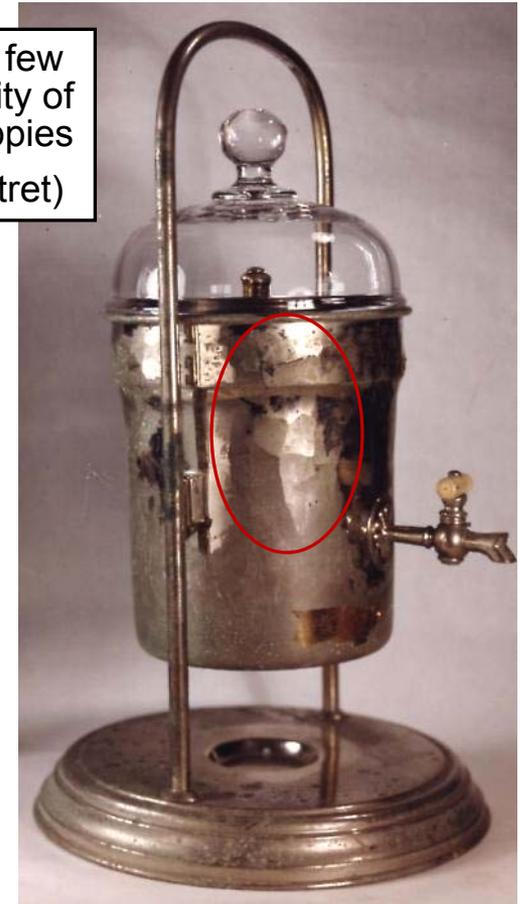
- ◆ Degradation of resistance to fatigue or creep by exposure to oxidizing gaseous atmospheres

Stress corrosion cracking

- ▶ Copper alloy in the presence of ammonia
 - ◆ Ex: Cu alloys in presence of ammonia

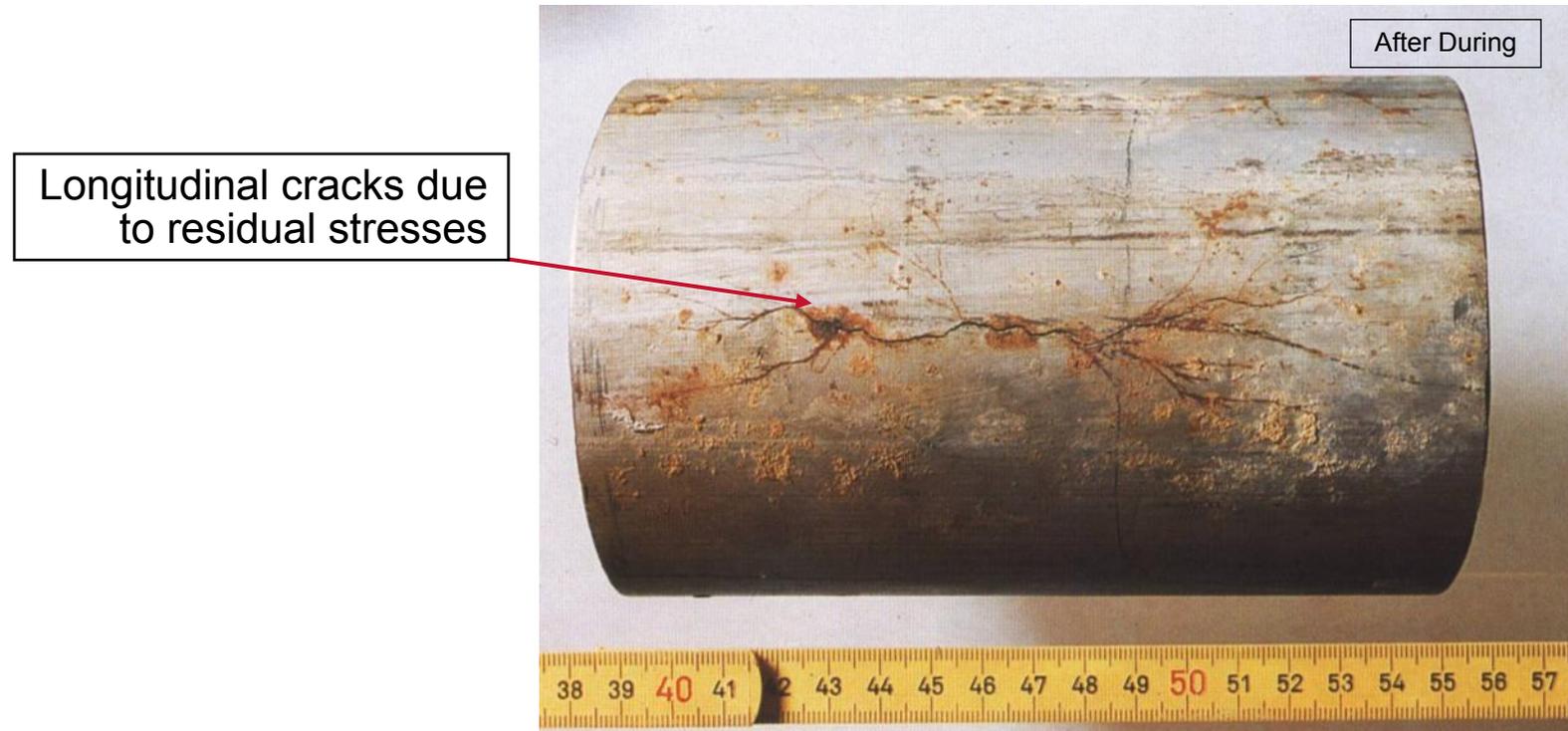
Coffee pot left for a few days in the vicinity of « polluted » baby nappies
(After A. Désestret)

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



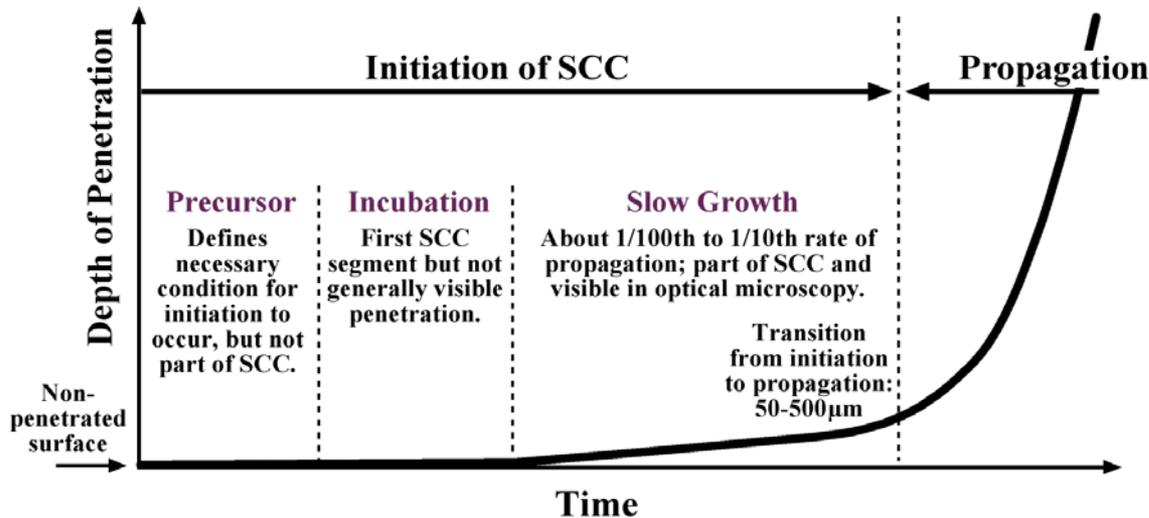
Stress Corrosion Cracking

- ▶ Ex: Type 316 SS under insulation (after During)
 - ◆ Penetration due to rinsing water with 60 ppm Cl⁻
 - ◆ Temperature 50-60 °C
 - ◆ SCC in a few months



Initiation and propagation

- ▶ SCC failures occur at the end of a sequence of events that is usually separated into initiation and propagation
- ▶ However, definition of « initiation » is not trivial and depends both on the scale and scope of observation



(no penetration)

Time associated with developing conditions necessary for initiation but does not propagate SCC: e.g.,

- Accumulation on superheat surfaces
- Lead accumulation
- Depletion of alloy species
- Surface abuse

Incubation (negligible penetration)

Time for incubation process to lead to slow growth, e.g.

- Intergranular penetration
- Change in film composition
- Local creep

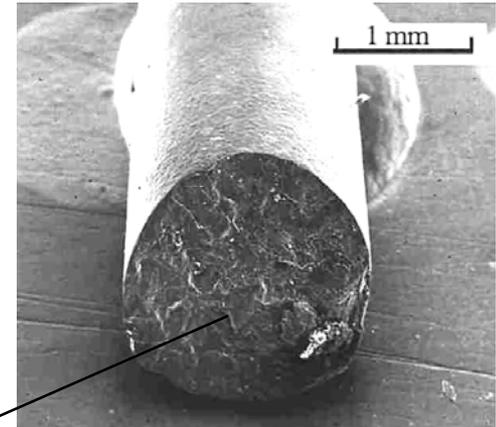
Slow Growth (slow and small penetration)

- Penetration of SCC to range of 50-500µm
- Rate much lower than propagation.
- Up to early coalescence

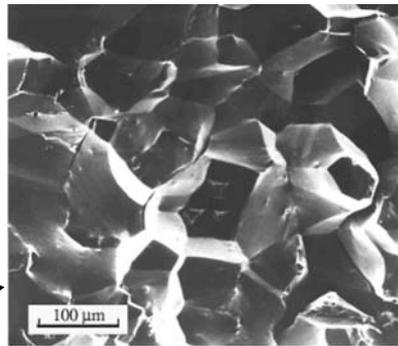
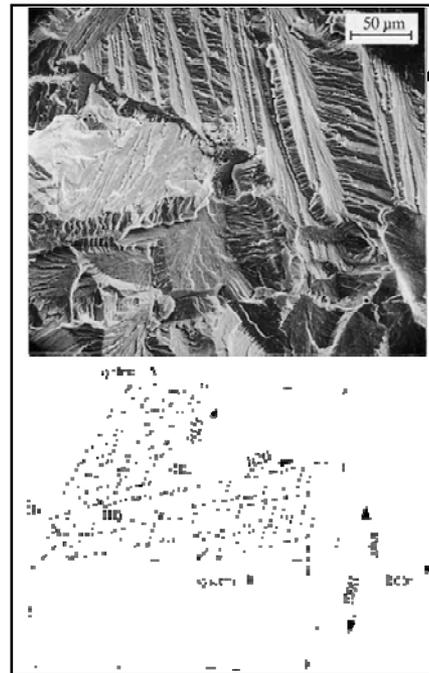
After Staehle

Crack morphology

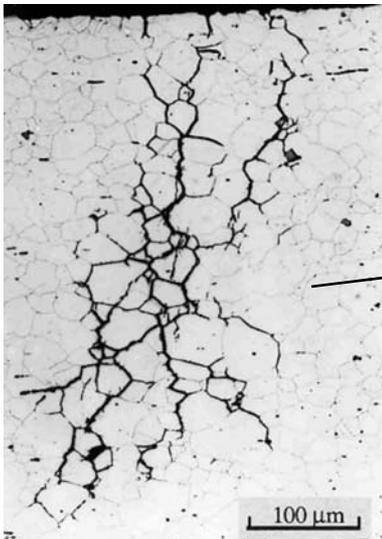
- ▶ Cracking generally perpendicular to the highest principal stress
- ▶ Brittle appearance even in very ductile materials
- ▶ Cracks can be intergranular, transgranular or mixed



Type 304 Stainless Steel
in boiling $MgCl_2$ solution



Intergranular Crack
of Type 904L Stainless Steel
in 50 % NaOH solution, at 200 °C



Intergranular Crack
of Type 316-Ti Stainless Steel
in 10 % NaOH solution, at 200 °C



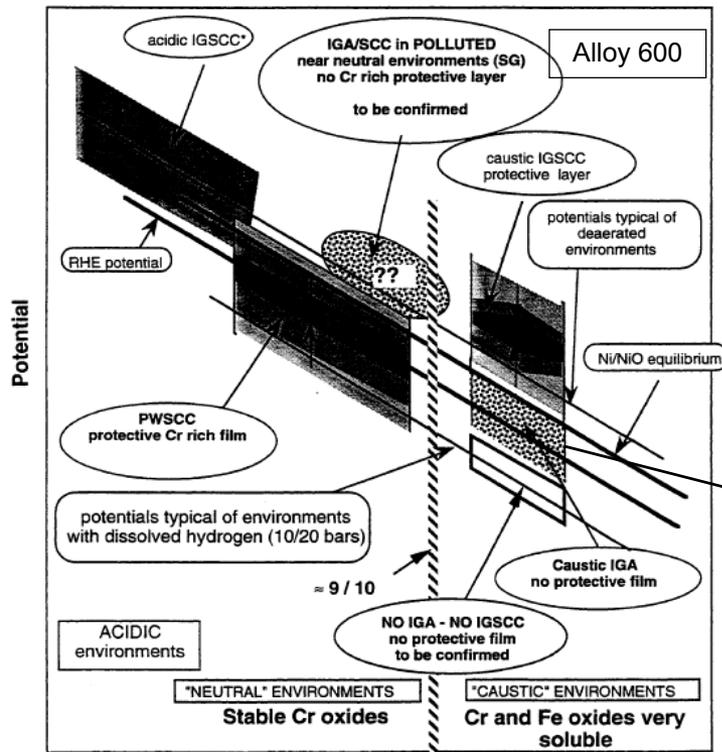
Transgranular Crack of Type 304 Stainless Steel
in aerated (8 ppm O_2)
chloride (100 ppm Cl^-) solution, at 200 °C

Some SCC systems of practical importance

Material	Environment	Temperature
Carbon Steels	<ul style="list-style-type: none"> - Caustic solutions - Carbonates-bicarbonates - Nitrates - Liquid ammonia 	<ul style="list-style-type: none"> > 80 °C ≥ RT ≥50/60 °C RT
Austenitic Stainless Steels	<ul style="list-style-type: none"> - Near neutral, diluted aerated chloride solutions - Very acidic chloride solutions - Chloride env. containing H₂S - Caustic solutions 	<ul style="list-style-type: none"> > 60/100 °C ≥ RT ≥ RT ≥ 80/120 °C
Ni-Base Alloys	<ul style="list-style-type: none"> - Caustic environments 	<ul style="list-style-type: none"> ≥ 100/200 °C
Ni-Base Alloys < 25-30 % Cr	<ul style="list-style-type: none"> - Deaerated, hydrogenated water 	<ul style="list-style-type: none"> ≥ 250/280 °C
Sensitized Stainless Steels and Ni-Base Alloys	<ul style="list-style-type: none"> - Aerated « pure » water - Solutions containing reactive sulfur species (polythionic acids, thiosulfates, thiosulfates, ...) 	<ul style="list-style-type: none"> ≥ 60/100 °C ≥ RT
Cu Alloys	<ul style="list-style-type: none"> - ammoniacal solutions 	<ul style="list-style-type: none"> RT
Al Alloys	<ul style="list-style-type: none"> - chloride environments 	<ul style="list-style-type: none"> RT
Ti Alloys	<ul style="list-style-type: none"> - alcoholic chloride solutions 	<ul style="list-style-type: none"> RT
Zr Alloys	<ul style="list-style-type: none"> - gaseous iodine and dissolved iodide 	<ul style="list-style-type: none"> RT

Preferential domains of cracking

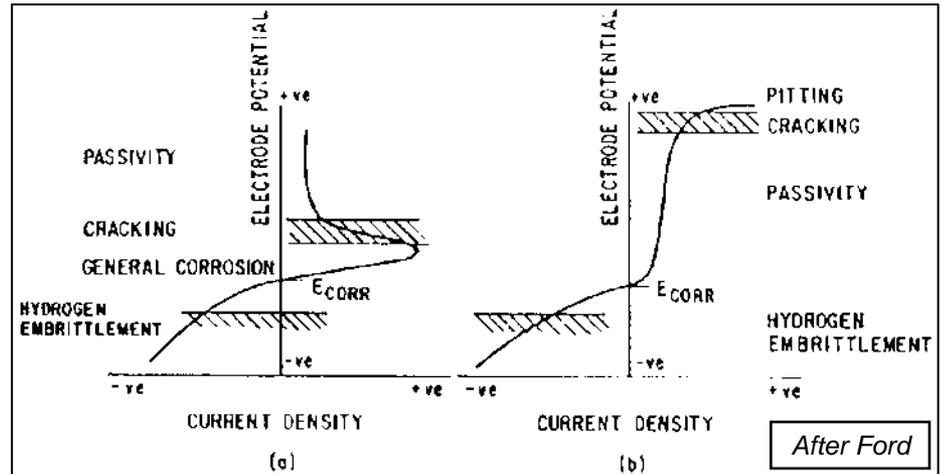
- ▶ In many cases SCC occurs in a limited domain of potentials often (but not always) corresponding to the onset of instability of protective films
 - ◆ Active-Passive transitions
 - ◆ Near localized corrosion potentials
 - ◆ Ex of Alloy 600 in HT environments



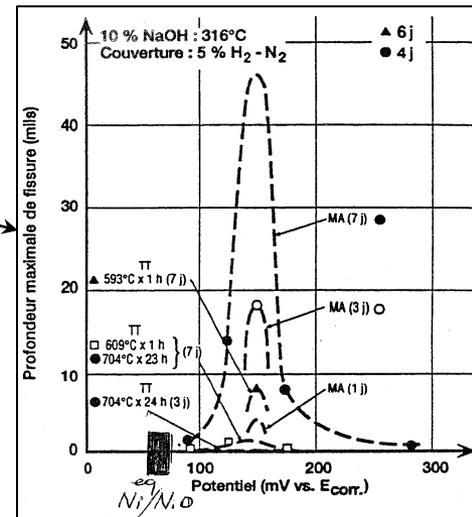
Arrows indicate an increase of the susceptibility to cracking

* The domain of acidic IGSCC is not very well established and it could be extended to lower potentials

After Combrade



After Ford



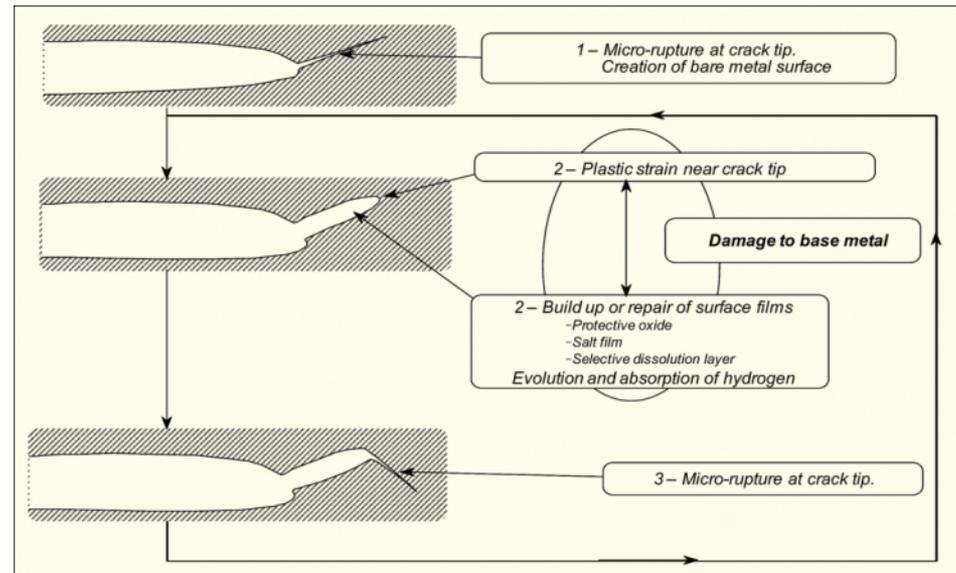
After Pessal

- ▶ **There is not a single mechanism responsible for all SCC phenomena**
- ▶ Most proposed mechanisms account better for crack propagation than for crack initiation
- ▶ Mechanisms for SCC in « low temperature » aqueous environments assume no mass transport in the base metal (except hydrogen)
- ▶ **Mechanisms for SCC in « high temperature » water should look at mass transport issues and subsequent damage in the base metal**
 - ◆ See “internal oxidation “ model for alloy 600

► Two basic classes of mechanisms

- ◆ Crack advance due to metal removal by dissolution (or oxidation)
 - Slip-dissolution (slip-oxidation) → see Peter Ford presentations
 - Stress Assisted IG corrosion (oxidation)
 - Probably the case of IGSCC of sensitized Stainless Steels and Ni-base Alloys by reactive sulfur species (polythionates, thiosulfates, ...)
 - Possibly at the origin of PWSCC even though GB embrittlement may be more complex
- ◆ Crack advance by micro-cracking which may be due to
 - Hydrogen embrittlement
 - Cleavage induced by the rupture of a nanoporous surface layer
 - Change of surface energy due to adsorption (not relevant for very ductile alloys)
 - Embrittlement due to the formation of nanovoids by vacancy condensation ???
 - See Arioka results for Low Alloy and Stainless Steels

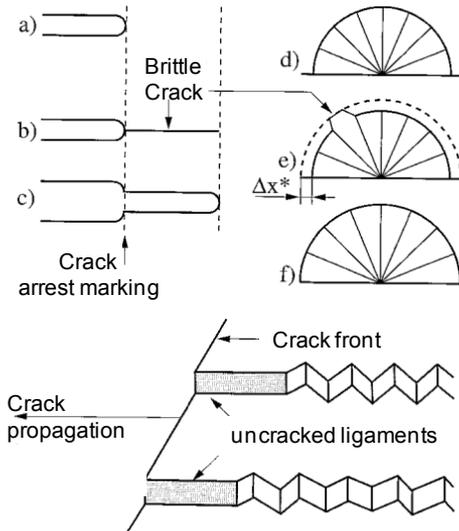
This type of mechanisms involves a repeated sequence of events



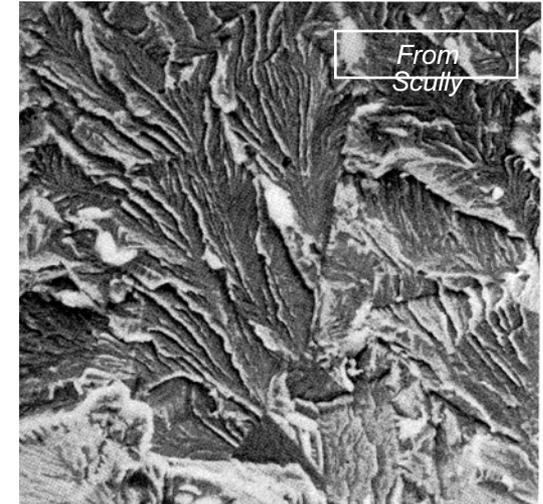
Possible SCC mechanisms

► Crack advance by micro-cracking (cont'd)

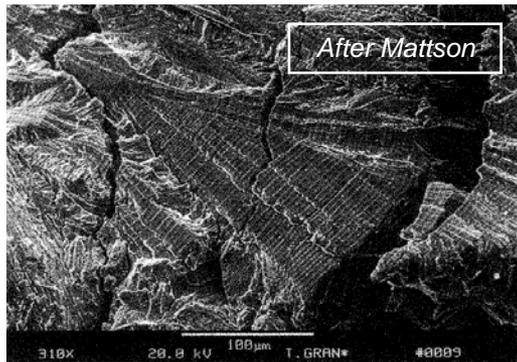
- ◆ Consistent with "fans" and "river markings" observed on many TG crack surfaces and with crack arrest markings on TG cracks



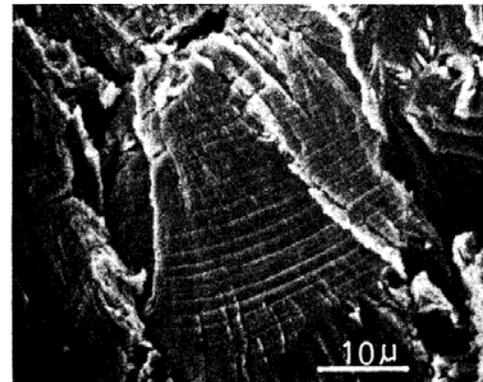
Stress Corrosion Crack surface
a Cu-Au alloy in NaCl solution



Crack surface on a Type 304 SS
exposed to a boiling $MgCl_2$ solution:
Note ductile tearing of ligaments
between brittle micro-cracks



Crack arrest markings on 70-30 brass
tested in pH 7.2 Mattson's solution



Crack arrest markings on
Type 304 SS exposed to
100 ppm Cl^- solution, at 288 °C
After Andresen and Duquette

Processes involved in crack propagation

▶ Surface reactions

- ◆ Dissolution
- ◆ Passive film build-up and/or repair
- ◆ Adsorption
- ◆ Reduction of protons
- ◆ Formation of brittle nanoporous layers by selective oxidation or dissolution

▶ Reaction and mass transport in the liquid phase

- ◆ Cation hydrolysis
- ◆ Electromigration of anions from and cations towards the bulk solution
 - Change in local environment → impurity concentration, pH and potential change

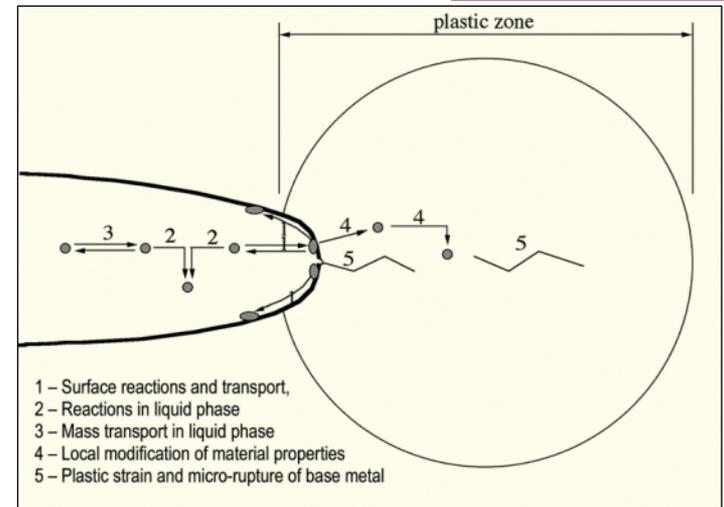
▶ Local modification of metal properties

- ◆ Hydrogen absorption → embrittlement and/or enhanced plasticity
- ◆ Vacancy injection, possibly stabilized by the presence of hydrogen
- ◆ IG oxidation or embrittlement

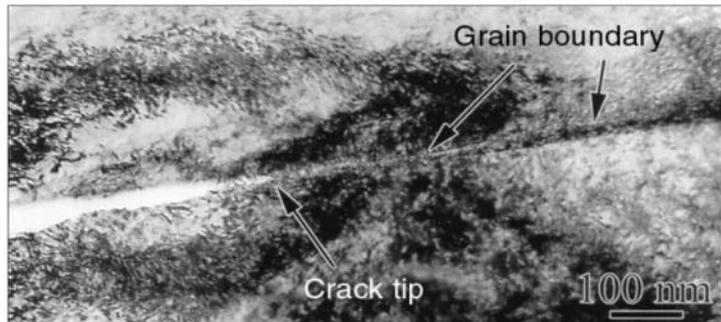
▶ Creep or relaxation possibly leading to periodical rupture of protective films

▶ Micro-cracking

- ◆ Surface layers
 - Protective films → slip-dissolution mechanism
 - Nanoporous layers created by selective oxidation or dissolution → film induced cleavage
- ◆ Base metal
 - Embrittled of base metal or GBs
 - Film induced cleavage



- ▶ TEM of SCC crack tips on austenitic materials cracked in HT water often shows radii much smaller than expected from linear elastic mechanics.
 - ◆ Pugh invoked the presence of uncracked ligaments behind crack front
 - ◆ Magnin suggested that crack tip dissolution (oxidation) along slip planes could cause preferential emission of dislocations from the surface (zone A) that maintains a propagating SC crack tip that is sharper than that of an uncorroded crack tip
 - ◆ Lynch suggested that hydrogen adsorption could weaken atomic bonds and promote the preferential emission of dislocations that tend to sharpen crack tips



PWSSC of Alloy 600: TEM examination showing very narrow crack tip with extensive plastic deformation

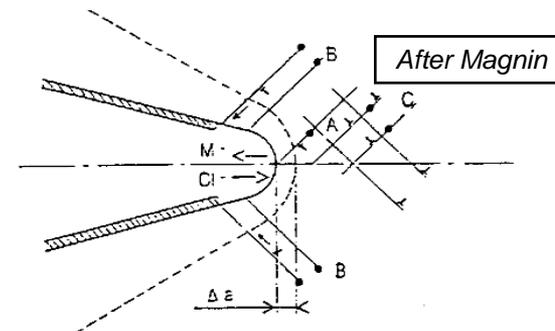


Fig. 7a. Schematization of the crack tip dislocation behaviour.

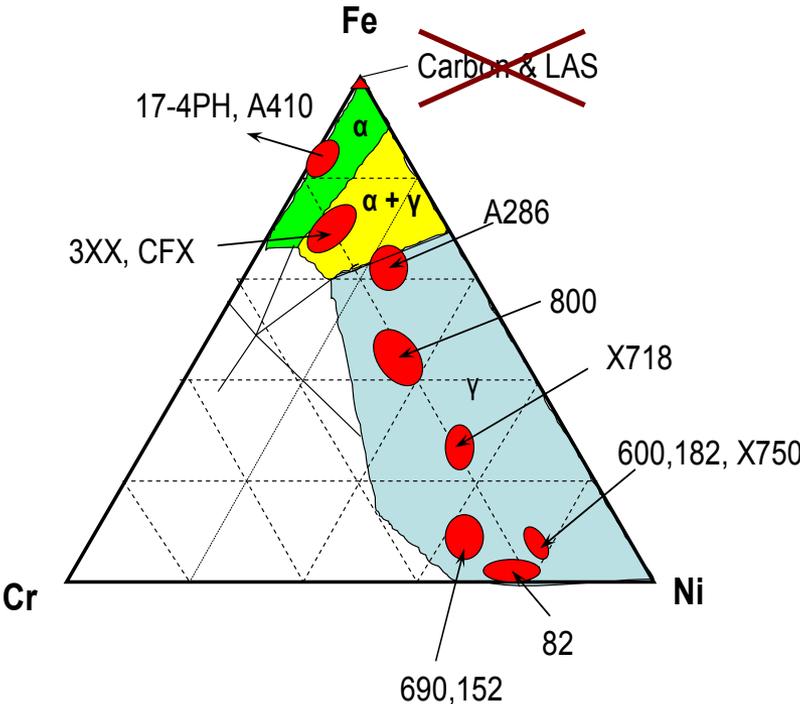
- ▶ Processes in very tight crack tips must be different from processes in larger volumes
 - ◆ Interaction with electrical double layers ??
 - ◆ Access of water ??, incomplete cation solvation ??
 - ◆ Thermodynamic equilibria ?? Nature of oxides ??
 - ◆ Transport processes: bulk versus surface ??
 - ◆ Oxide wedge effects ??

Corrosion problems in LWRs

Main Materials in PWR plants

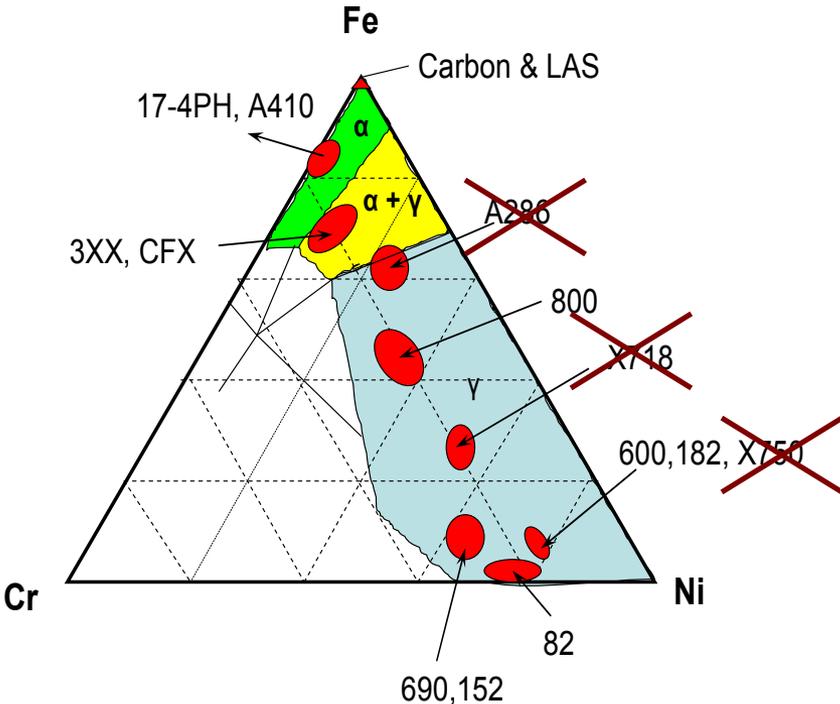
Primary circuit

- ◆ **No Carbon and Low Alloy Steels**
- ◆ Stainless Steels
- ◆ Nickel Base Alloys
- ◆ Zr alloys



Secondary circuit

- ◆ Carbon and Low Alloy Steels
- ◆ Stainless Steels
- ◆ Copper Alloys or Titanium alloys



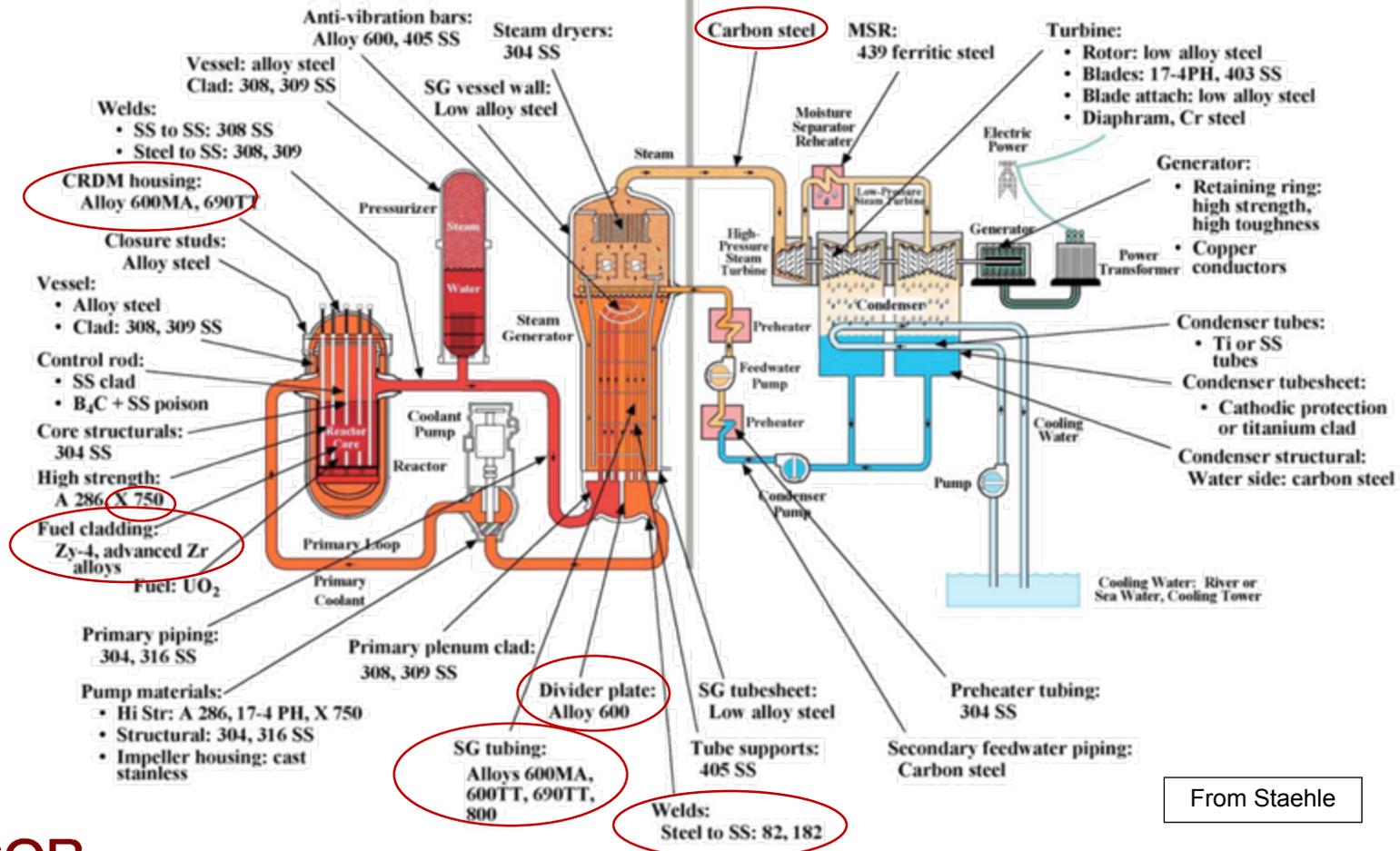
Main Materials in PWR plants

► Primary circuit

- ◆ **No Carbon and Low Alloy Steels**
- ◆ Stainless Steels
- ◆ Nickel Base Alloys
- ◆ Zr alloys

► Secondary circuit

- ◆ Carbon and Low Alloy Steels
- ◆ Stainless Steels
- ◆ Nickel Base Alloys
- ◆ Copper Alloys or Titanium alloys



From Staehele

Main corrosion problems in PWR primary circuits

- ▶ **Intergranular Stress Corrosion Cracking (IGSCC) of Alloy 600 and related weld metals i.e. Alloys 182 and 82**
 - ◆ Secondary side IGA/SCC of steam generator tubes
 - ◆ Primary Water Stress Corrosion Cracking (PWSCC)
- ▶ IGSCC of Alloy X-750
 - ◆ Rupture of control drive pins
- ▶ **IGSCC of irradiated Stainless Steels**
 - ◆ See G. Was presentation for irradiation damage
- ▶ SCC of Cold Worked Stainless Steels
 - ◆ Not extensive but recurrent problem
 - ◆ Affects material with elevated hardness – Hv > 300/310
 - ◆ May be definitely enhanced due to dissolved oxygen transients in primary water
- ▶ **Cation release**
 - ◆ Due to general corrosion of nickel base alloys and stainless steel surfaces
 - ◆ Release of nickel and cobalt are that can be activated into ^{58}Co and ^{60}Co in the core

- ▶ **Flow assisted corrosion of carbon steel in the secondary circuit**

Cation release in PWR primary water

▶ Main source = Steam Generator tubings

- ◆ Nickel Base Alloy (Alloy 600 or 690)
- ◆ Total area ~ 15 000 to 30 000 m²

▶ Mechanism of cation release

- ◆ "Duplex" structure of the oxide grown on Stainless Steels and Ni-Base Alloys in HT water

- **Cr rich, protective inner layer – insoluble**
- **External, Cr free oxide layer – soluble**
 - Grown by precipitation of dissolved ions coming from base metal and from environment

- ◆ Activation of the circuit arises from

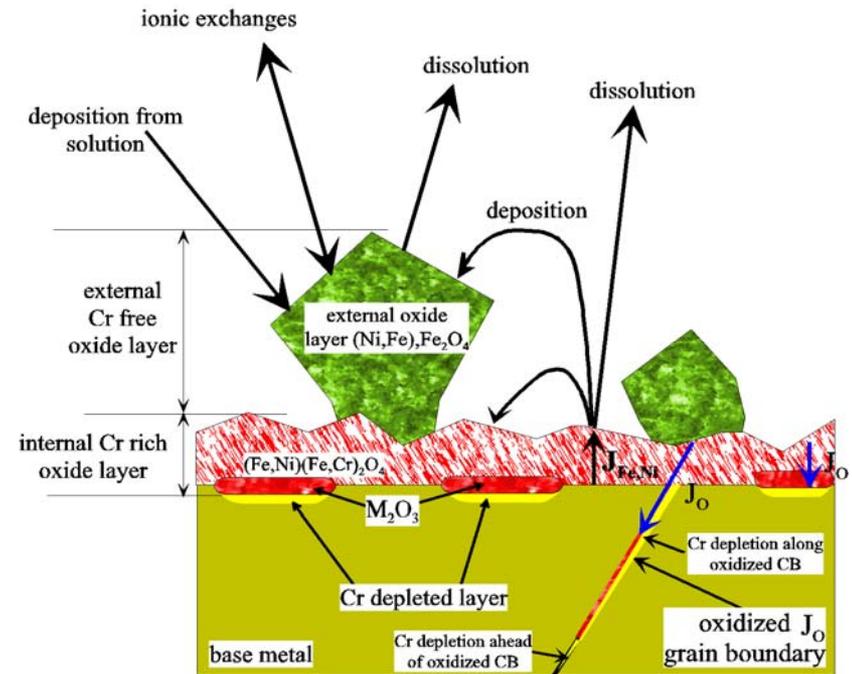
- Cations diffusing from base metal through protective inner oxide layer
- Growth or dissolution of external oxide layer depending on the temperature differences between core and primary circuit surfaces.

- ◆ Kinetics

- Oxidation rates seem to obey power laws for short exposure times
 - M_{ox} or $M_{rel} \propto t^n$ with $n \sim 1/3$ to $1/2$
 - Corrosion rates ~tenth of $\mu\text{m}/\text{y}$ for long exposures
 - **Release rates ~tens of kg/y**

▶ Mitigation of cation release

- ◆ Optimization of pH
- ◆ Optimization of surface condition
- ◆ Addition of Zn that leads to thinner and more protective oxide layers



Intergranular Stress Corrosion of Ni-Base Alloys in PWRs

► Nickel-base alloys

◆ Composition

- Alloy 600 : 75 % Ni, 15 % Cr, 8 % Fe, and corresponding weld metals, Alloy 182 and 82
- Alloy 690 : 60 % Ni, 30 % Cr, 10 % Fe

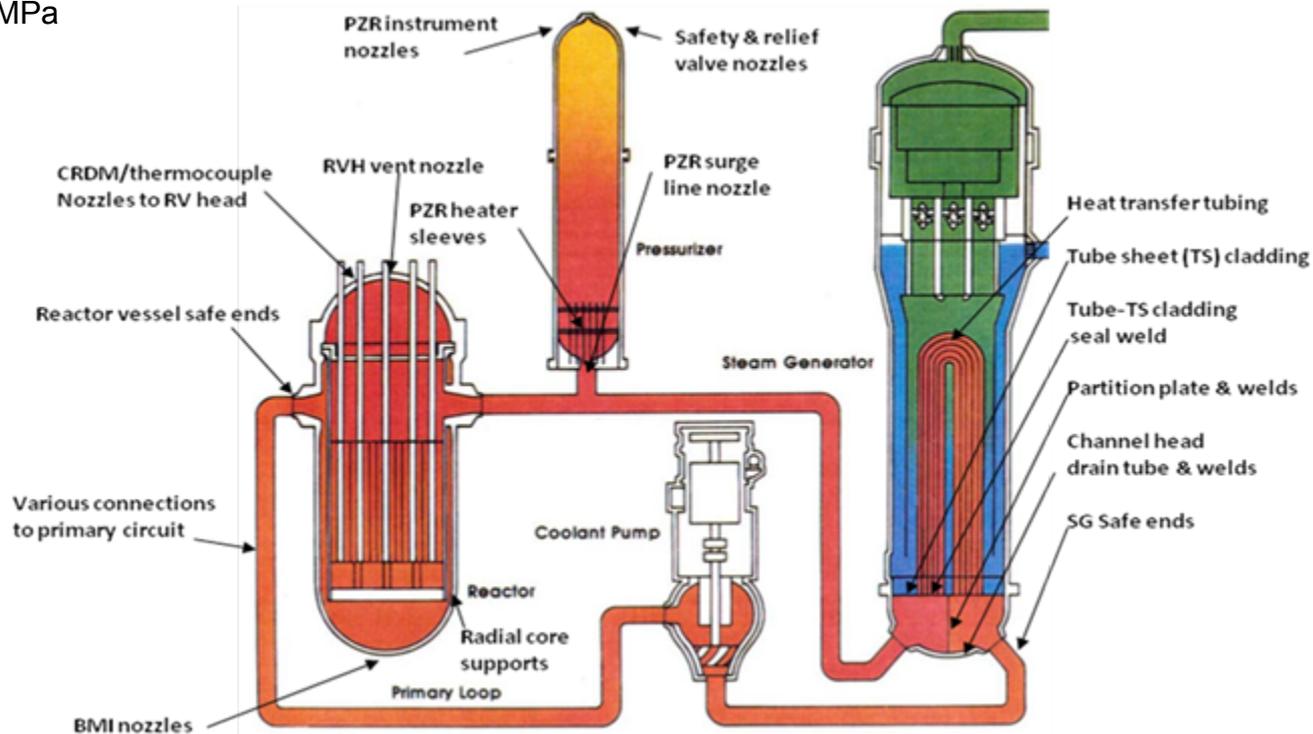
◆ Microstructure

- Austenitic (FCC)
- Low carbon solubility → Chromium carbides

◆ Mechanical properties - not cold worked

- $\sigma_{0,2}$ ~250 to 350 MPa

Alloys 600, 82 and 182
in PWR Primary Circuits



Brief History of the Introduction of Nickel Base Alloys into PWRs

▶ Cracking in service of Alloy 600 from the 1970s onwards

- ◆ 1980s : Steam generator tubes and Pressurizer sleeves
- ◆ 1990s : Upper Head CRDM nozzles
- ◆ From 2000 : Alloy 182 welds and steam generator divider plates

▶ Remedies

- ◆ Mid 1970s – Thermal treatment of Alloy 600 for steam generators tubes at $\sim 700^{\circ}\text{C}$ → Alloy 600 TT - Generally good operating experience
- ◆ Mid 1980s – decision to use Alloy 690 → excellent operating experience – no in-service cracking to date

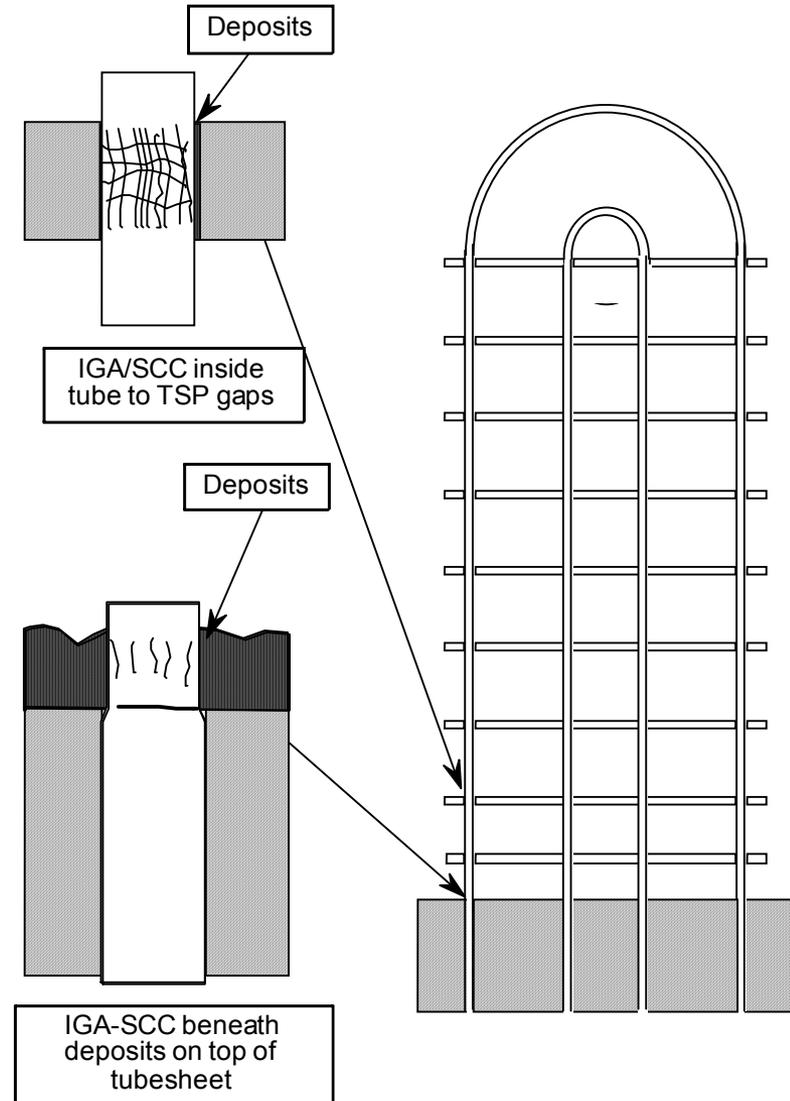
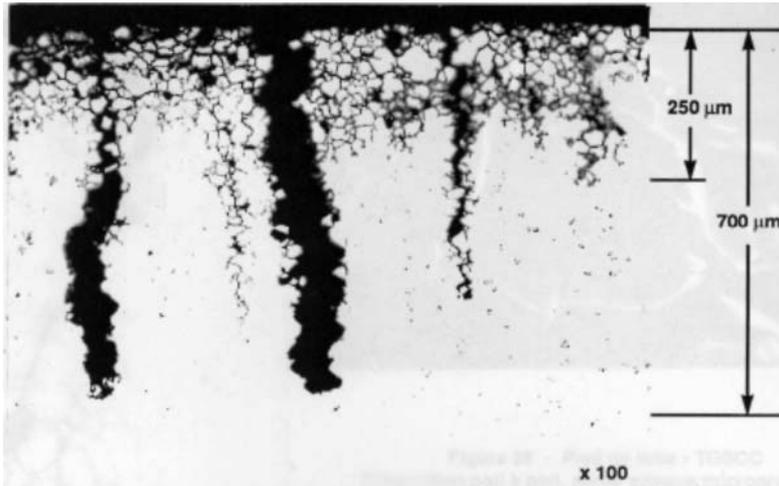
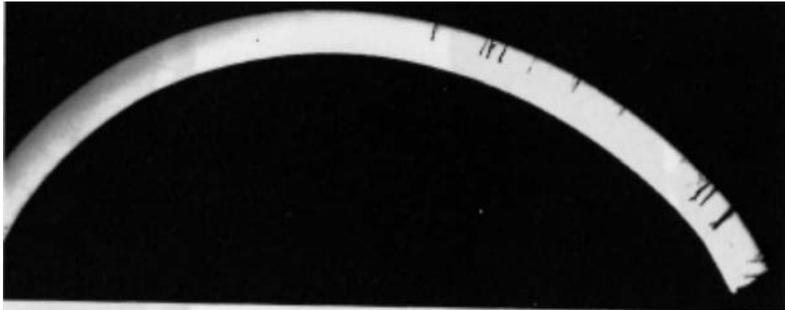
▶ From the 1980s to date – management of Alloy 600 in service

- ◆ Development of NDE techniques
- ◆ Empirical models for predicting in-service cracking

▶ From the early 1990s to date – extent of reliability of Alloy 690 examined

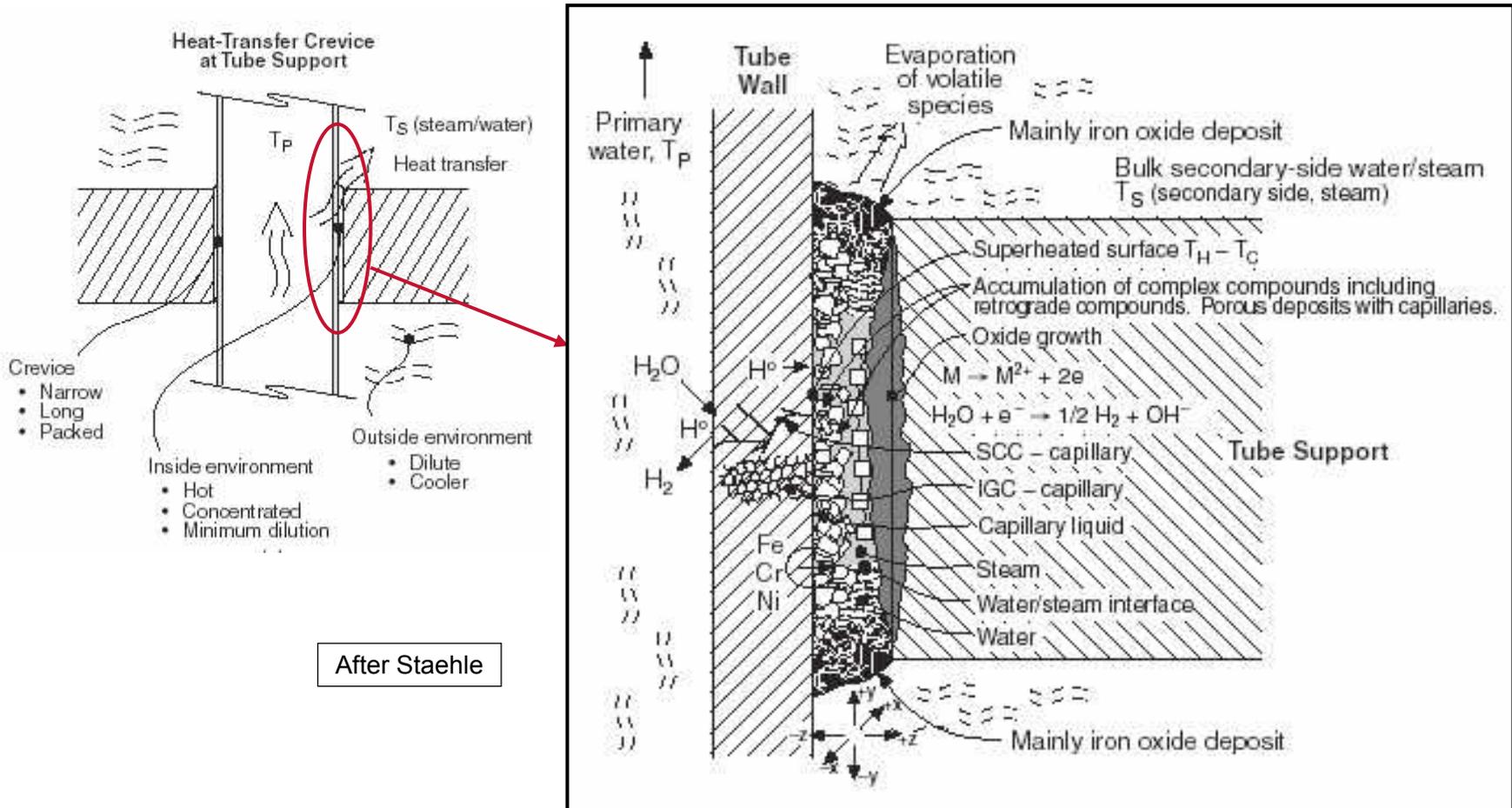
Secondary side cracking of Alloy 600 Steam generator tubes

- ▶ ICA-SCC under deposits formed inside Tube to Tube Support Plate (TSP) gaps or on top of tubesheet



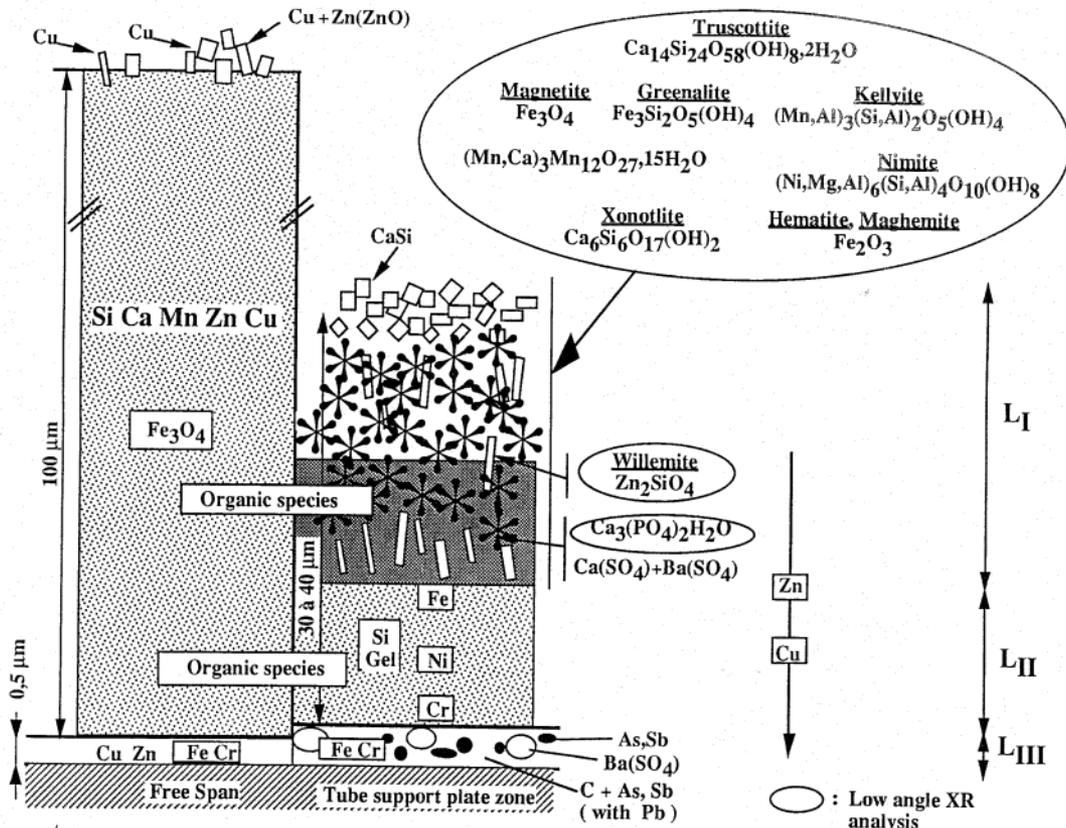
Secondary side cracking of Alloy 600 Steam generator tubes

- ▶ IGA-SCC is due to progressive accumulation of magnetite and impurities in overheated zones

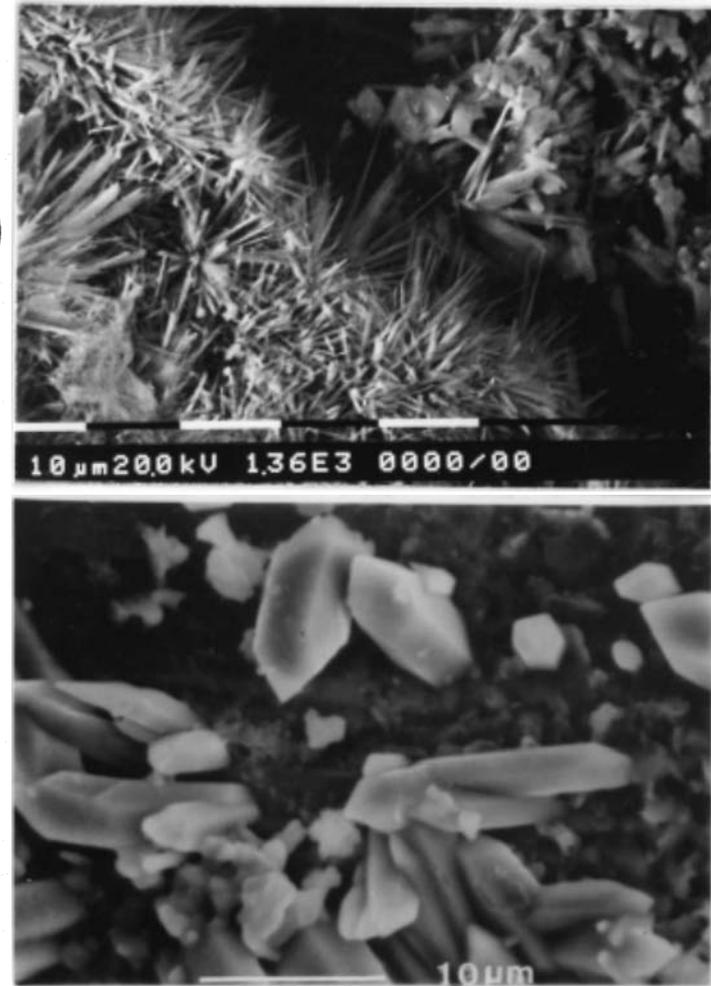


Secondary side cracking of Alloy 600 Steam generator tubes

► Example of deposits inside a tube to TSP gap



From Sala et al.



Secondary side cracking of Alloy 600 Steam generator tubes

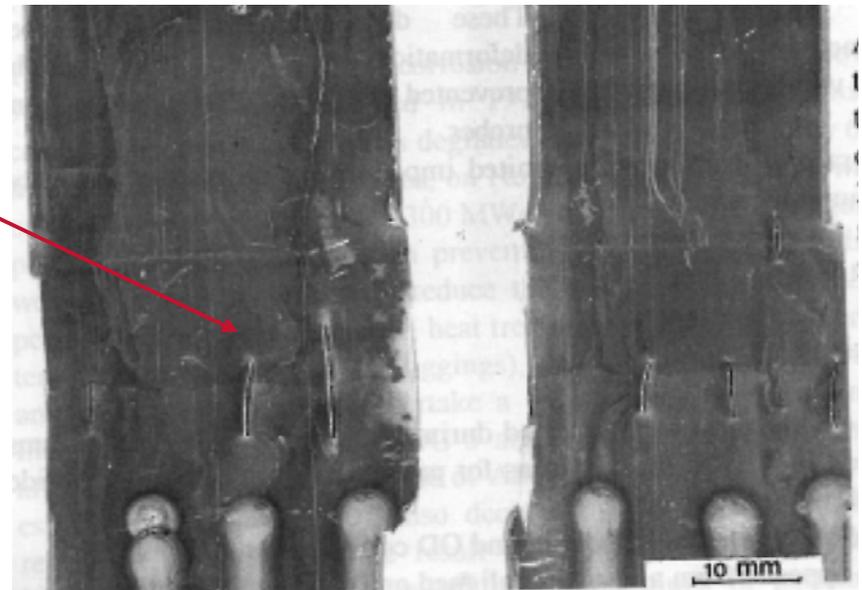
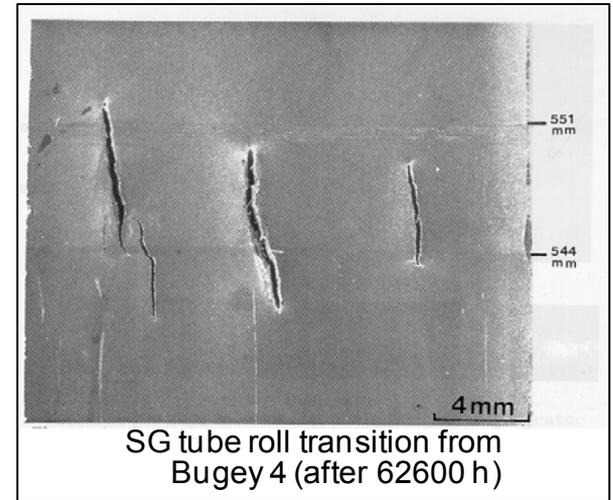
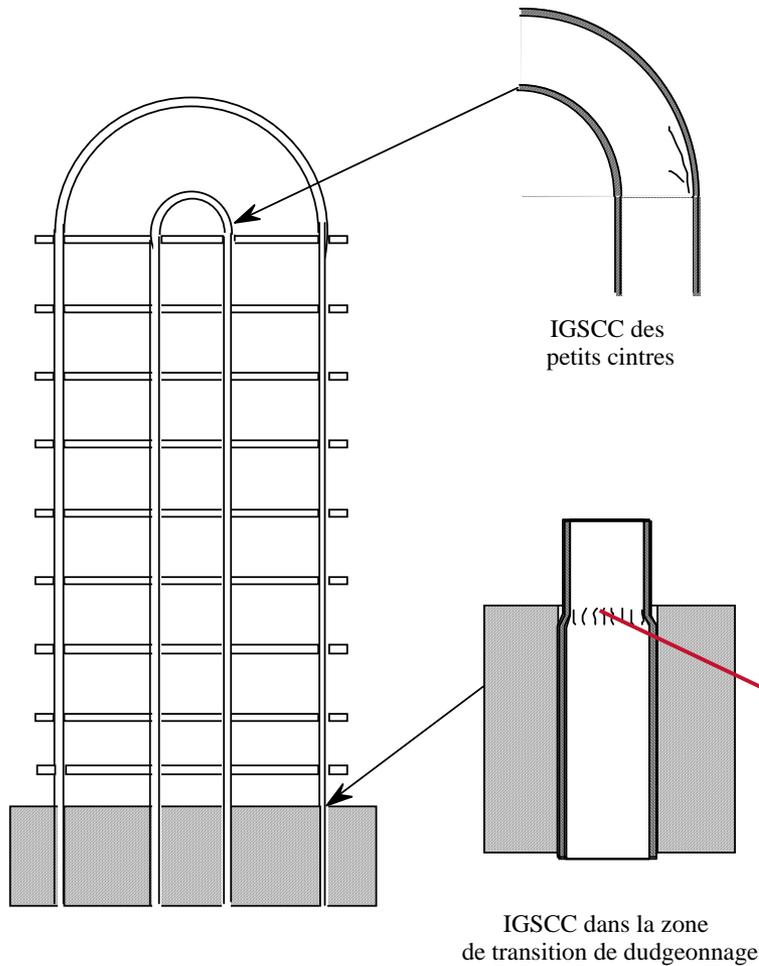
▶ Environments responsible for IGA-SCC

- ◆ Dependent on water chemistry, nature of cooling water (sea water vs river water) inleakages and nature of condenser tubes (copper alloys vs SSs or Ti)
- ◆ Not clearly identified

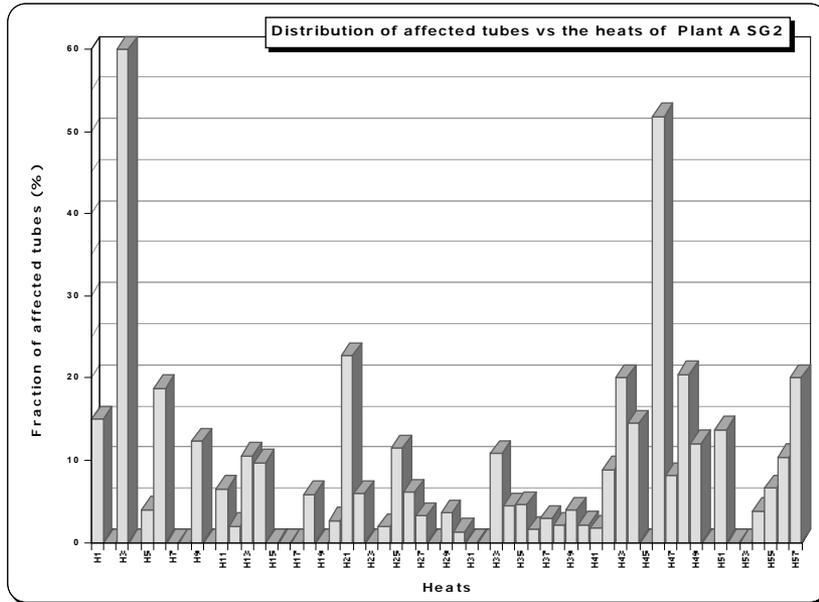
▶ Species suspected to be responsible for IGA-SCC

- ◆ Caustic
- ◆ Acidic
- ◆ Chloride and sulfur species
- ◆ Complex alumino-silicates
- ◆ LEAD

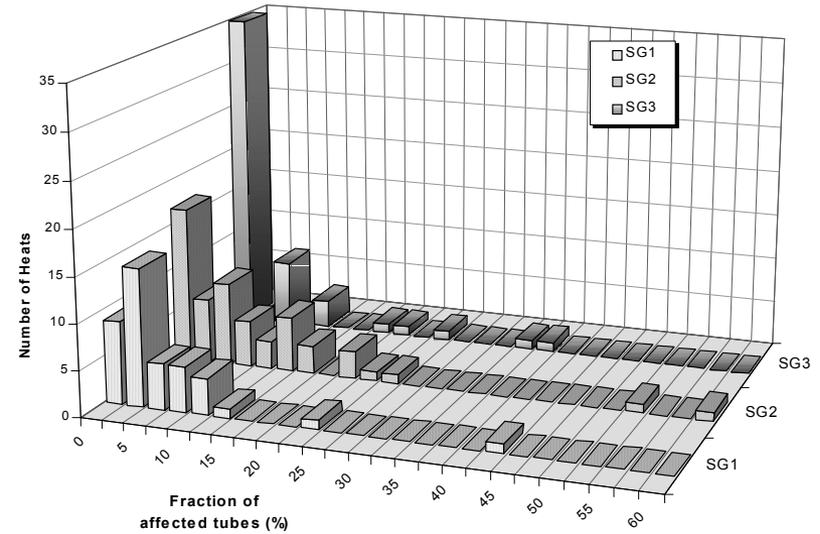
PWR Primary Side Steam Generator Tube Cracking



Heat to Heat Susceptibility of Alloy 600 to IGSCC in PWR Primary Water

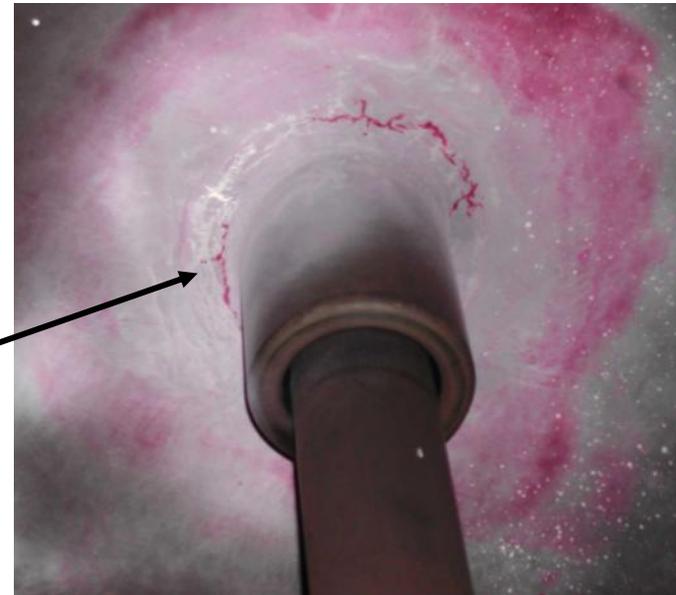
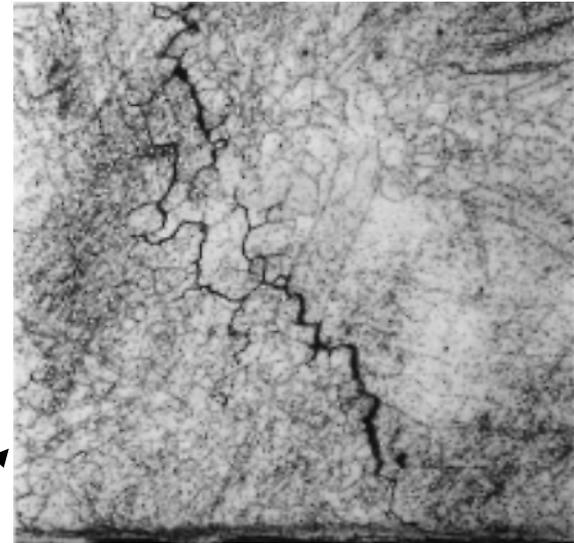
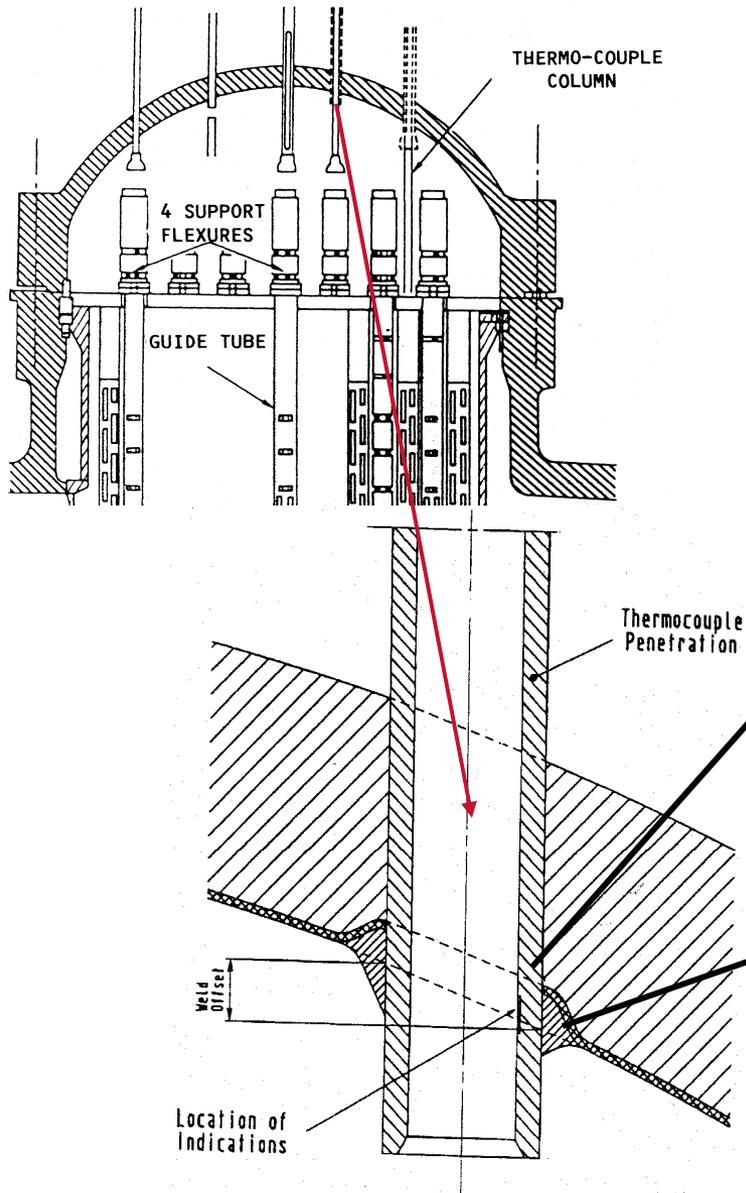


Histogram of percentage of tubes of each heat of alloy 600 in order of manufacture affected by IGSCC on the primary side of roll transitions in a steam generator tube bundle after ~40,000 hours service.



Distribution of heats of alloy 600 by susceptibility to IGSCC on the primary side of tube roll transitions in three steam generators of the same plant.

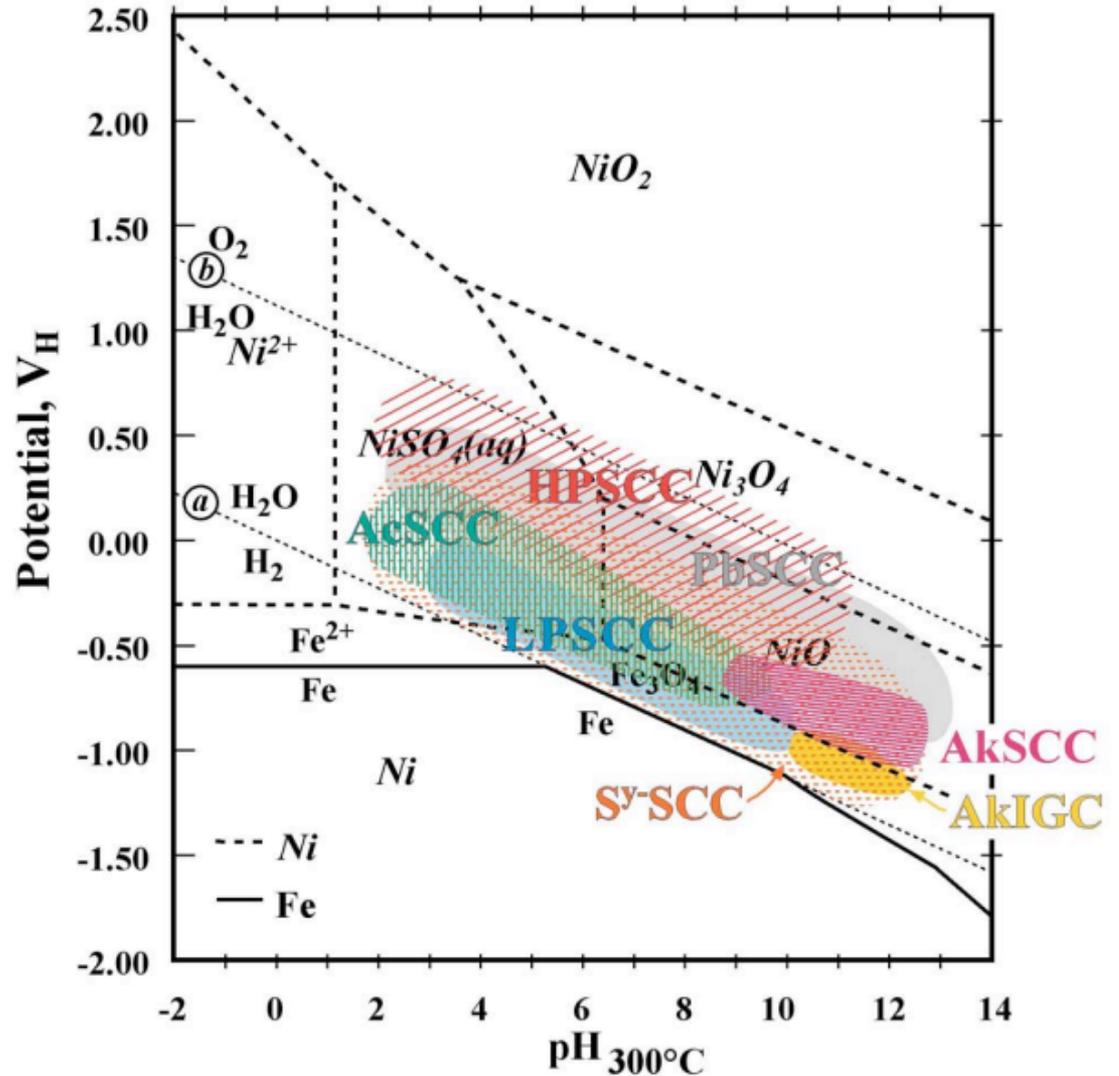
PWSCC in Upper Head CRDM Penetrations



Sub-modes of SCC for Alloy 600 in HT water (after Staehle)

Other contributors to the “mode diagram” concept

- Parkins
- Pourbaix
- Combrade
- Tsujikawa
- Nagano

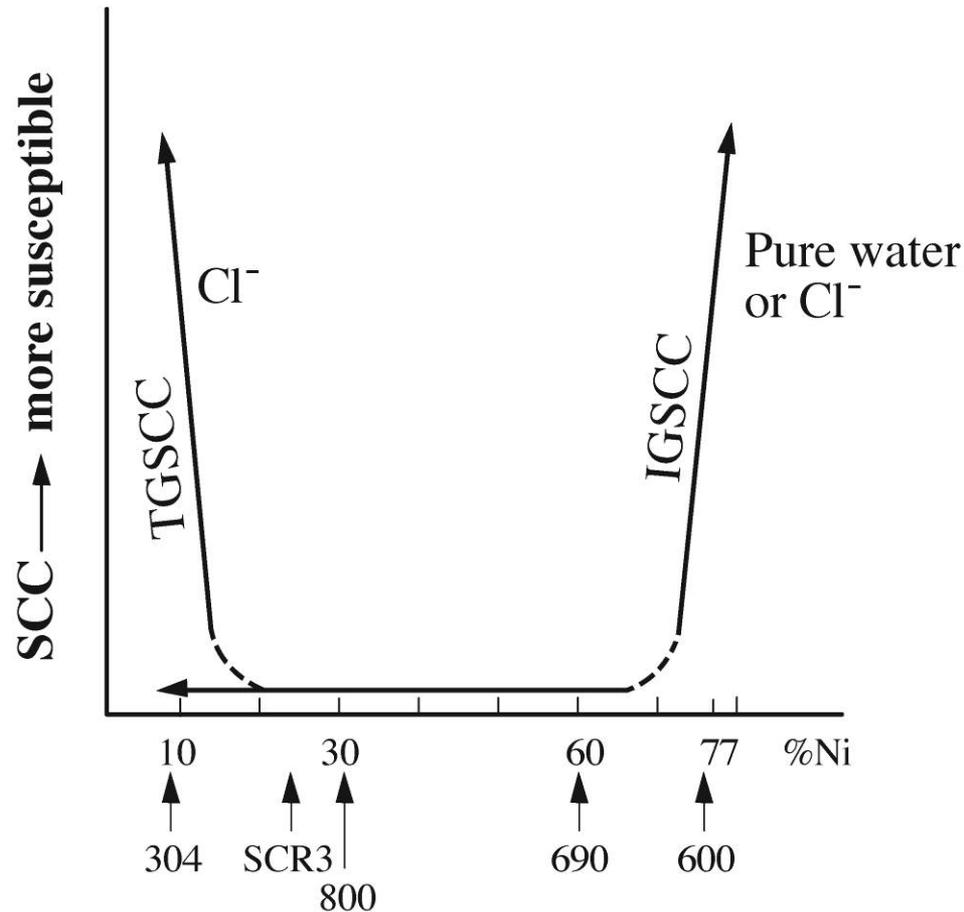


IGSCC of Alloy 600 in PWR primary water (PWSCC)

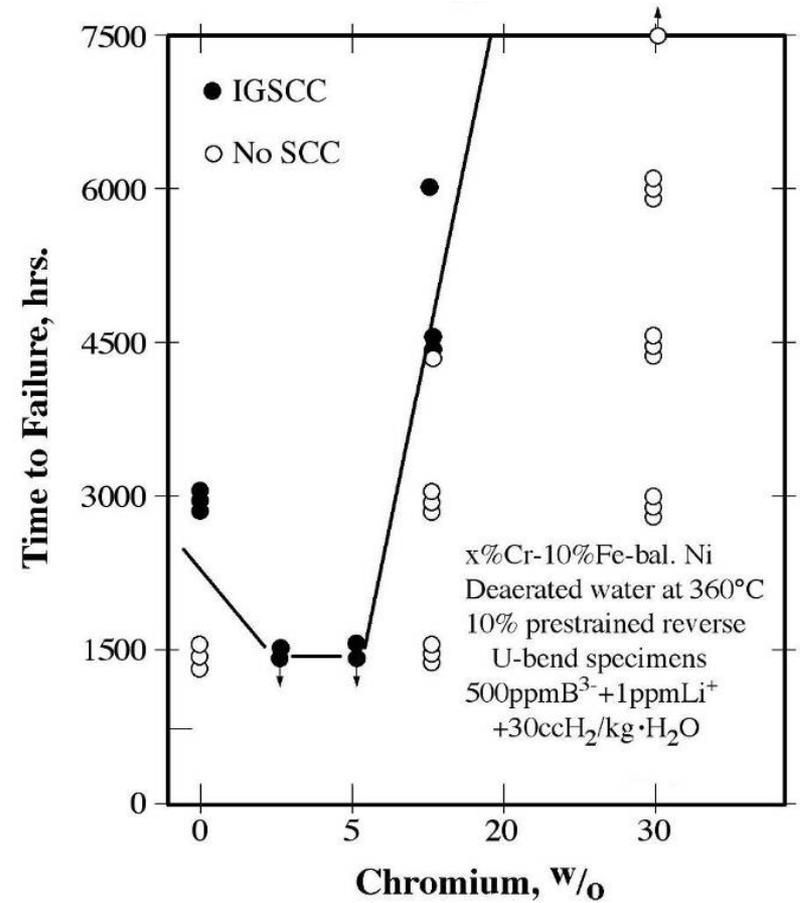
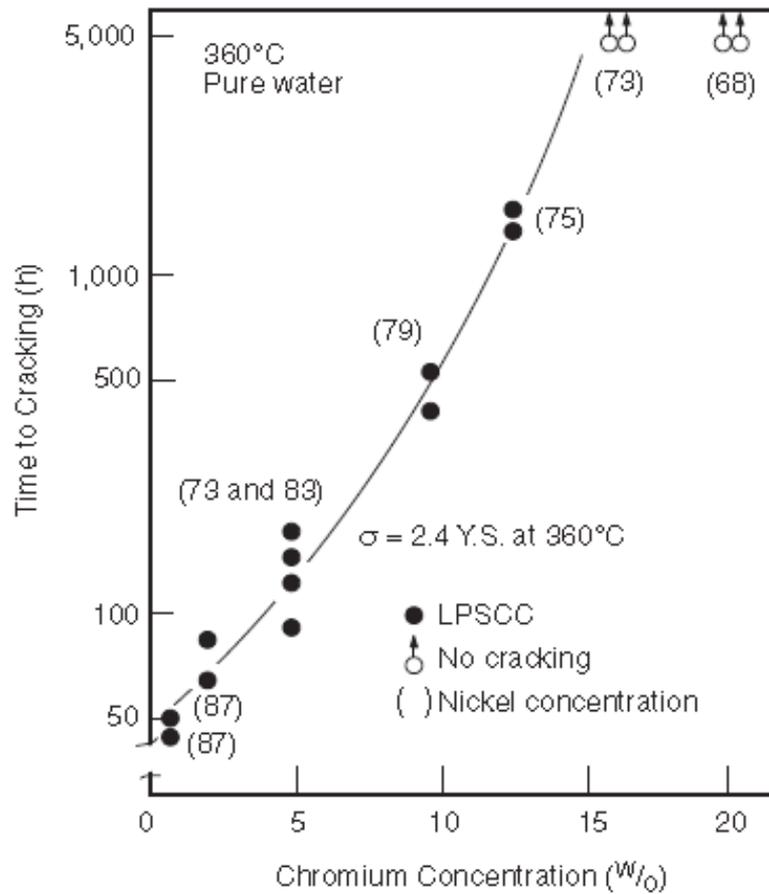
PWSCC – Influence of Ni content

- ▶ Influence of nickel content on SCC of austenitic alloys containing 15 to 30%Cr

- ◆ Coriou 1969

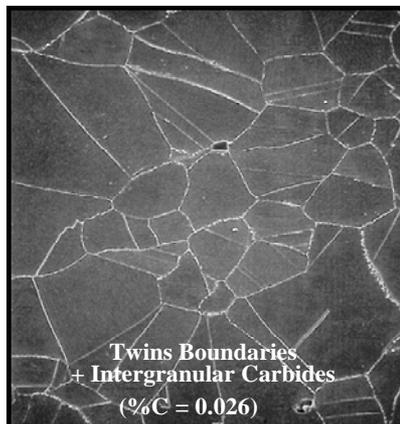


PWSCC - Effect of Cr content



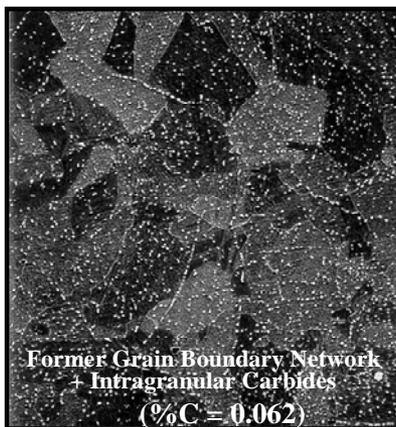
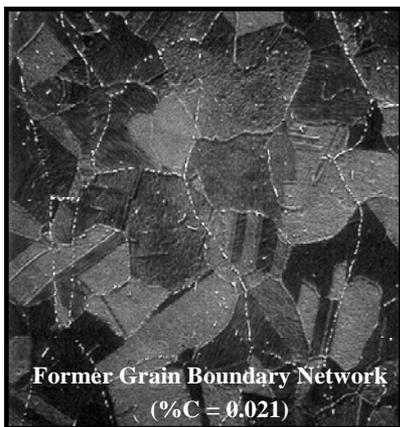
PWSCC of Alloy 600 - Influence of Microstructure

- ▶ Favorable influence of a network of fine, semi-continuous intergranular carbides

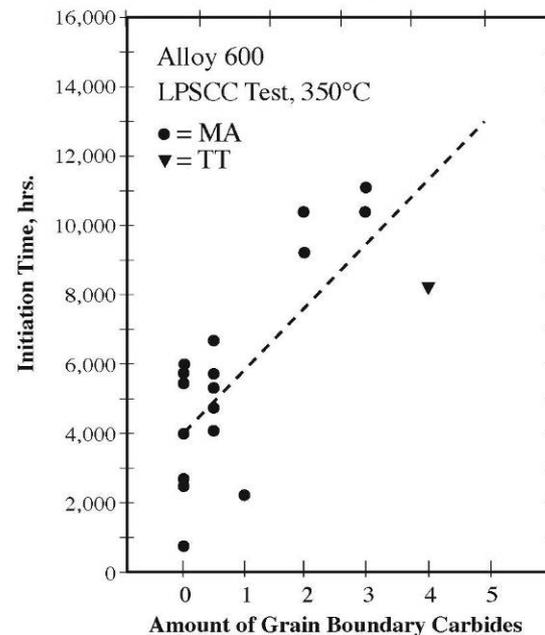


Structure not very susceptible to cracking

- ▶ Unfavorable role of intragranular carbides

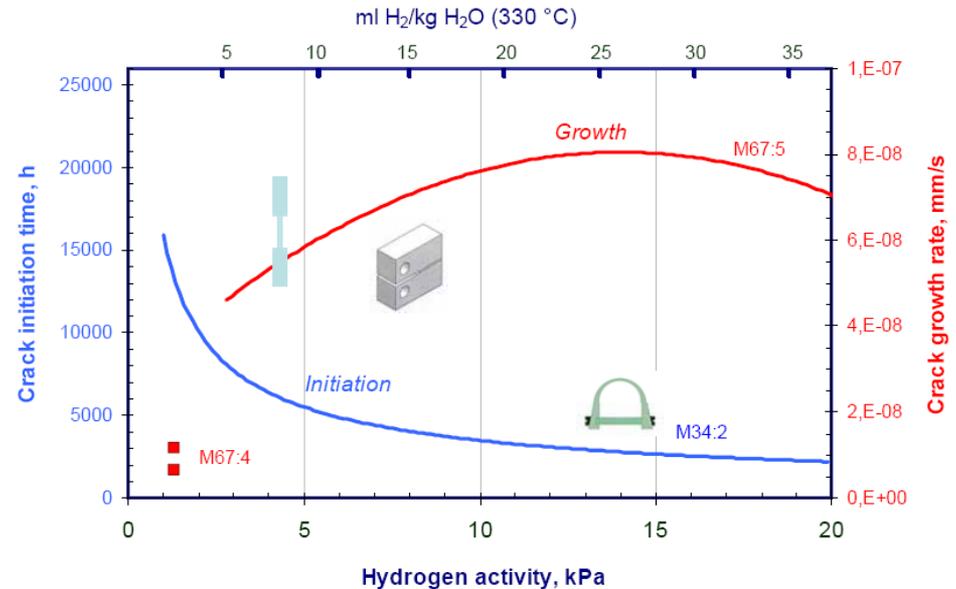
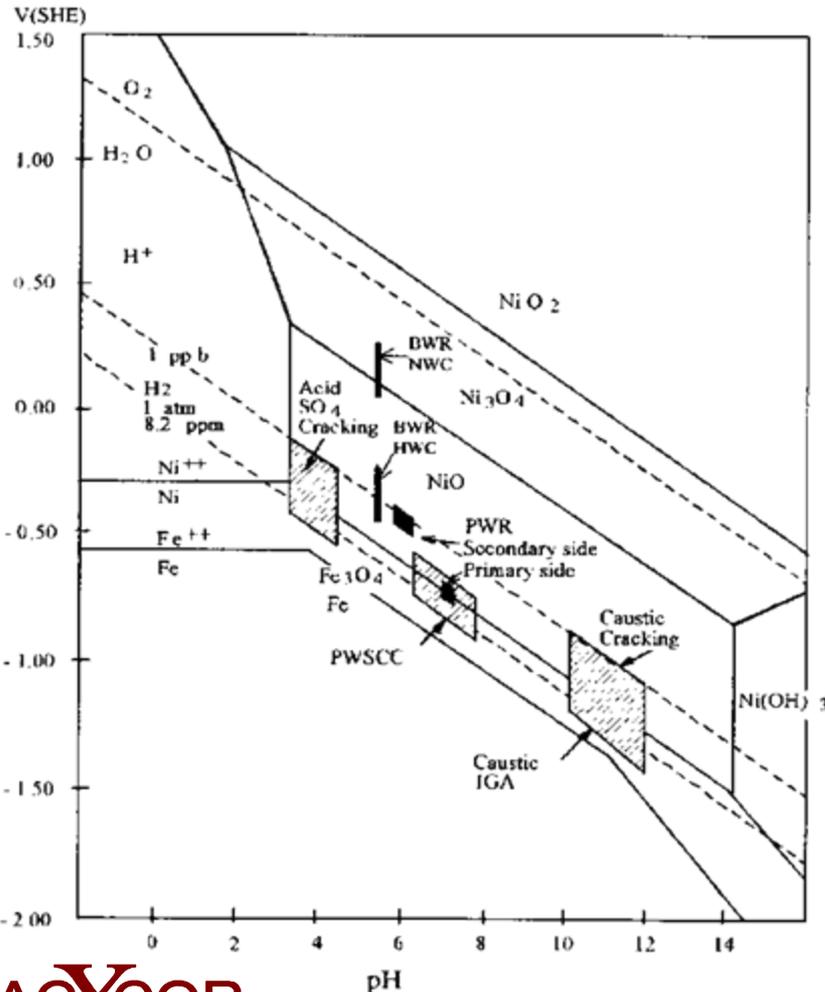


Structures more susceptible to cracking



PWSCC - Role of corrosion potential i.e. of dissolved hydrogen

- ▶ PWSCC occurs in a very limited range of corrosion potential i.e. of dissolved hydrogen
 - ◆ But crack initiation and crack growth do not depend in the same way of dissolved hydrogen content
 - ◆ This raises problems to optimize dissolved hydrogen in plants using Alloy 600 and related weld metals

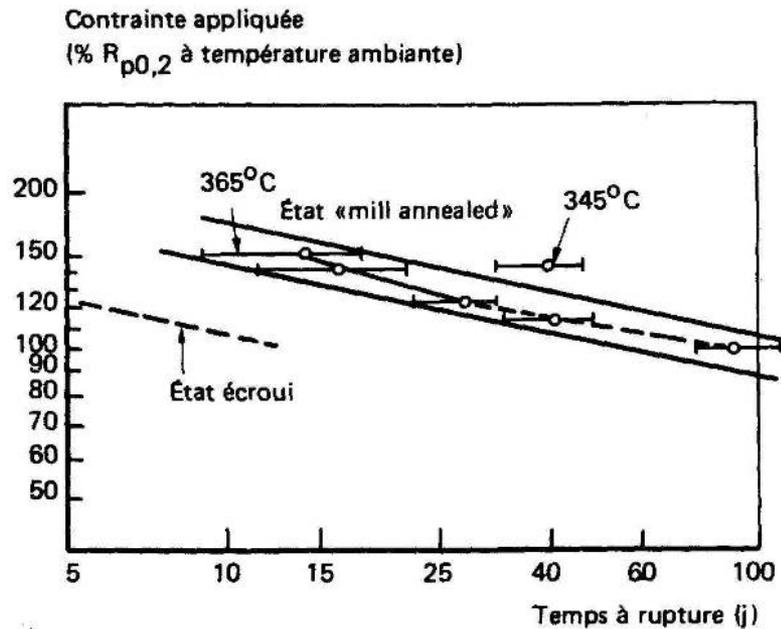


From Molander et al.

PWSCC – Effect of Stress and Cold work

► Strong influence of stress on crack initiation

- ◆ No cracking if $\sigma < \sim 250$ MPa
- ◆ Initiation time proportional to σ^{-4}

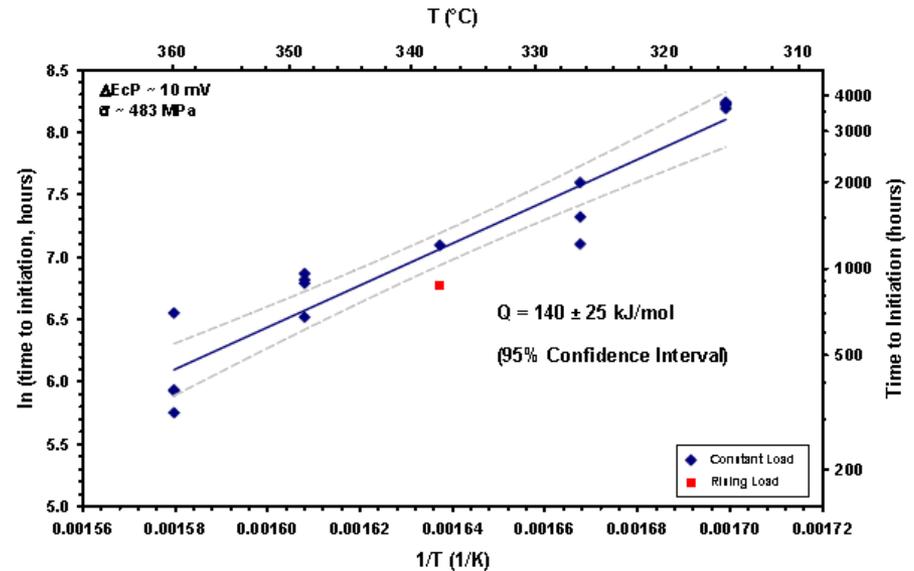
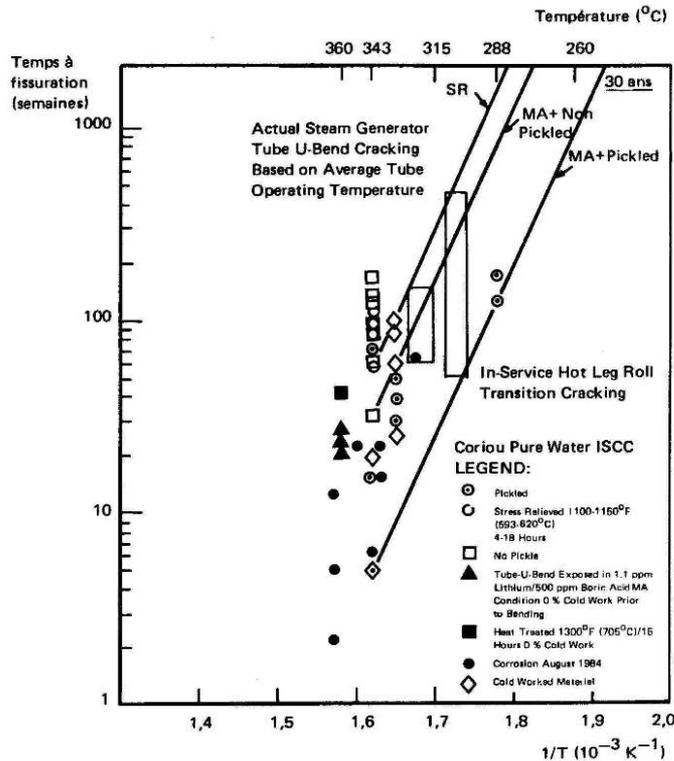


- ◆ Strong effect of cold work, especially surface cold work on initiation times
 - Role of machining, grinding etc

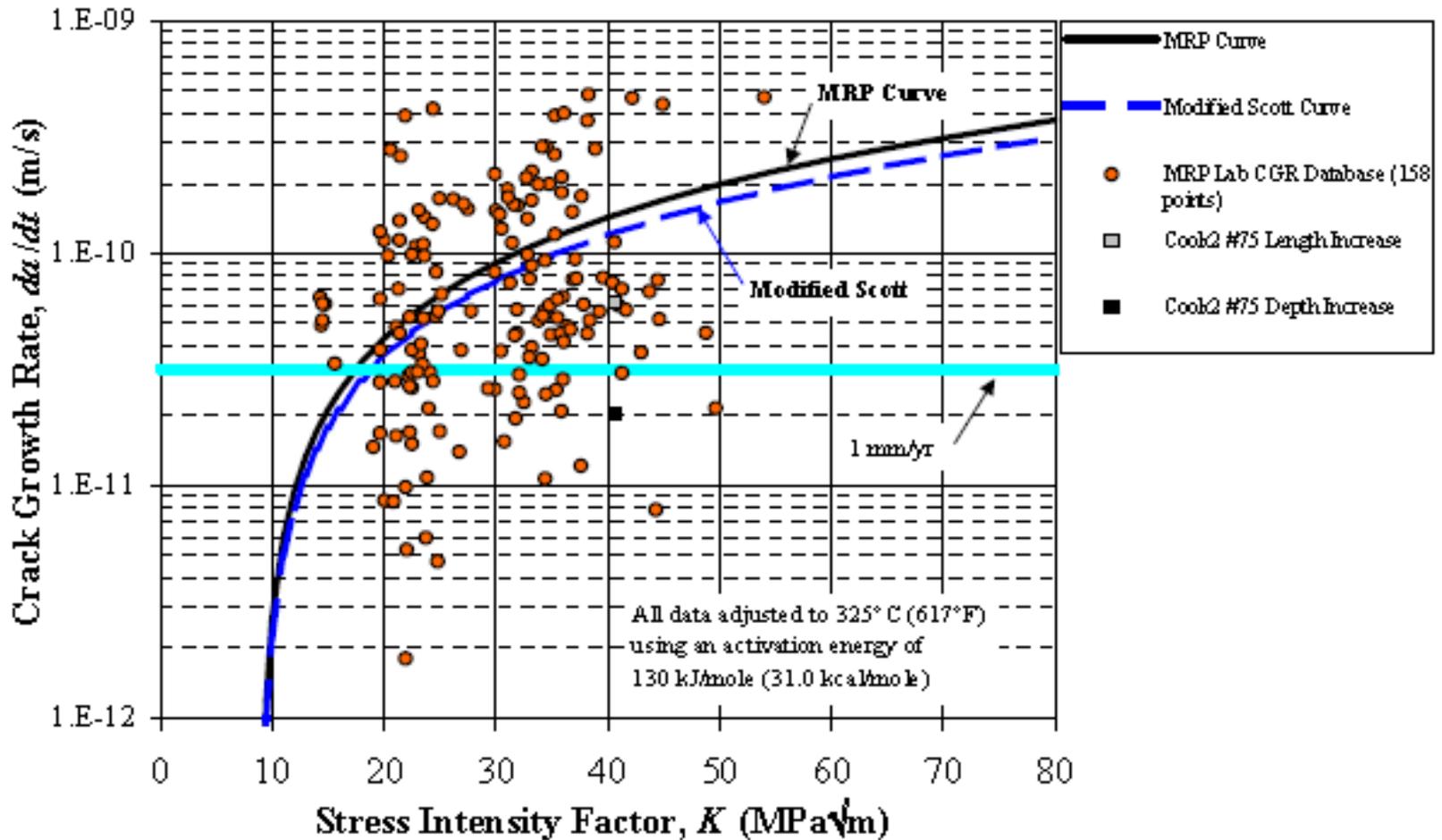
PWSCC – Effect of temperature

► Usually represented by an "apparent " activation energy

- ◆ ~ 185 kJ/mole for initiation
- ◆ ~110 to 130 kJ/mole for propagation



PWSCC – Propagation rates for Alloy 600



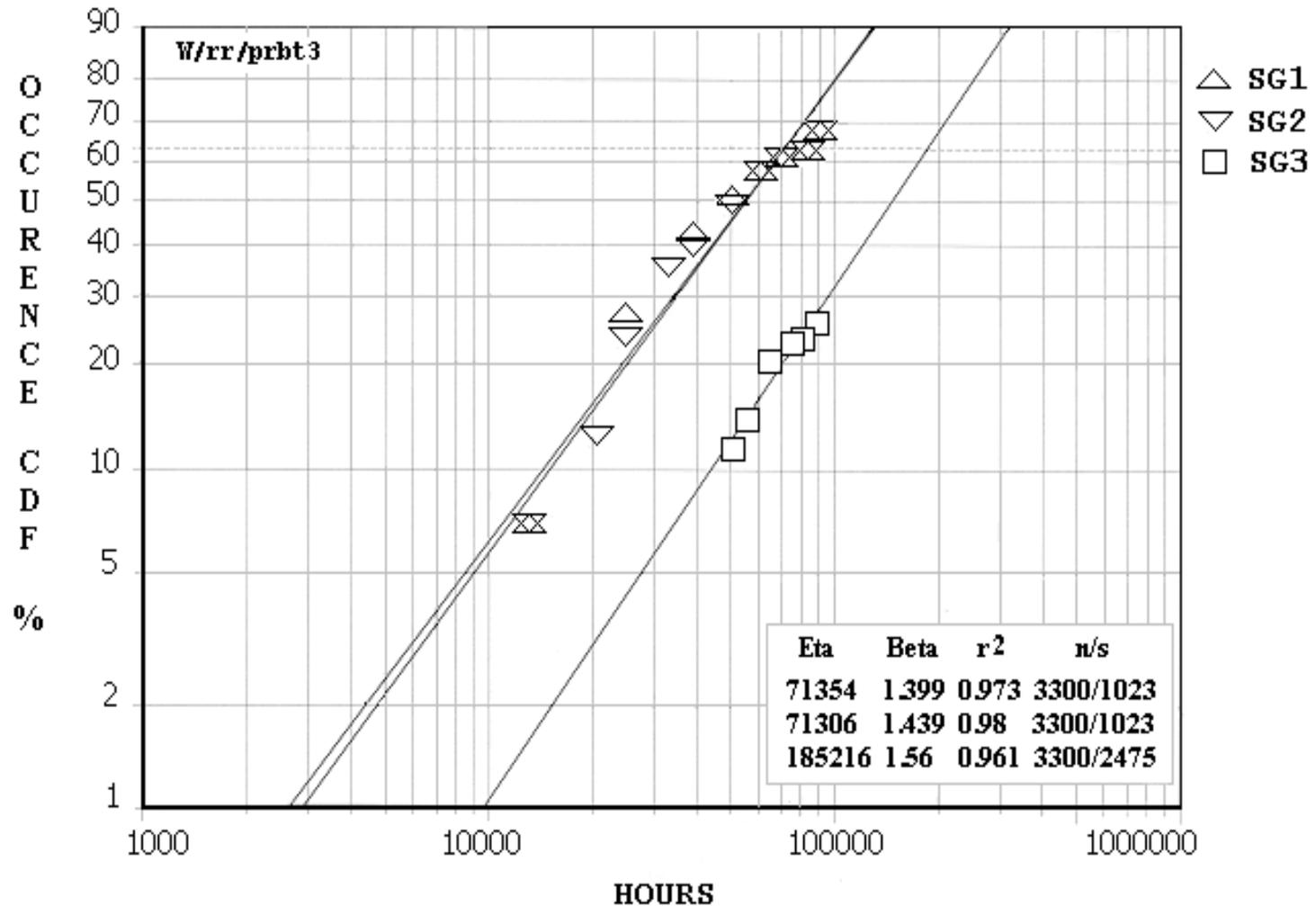
PWSCC in Alloy 600 - Summary of Main Observations

- ▶ Apparent initiation times in plant have been up to 25 years with a huge heat to heat variability observed in service
 - ◆ Crack incubation times can vary by a factor of 50, even when all other important influencing parameters remain constant
- ▶ Apparent continuous mechanism of cracking between 300°C water and 400°C steam
- ▶ Important influence of hydrogen partial pressure → maximum growth rate in range $E_{\text{Ni/NiO}} \pm 80$ mV
- ▶ High activation energy ≈ 140 to 180 kJ/mole
- ▶ Strong effect of carbide morphology and cold work
- ▶ High stress exponent of ≈ 4
- ▶ No consensus on mechanism of IGSCC

- ▶ Different approaches all purely empirical
 - ◆ Extrapolation of the Weibull distribution fitted to a sequence of early 'failures'; i.e. components identified to be leaking or to have macroscopic cracks detectable by non-destructive examination
 - ◆ Deterministic application of time to failure equation as a function of stress, temperature and material susceptibility index – it is generally accepted that material variability is an important input into determining the likelihood of crack initiation
 - ◆ Monte Carlo modelling using distributed values for stress, material susceptibility indices and temperature

Application of Weibull distribution

- ▶ Application of Weibull Distribution to Primary Side IGSCC of Roll Transitions of Alloy 600 SG



Revised MRP Approach for CRDM Nozzle Cracking in U.S. PWRs (MRP-48)

Effective Degradation Years (EDYs) are computed in accordance with the following activation energy equation^x

$$EDY_{600^{\circ}F} = \sum_{j=1}^n \left\{ \Delta EFPY_j \exp \left[-\frac{Q}{R} \left(\frac{1}{T_{head,j}} - \frac{1}{T_{ref}} \right) \right] \right\} \quad [Equation A - 1]$$

Where:

$EDY_{600^{\circ}F}$	=	total effective degradation years through February 2001, normalized to a reference temperature of 600°F
$EFPY$	=	effective full power years
Q_j	=	activation energy for crack initiation (50 kcal/mole)
R	=	universal gas constant (1.103×10^{-3} kcal/mol-°R)
$T_{head,j}$	=	100% power head temp. during time period j (°R = °F + 459.67)
T_{ref}	=	arbitrary reference, temperature (600°F = 1059.67°R)
n	=	number of different head temperatures during plant history

Empirical Equations for Component Life Estimation

$$t_f = C \frac{\sigma^{-4}}{I_m} \exp\left(\frac{E}{RT}\right)$$

t_f is the failure time (hours)

C is a constant

σ is the applied stress (MPa)

I_m is a material susceptibility index

E is the apparent activation energy (180 kJ/mole)

R is the universal gas constant (1.987 cal/mole/°K)

T is the absolute temperature (°K).

Note by definition from early experience with roll transition zones of mill annealed Alloy 600 SG tubes, $I_m = 1$ for $t_f = 10,000$ h when $\sigma = 450$ MPa at 325°C.

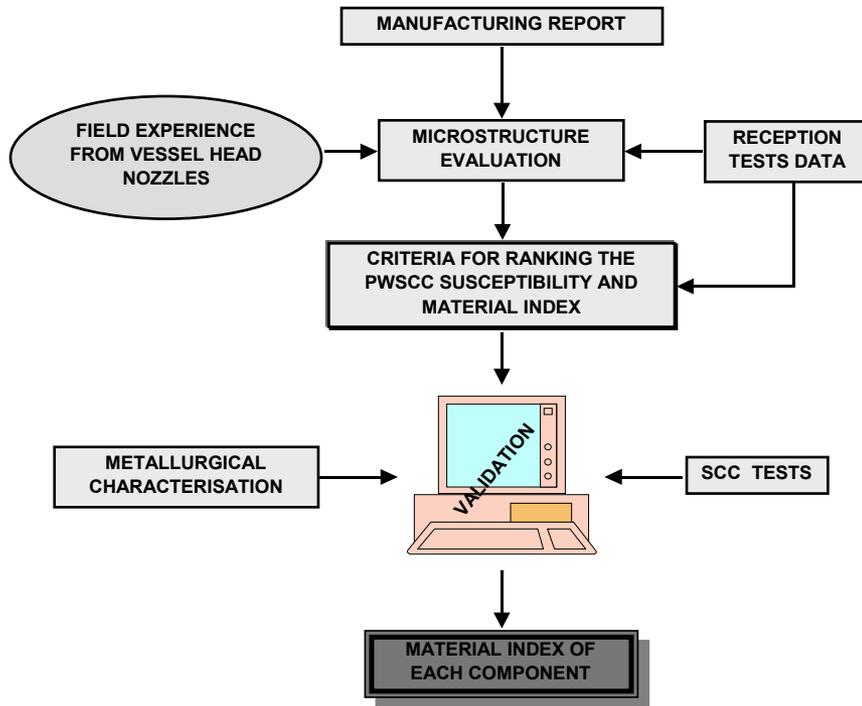
⇒ AREVA NP and EDF approach

$$t_f = \frac{10000}{I_m \cdot I_\theta \cdot I_\sigma} \text{ hours}$$

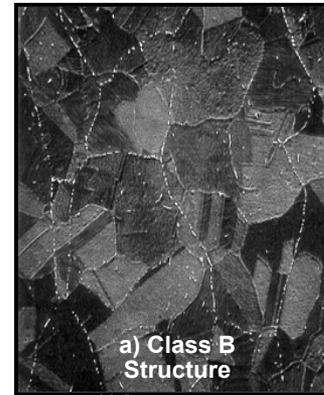
$$I_\sigma = \left(\frac{\sigma}{450}\right)^4 \quad I_\theta = \exp\left[\left(\frac{-E}{R}\right)\left(\frac{1}{T} - \frac{1}{598}\right)\right]$$

Improved Estimation of I_m for Alloy 600 (Developed for Upper Head Penetrations by C. Benhamou)

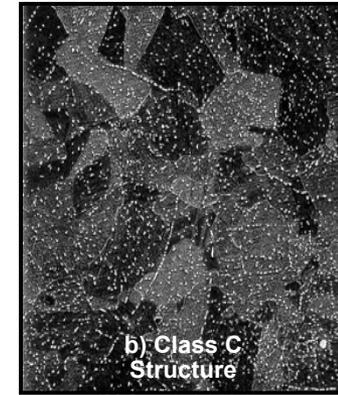
Importance of carbide morphology first established for SG tubing and then applied to Pressurizer nozzles and Upper Head penetrations



Criteria: carbon content, temperature at the end of forging or rolling operations, yield strength after hot-working



a) Class B Structure



b) Class C Structure

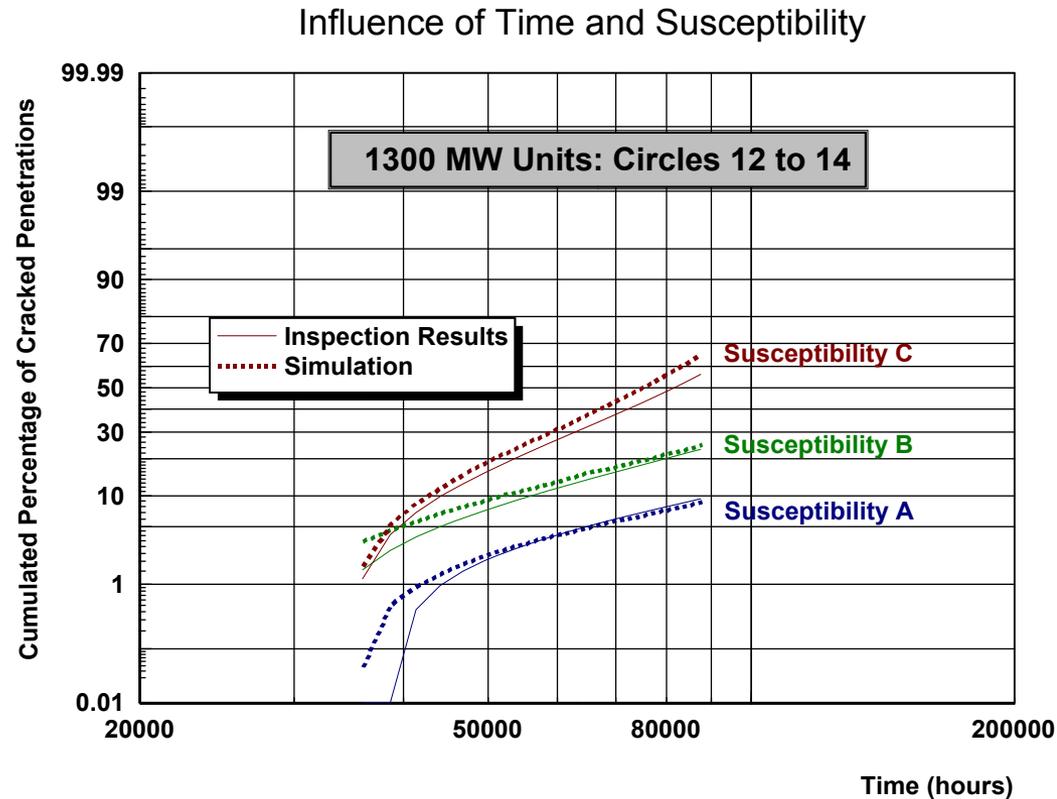
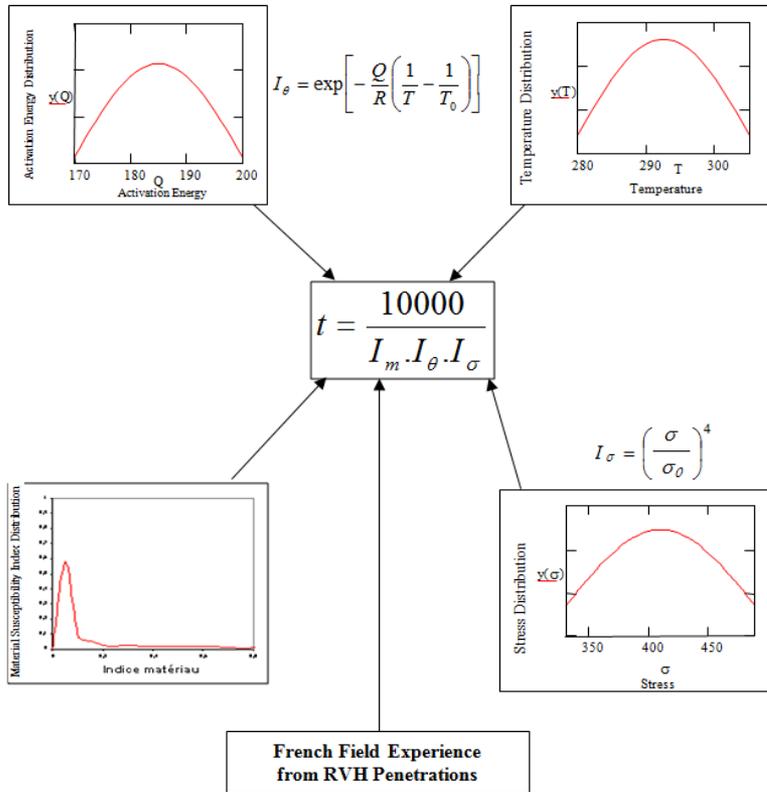
20 μ m

Class A with mainly intergranular carbide precipitates

Class B re-crystallized with carbides mainly on a prior grain boundary network

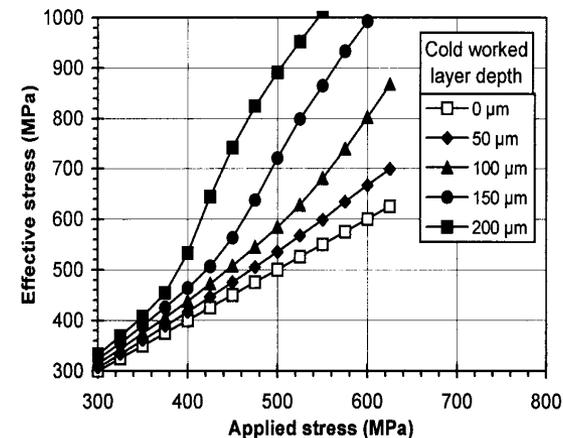
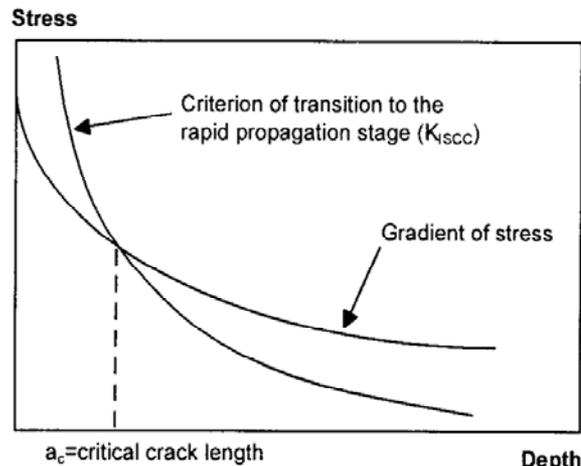
Class C re-crystallized with randomized intragranular carbides as well as carbides on prior grain boundaries

Monte Carlo Simulation of Upper Head Penetration Cracking



Effect of Surface Cold Work (After Le Hong)

- ▶ Quantitative treatment of effect of surface cold work on stress corrosion cracking is based on three principles:
 - ◆ Crack growth rates increase with cold work when strained beyond the yield point
 - ◆ Cracks evolve in three stages; incubation, slow crack growth, fast growth ($K_I > K_{I_{SCC}} = 9 \text{ MPa}\sqrt{\text{m}}$)
 - ◆ Crack growth rates, slow and fast, are a function of strain rate



- ▶ When a cold worked layer is put into tension by straining the more ductile substrate beyond the yield point, very high stresses up to 1000 MPa are generated in the surface layer
- ▶ If the surface cold worked layer is relatively thick, the slow to fast transition in growth rates occurs within it at high stress and the lifetime to failure is significantly reduced

- ▶ Parametric prediction tools have been developed based on laboratory studies for wrought Alloy 600 components and qualified against known operating experience.
- ▶ They have been important for ensuring the safe and orderly organization of repair and maintenance activities
- ▶ Parametric equations for PWSCC growth rates in Alloys 600, 132/182 and 82 have also been developed to permit conservative evaluations of the growth of any defects found by non-destructive examination
- ▶ However, the relatively poor knowledge of the mechanism reduces confidence in the reliability of empirical predictive models and extrapolations beyond current empirical databases

Remedies to PWSCC of Nickel-Base Alloys

- ▶ Step 1 – Alloy 600 Thermally treated (700 to 715 °C for 10 to 15 h)
 - ◆ Applied to SG tubes
 - ◆ Produces fine and semi-continuous network of Cr carbides
 - ◆ Relieves straightening residual stresses

- ▶ Step 2 – replacement by Alloy 690 and corresponding weld metals Alloys 52 and 152
 - ◆ Compared to Alloy 600 these alloys have high Cr content (close to 30 %)
 - ◆ Specified Alloys 690 have optimized microstructure with fine and semi-continuous network of Cr carbides obtained by heat treatment at 700-715 °C

 - ◆ Planned to be applied to all parts previously in Alloy 600 and corresponding weld metals Alloys 82 and 182

 - ◆ Anticipated lifetime improvement factors
 - of over 40 to 100 in primary water
 - of at least 7.5 in secondary water
 - Main weak point is resistance to lead pollution that can be present in the secondary side of SG tubes

 - ◆ Field experience of more than 20 years with no known problems

Water chemistry is a very important factor
in minimizing corrosion problems

Water chemistry in PWR primary circuit

▶ Aims of primary water chemistry

- ◆ Corrosion problems:
 - Avoid water radiolysis to obtain low corrosion potentials
 - Optimise behaviour of Zr alloys regarding oxidation
- ◆ Minimise activity of circuits and crud deposition on fuel

	Typical
Pressure (MPa)	14.2
Temperature (°C)	286-323
Oxygen (ppm)	<0.1
Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	1-40
Hydrogen (ml/kg) at STP	20-50
Lithium (ppm) as LiOH	0.1-3.5
Boron (ppm) as H_3BO_3	0-2300
Chloride (ppm)	<0.15
Fluoride (ppm)	<0.15
SiO_2 (ppm)	<0.20
pH_T	6.8-7.4

Water chemistry in PWR primary circuit

► Pressure

- ◆ High enough to avoid boiling
- ◆ However, nucleate boiling may occur on some fuel pins in « high duty » cores
 - Favours the formation of deposits and may lead to the Axial Offset Anomaly (AOA)

► Boric acid

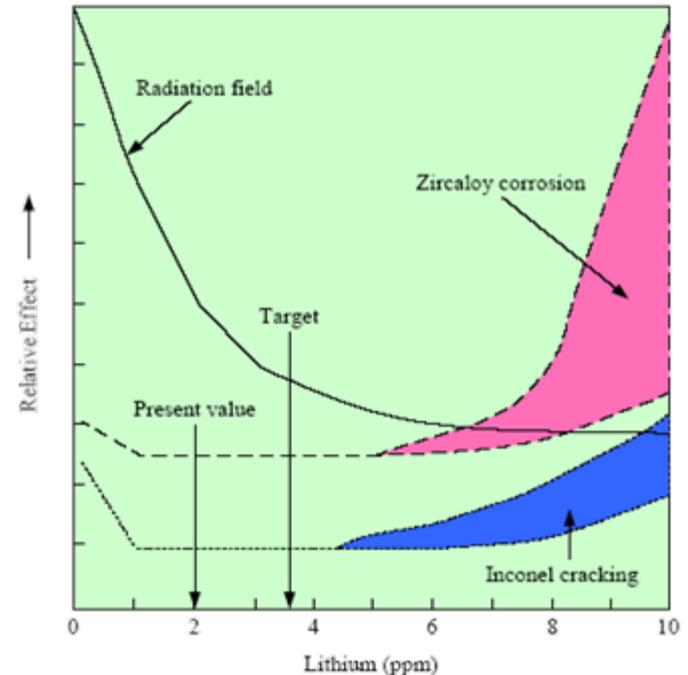
- ◆ Controls the nuclear reaction
 - Use of enriched B¹⁰ is considered to reduce the required amount of boric acid
- ◆ Decreases throughout the fuel cycle from ~1000/1800 ppm B to ~0

► Lithium hydroxide

- ◆ Control of pH
- ◆ Selected because
 - it is a relatively weak base and
 - it is a product of nuclear reaction with B
- ◆ Concentration
 - Formerly limited to 2.1 - 2.2 ppm Li to avoid damage to Zr alloys
 - Now the trend is to increase to 3.5 ppm (or even higher) to decrease activity of primary circuits and to allow longer fuel cycles

► Oxygen

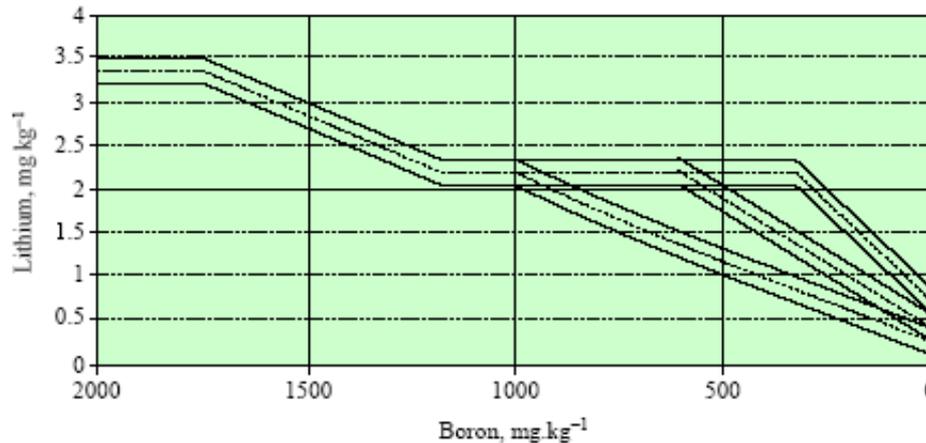
- ◆ Specification is < 0.1 ppm
- ◆ In service values are much lower



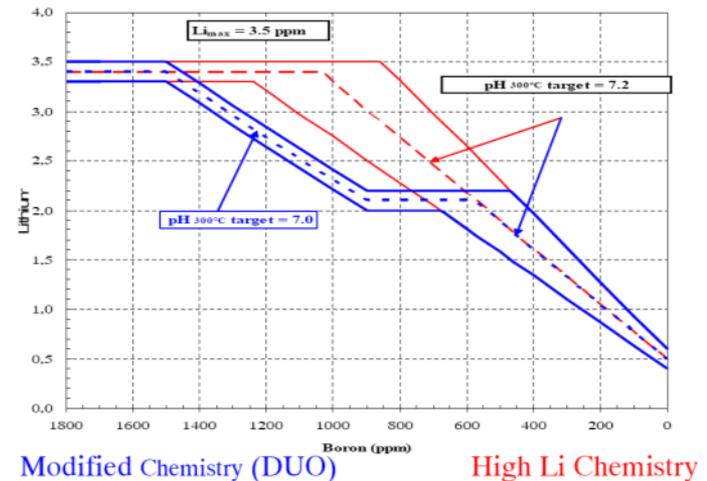
Water chemistry in PWR primary circuit

► Coordinated Li/B chemistries

- ◆ Goal is to optimise HT pH in order to minimise the activity of primary coolant circuits and to ensure safe behaviour of materials, particularly Zr alloys
 - Initially the optimum $\text{pH}_{300\text{ }^\circ\text{C}}$ was assumed to be 6.9
 - based on Fe solubility data
 - Now the optimum $\text{pH}_{300\text{ }^\circ\text{C}}$ is thought to be higher, ~7.2 to 7.4*
 - by taking into account Ni solubility (NiO and nickel ferrites)
 - This requires higher Li concentration at the Beginning Of Cycles (BOC)



Coordinated Li/B water chemistry
for pH 7.0, 7.2 and 7.4 (from Garbett)



French coordinated chemistries
(from Bretelle et al)

▶ Dissolved H₂

- ◆ Scavenges radiolysis oxidising products
- ◆ Maintains a low corrosion potential
 - A few cc/kg are sufficient to reach this goal
- ◆ Present specification 25-50 cc/kg
- ◆ Debate in progress to optimise the H₂ concentration
 - Effect on PWSCC
 - US position - Increasing H₂ slows Alloy 600 crack propagation
 - Europe and Japan – decreasing H₂ delays Alloy 600 crack initiation
 - Effect on primary circuit activity
 - Not clear
 - Recent results tend to show that decreasing H₂ could decrease activity
 - Minimum H₂ level in EPR will be 17 cc/kg

▶ Addition of Zn

- ◆ Considered to reduce activity of the circuits
 - 5 to 15 ppb targeted in plants with no Alloy 600 and related weld metals
 - Higher levels in plants with Alloy 600 and related weld metals to reduce risk of PWSCC initiation

Water chemistry in PWR secondary circuit

► Aims of secondary side water chemistry:

- ◆ Minimise corrosion problems
 - IGA-SCC of SG tubes
 - Avoid FAC of C-steels
 - Minimise corrosion of condenser tubing if using Cu alloys
 - Role of pH and amines
- ◆ Minimise formation of deposits
 - Fouling of tube free spans that decrease boiling efficiency
 - Blockage of TSPs that perturbs SG thermal hydraulics and can cause vibration problems
- ◆ Minimise costs and waste release

	Typical
Pressure (MPa)	5.4 – 7.2
Temperature (°C)	284 - 305
Oxygen (ppm)	<0.005
Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	<0.5
NH ₃ , morpholine or ethanolamine	As required for pH _T
Hydrazine (ppb)	Initially [O ₂]+ 5 Now 50 to 100 Or > 20 and > 8X[O ₂] (EPRI)
Sodium (ppm)	<0.005
Chloride (ppm)	<0.03
SiO ₂ (ppm)	<1
pH ₂₅	8.9 - 10

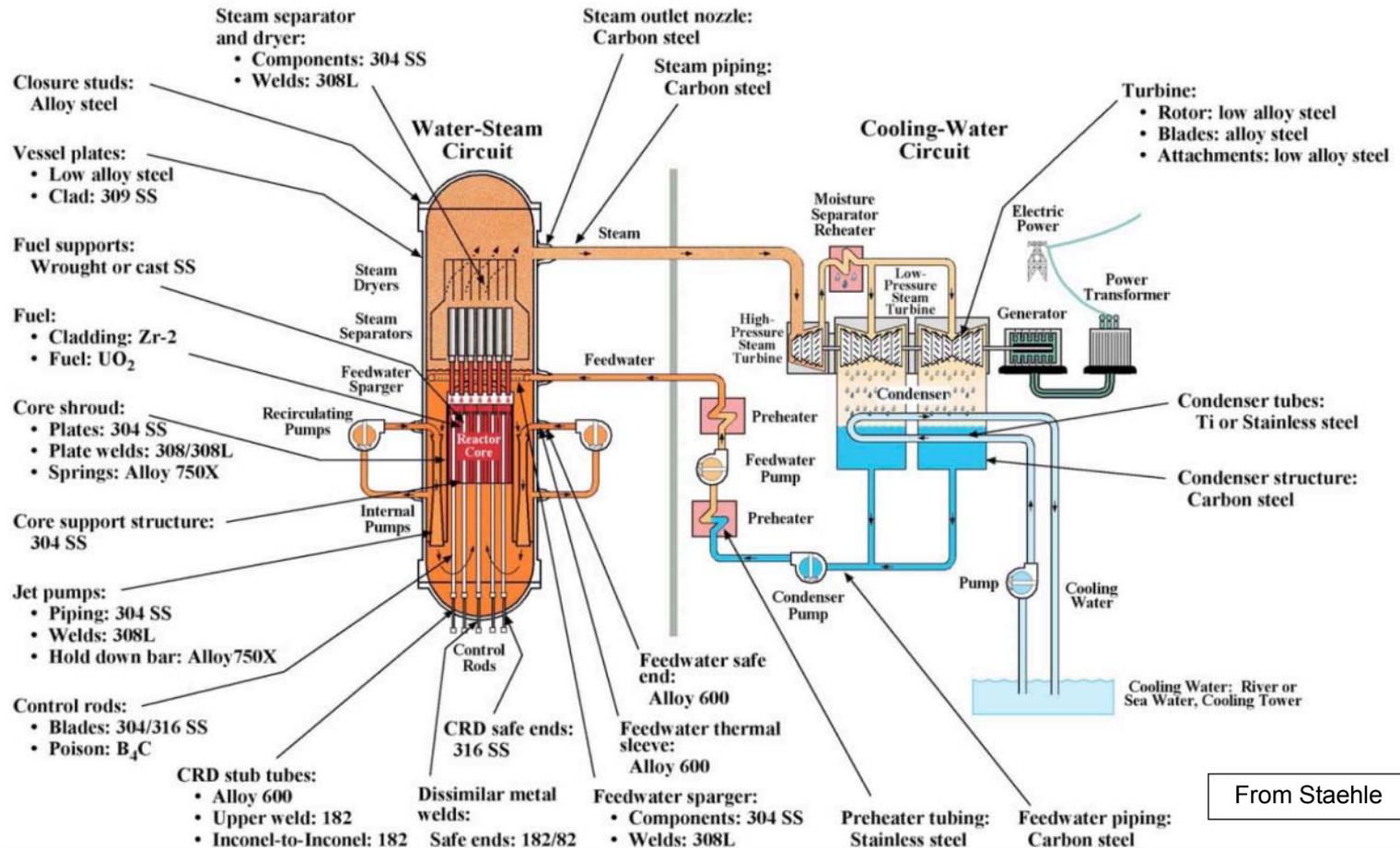
Corrosion in LWRs

BWRs

Main Materials in BWR plants

Water-Steam circuit

- ◆ Stainless Steels
- ◆ Nickel Base Alloys
- ◆ Carbon Steels
- ◆ Zr alloys



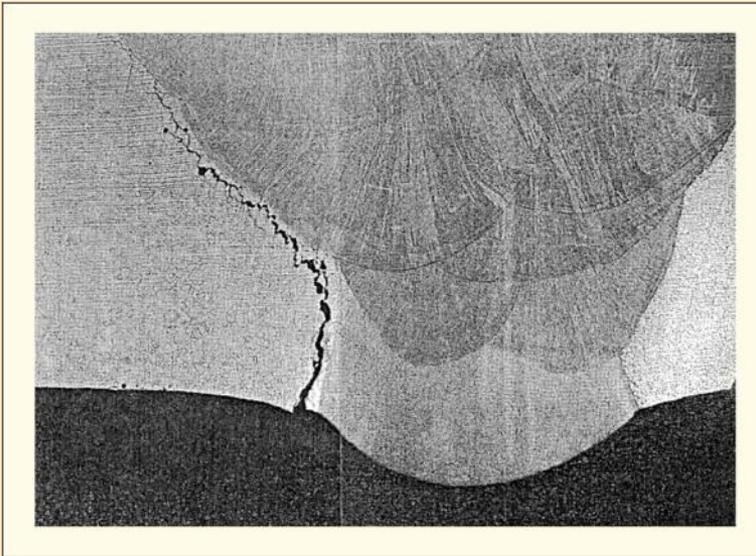
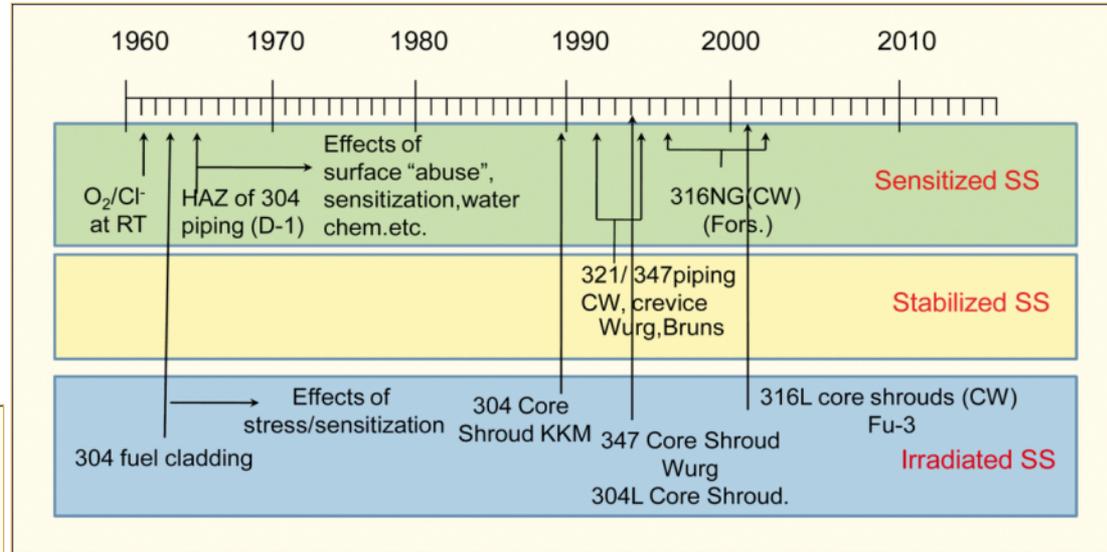
From Staehle

Main corrosion problems in BWR primary circuits

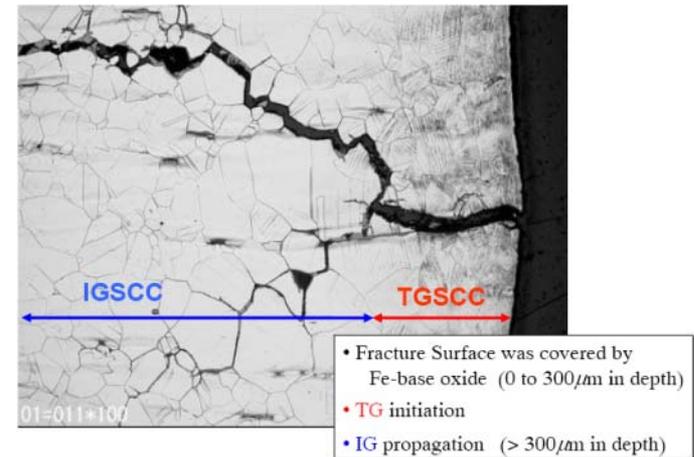
► Intergranular Stress Corrosion Cracking (IGSCC) of stainless steels

- ◆ Sensitized
- ◆ Bulk and Surface Cold worked
- ◆ Irradiated

► Cation release



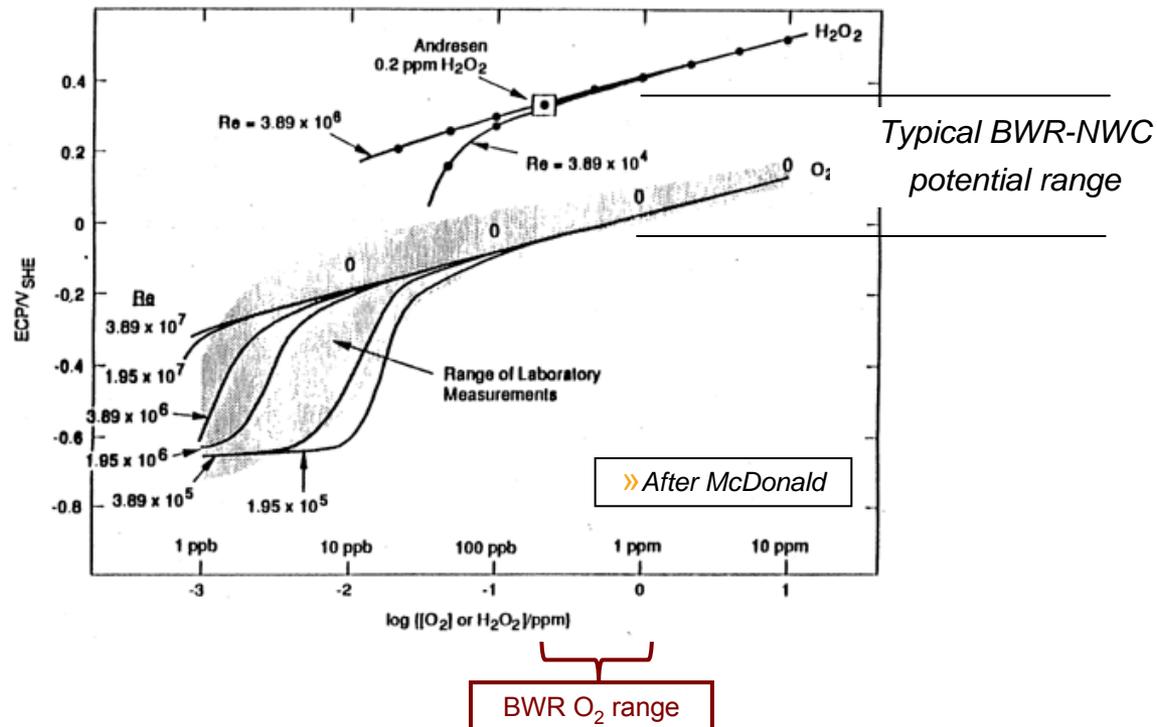
Pipe test results showing IGSCC in a 400mm. (16 ins.) Type 304 pipe HAZ (After Gordon & Gordon)



Cracking of SS HAZ initiated by severe surface cold work (After Suzuki)

Corrosion potential in BWR circuits

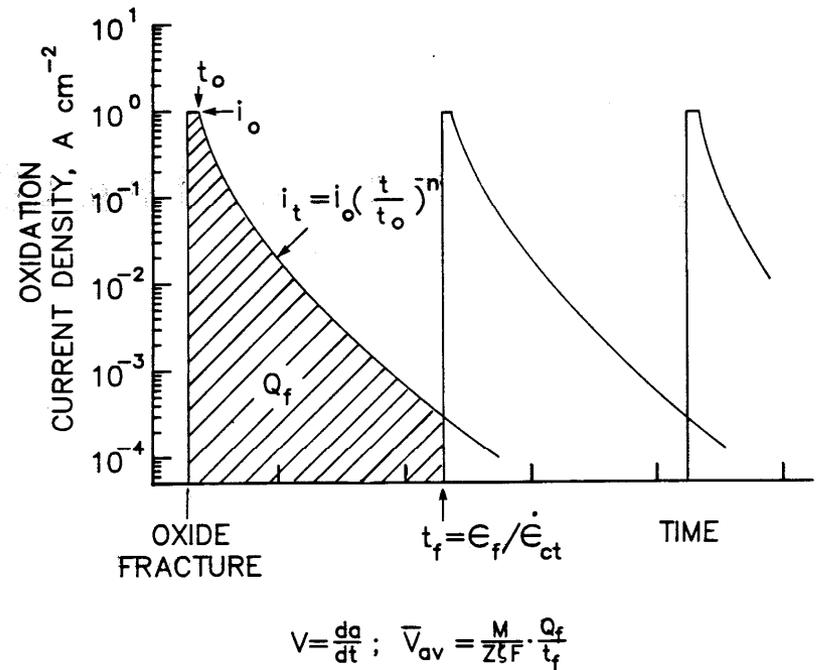
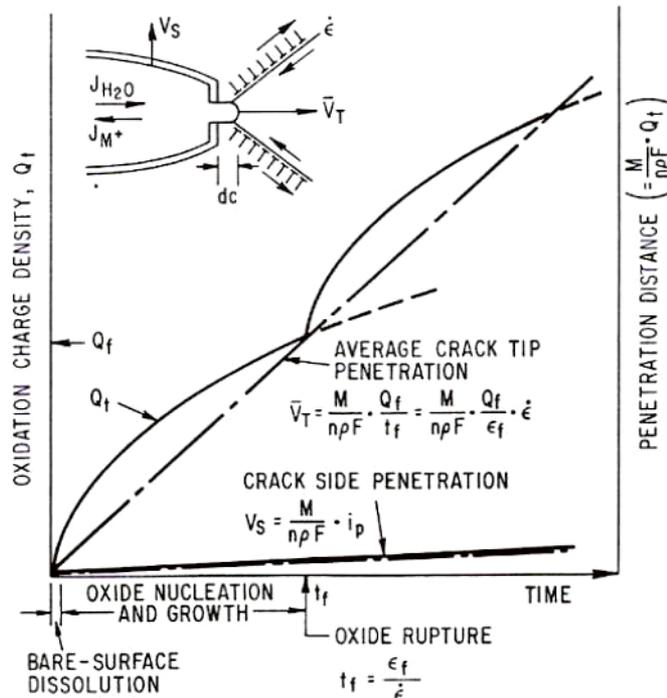
- ▶ BWR water contains dissolved oxygen and often oxygen peroxide sur to water radiolysis in the core
- ▶ This result in "high" corrosion potentials of materials in the circuits under Normal Water Chemistry



Modeling IGSCC of Stainless Steels in BWR water (GE PLEDGE model)

- Modeling based on a mechanistic assumption = SCC is due to a "slip-oxidation mechanism"

After Ford

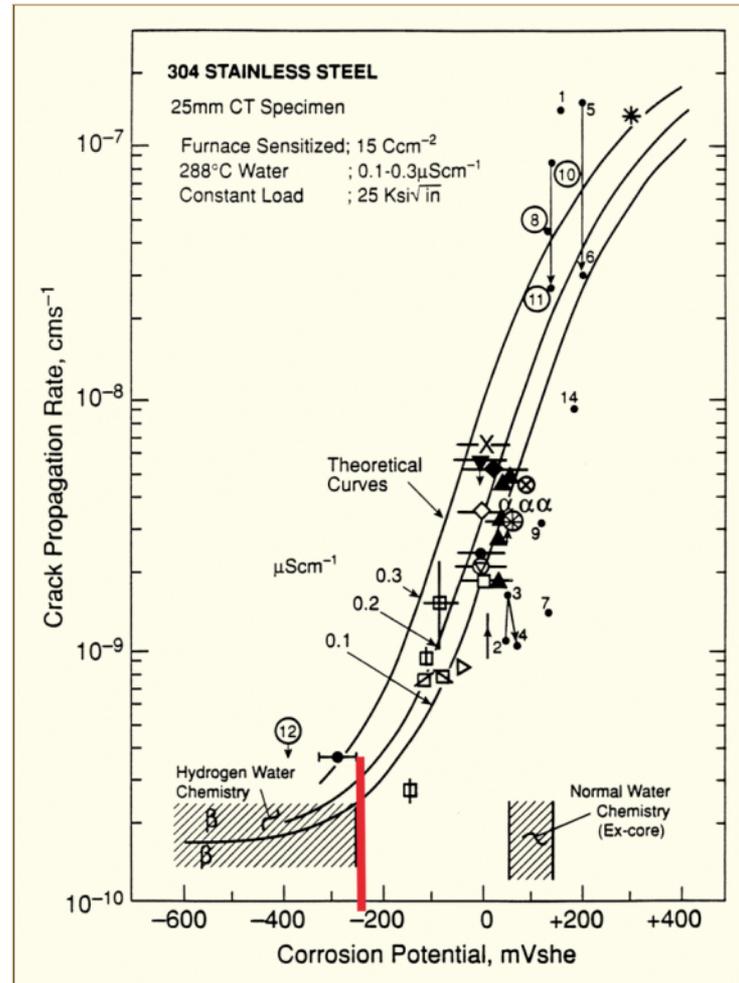


(a) Schematic oxidation charge density-time relationship for a strained crack tip and unstrained crack sides

(b) Changes in oxidation current density following the rupture of the oxide at the crack tip

Effect of potential on IGSCC of Stainless Steels in BWR water

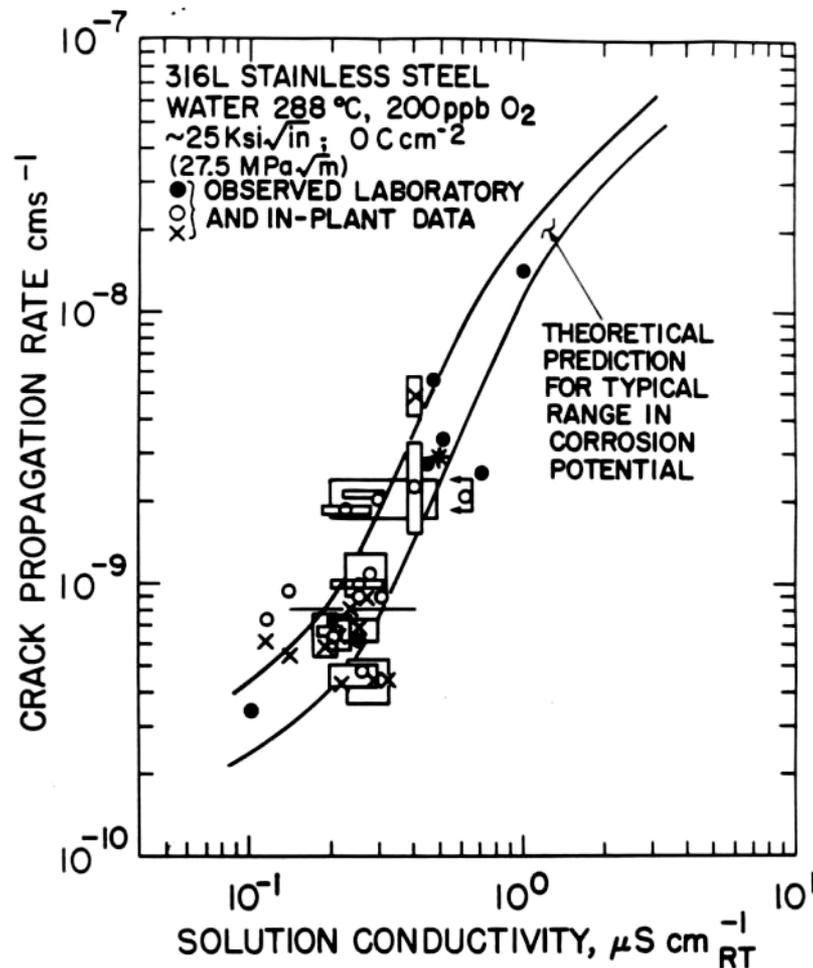
- ▶ Crack propagation rate increases dramatically in a potential range -200 - + 200 mV/SHE
- ▶ A practical critical potential has been defined at - 230 mV/SHE



After Ford

Effect of water purity on GSCC of Stainless Steels in BWR water

- ▶ High water purity strongly decreases crack propagation rates



Mitigation of IGSCC of Stainless Steels in BWRs

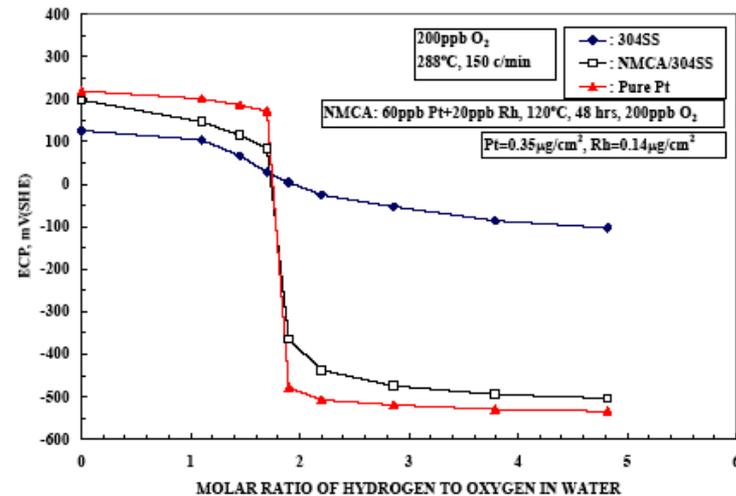
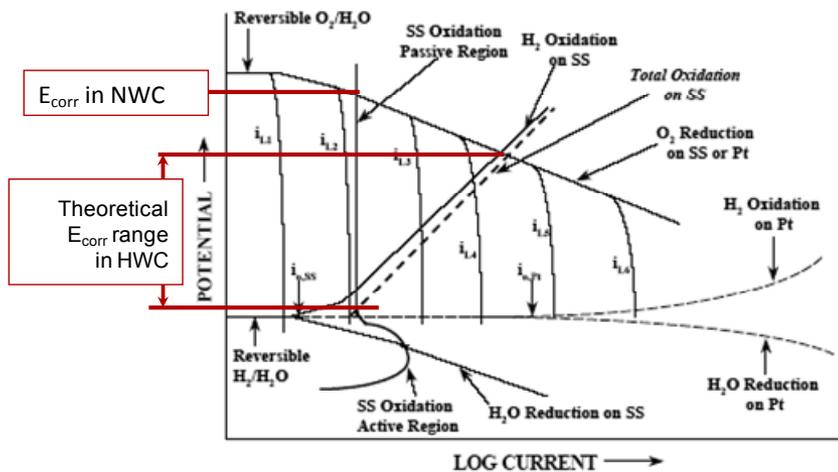
► Improvement of materials

- ◆ Use of Nuclear Grade and/or stabilized Stainless Steels materials
 - That are not sensitized by welding operations
- ◆ Improve surface conditions by avoiding excessive cold work during finishing operations
- ◆ For in-service plants, add corrosion resistant overlays on susceptible areas

Mitigation of IGSCC of Stainless Steels in BWRs

► Improvement of water chemistry

- ◆ Purity = BWR water of most plants now approaches the theoretical conductivity of pure water
- ◆ Hydrogen Water Chemistry (HWC = Addition of Hydrogen to decrease the corrosion potential below a critical value for IGSCC (around - 230 mV/SHE)
 - H_2 scavenges the radiolysis products of water in the core
 - H_2 recombines with O_2 on circuit surfaces
- ◆ NobleChem™ in addition to Hydrogen injection, noble metal particles on the surface catalyse the H_2/O_2 recombination reaction



After Kim

► Typical specifications under power operation (After Lundgren)

◆ Water in the circuits

	EPRI Recommended Goals			VGB Guidelines
	NWC	Moderate HWC	Noble Metal Chemical Addition	NWC
Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	<0.30 (note 1)	<0.08	<0.08	<0.15
Chloride (ppb)	<5 (note1)	<1	<1	<10
Sulphate (ppb)	<5 (note1)	<2	<2	<10
Silicate (ppb)				<200
Zn (ppb)		>5		
Cu (ppb)		<1	<1	
ECP (mV_{SHE})		<-230	<-230	
H ₂ /O ₂ molar ratio			3:1	

Note 1: Action level 1 values

◆ Feedwater

	EPRI Recommended Goals			VGB Guidelines
	NWC	Moderate HWC	Noble Metal Chemical Addition	NWC
Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	<0.065 (note 1)	<0.060	<0.060	<0.06
Zn (ppb)	<0.6 (note 1)	<0.4		
Cu (ppb)	<0.2 (note 1)	<0.05	<0.05	<0.3
H ₂ (ppm)	plant specific (<2.0)	0.15-0.4		
Fe (ppb)	<5 (note 1)	0.1-1.0	0.1-1.0	<2.0
O ₂ (ppb)	>30, <200 (note 1)	30-100	30-100	20-200

Note 1: Action level 1 values

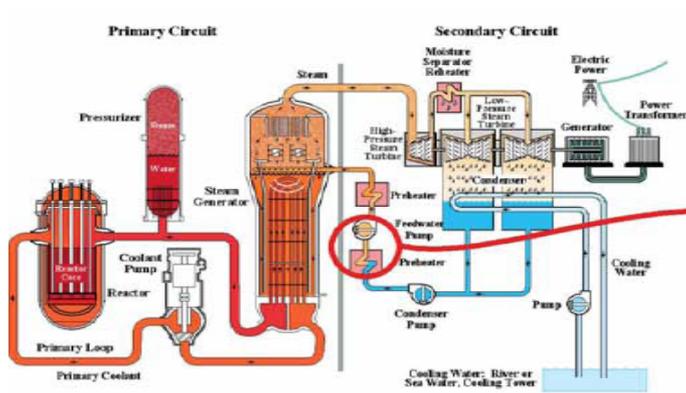
Flow Assisted corrosion

- ▶ Flow Assisted Corrosion (FAC) is a kind of General Corrosion enhanced by flow velocity
 - ◆ with no mechanical erosion
- ▶ FAC occurs on components made of Carbon-steel with very low Cr content
 - ◆ $Cr < 0.1 \%$
- ▶ FAC occurs:
 - ◆ In deaerated neutral water (oxygen < 5 ppb)
 - ◆ In a temperature range from 100 to 300° C
 - ◆ In single phase flow
 - ◆ In wet steam flow, if a liquid film is present on the metallic walls (no FAC can occur in dry steam).
- ▶ FAC causes loss of thickness with linear corrosion rates increasing with flow velocity which may be as high as several mm/year.

Thus, FAC may lead to the in service **rupture of components**.

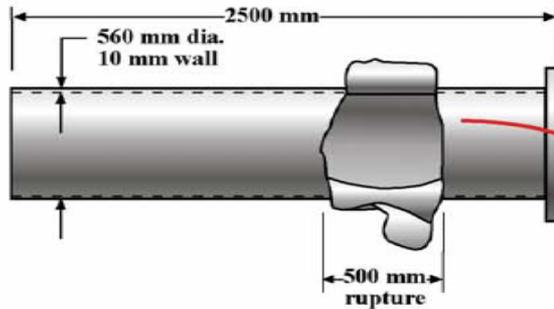
This raises a **safety problem for working people and plant components**

Mihama 3 FAC Incident, 2004



(c)

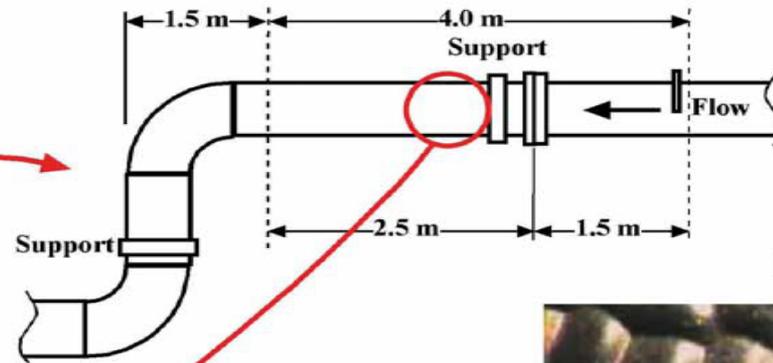
- 22 m/s, 0.93MPa, 142°C, 8.6-9.3pH
- 185,700 hr. operation



(d)



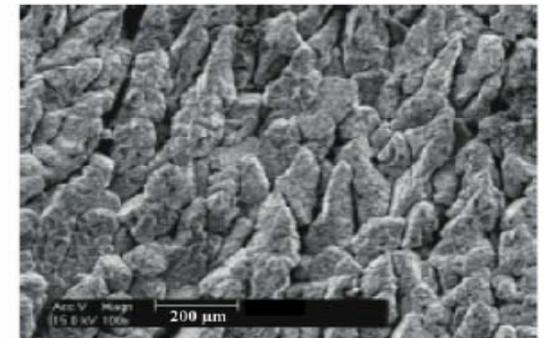
(b)



(e)

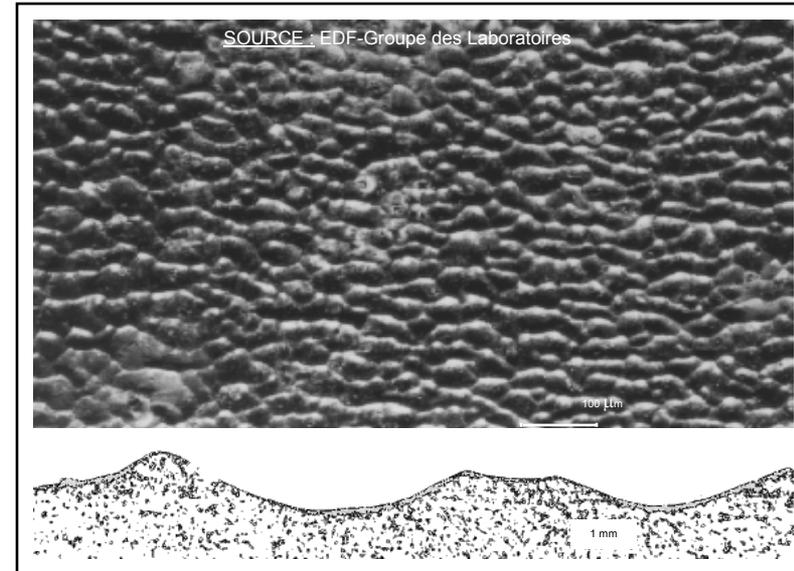
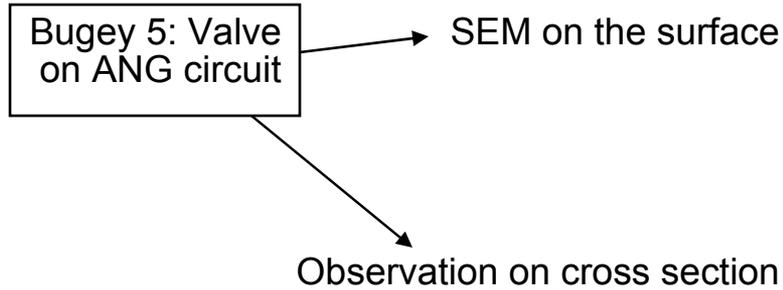


(f)

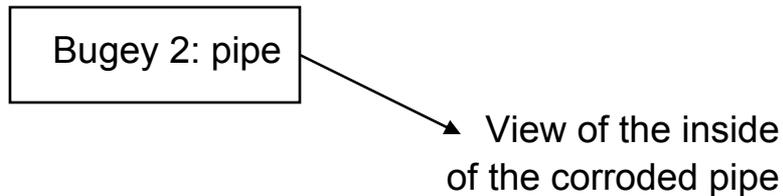


FAC of Carbon-steel - Aspect of corroded surfaces

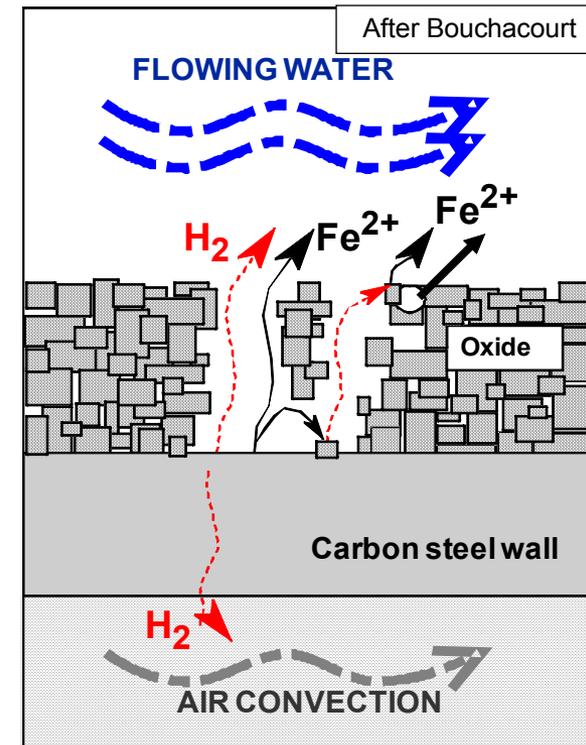
► Horse shoe pits in single phase flow



► Tiger striping in wet steam flows



- ▶ FAC is associated with changes in the mass-transport controlled oxidation and reduction electrochemical reaction rates occurring on an oxidized surface next to flowing water or wet steam.
- ▶ On Carbon steel, the thickness of protective magnetite layer results from a balance between
 - ◆ Formation of magnetite at or near the Metal/Oxide interface
 - ◆ Reductive dissolution of magnetite at the oxide/solution interface
$$\frac{1}{3} \text{Fe}_3\text{O}_4 + (2-b) \text{H}^+ + \frac{1}{3} \text{H}_2 \leftrightarrow \text{Fe}(\text{OH})_b^{(2-b)+} + (\frac{4}{3}-b)\text{H}_2\text{O}$$
- ▶ Mass transfer at metal/solution interface affects the dissolution rate of magnetite
- ▶ Increasing flow rate
 - ◆ increases the rate of reductive dissolution of magnetite
 - ◆ leads to thinner protective magnetite layer
 - ◆ increases the mass transport rates through the protective layer
 - ◆ And, thus, increases the corrosion rate of carbon steel



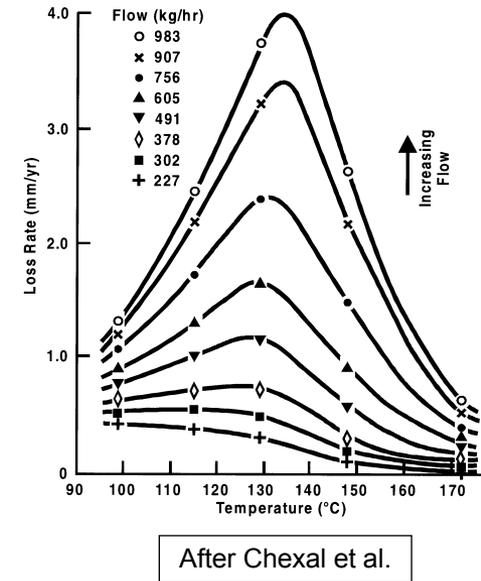
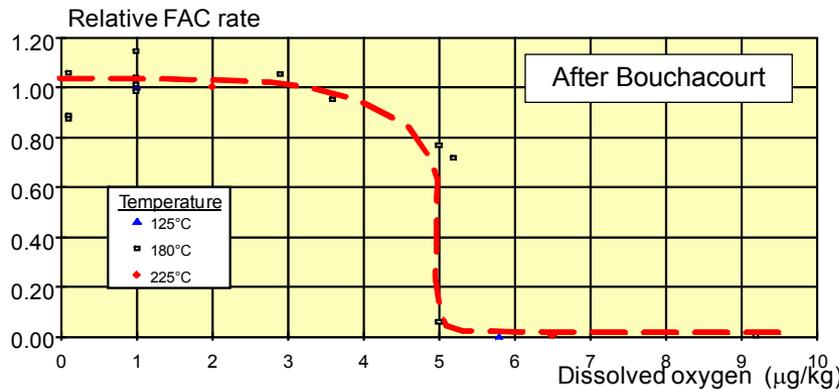
Model with porous oxide layer

▶ FAC is enhanced by dissolved hydrogen in solution

- ◆ Since it results from a reductive dissolution of magnetite

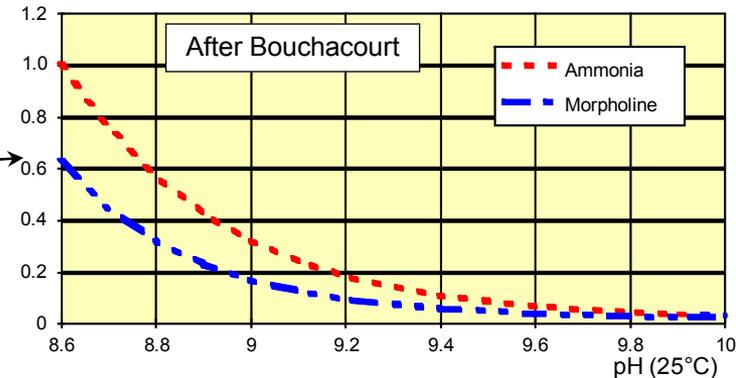
▶ Other influencing variables are:

- ◆ Flow rate and temperature
- ◆ Oxygen concentration (corrosion potential)
 - FAC is stopped as soon as hematite Fe_2O_3 becomes stable



◆ Water chemistry and pH

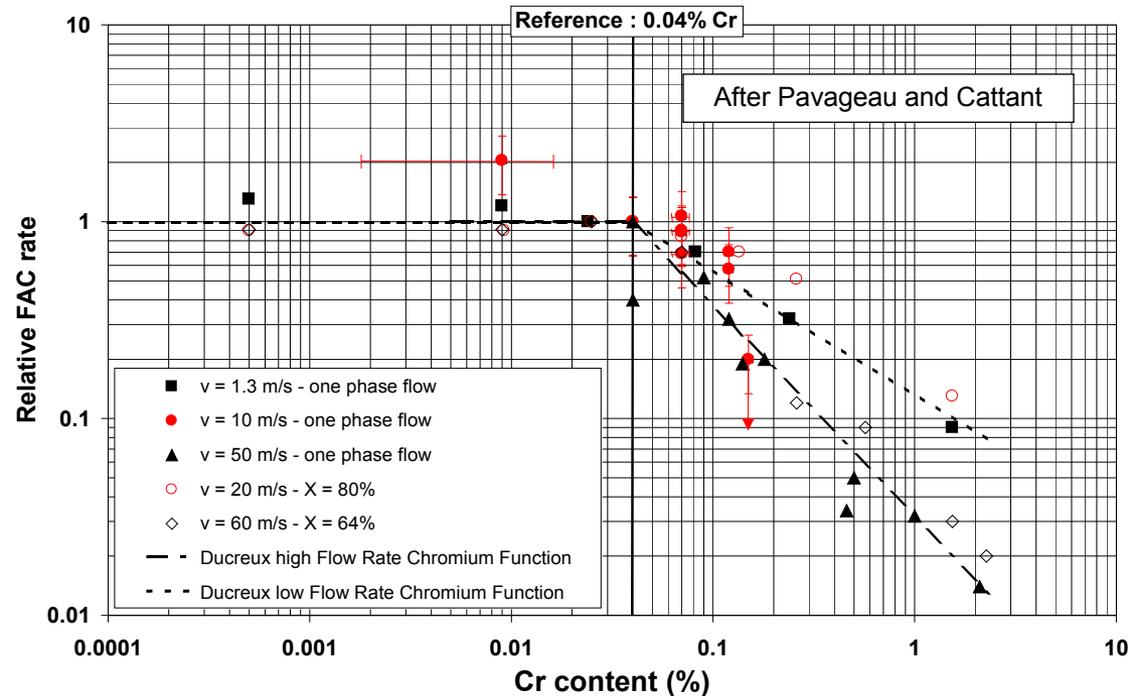
- Decreasing solubility of magnetite, decreases FAC rate
 - In near neutral environments (PWR secondary water increasing pH slows down FAC)
 - In slightly alkaline environments (CANDU primary water) increasing pH enhances FAC



Effect of steel composition

► Cr – Increasing Cr content slows down or stops FAC

- ◆ Current practice is to specify chromium levels of >0.15 or 0.2 wt% for the construction of PWR secondary side feed water piping.
 - Note that welds in 1¼Cr Mo or 2¼Cr Mo require stress relief → increase in cost.



► Other elements

- ◆ Cu and to a lesser extent Mo slow down FAC

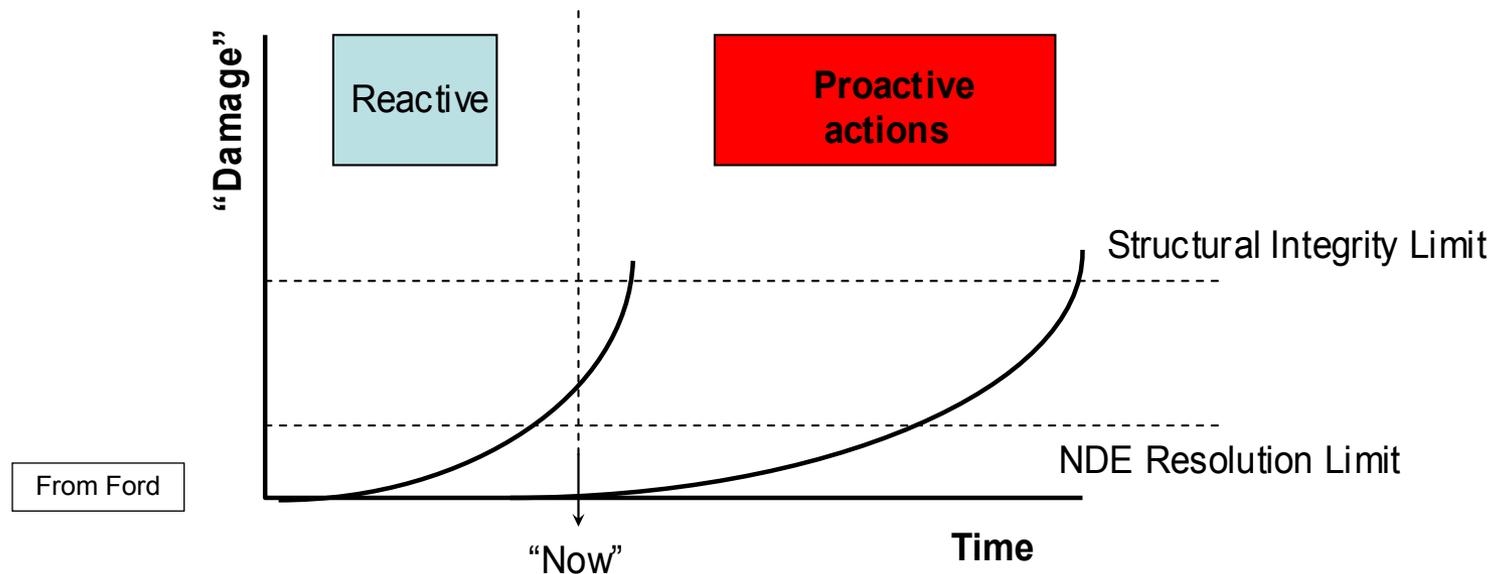
- ▶ EPRI CHECWORKS™ code – empirical statistical fits
- ▶ AREVA NP GmbH COMSY code – empirical statistical fits
- ▶ EdF BRT-CICERO code - physical model of ferrous ion transfer between the boundary layer in equilibrium with magnetite reduction and the ferrous ion concentration in the bulk water → metal loss rate roughly proportional to mass transfer rate
- ▶ British Energy (formerly CEGB) in-house code – same principles as the EdF code but includes flow effects on the cathodic reaction rate → predicts an accelerating non-linear dependence of FAC kinetics at high mass transfer rates

- ▶ Selection of materials for LWRs has been relatively successful from the point of view of corrosion resistance. Nevertheless, several critical problems have occurred in the last 30 years
 - ◆ The most important have been Stress Corrosion Cracking
 - Alloys 600, 182 and 82 in PWR primary water
 - SG tubes in PWR secondary water
 - Sensitized and cold worked Stainless Steels in BWRs

- ▶ These SCC problems led to extensive R&D to ensure safe life of components
 - ◆ Very important improvement of NDE techniques in order to detect flaws in components sooner and more reliably
 - ◆ Analyses of field experience and laboratory studies
 - to obtain a parametric description of the phenomena
 - to try to identify the underlying mechanisms
 - ◆ Modeling of phenomena in order to predict the most critical areas and to improve NDE campaigns
 - Empirical models for SCC of Alloys 600 and 182 in PWR primary water have been developed in the absence of a consensus on mechanisms
 - Mechanistically based modeling has been developed for Stainless Steels in BWRs
 - ◆ Prepare and implement repair and mitigation solutions

- ▶ As for most corrosion problems, solutions are not unique but involve combinations of improvements
 - ◆ Change of materials
 - Type 304 and 316 → type Nuclear Grade or stabilized Stainless Steels
 - Alloys 600, 182 and 82 → Alloys 690, 152 and 52
 - ◆ Improvement of material microstructure
 - X 750
 - Alloy 600 TT
 - ◆ Design of component
 - Alloy X 750 pins
 - Steam generator TSPs, row 1 to 3 tight U-bends...
 - ◆ Better control of fabrication process
 - Improved welding procedures
 - **Improved final surface conditions**
 - **Surface cold work minimized**
 - **Improved surface cleanliness**
 - ◆ Improved water chemistry
 - Water purity
 - Improved pH control
 - Improved corrosion potential control
 - HWC and NobleChem™ in BWRs
 - Addition of chemicals
 - Zn in primary circuits to reduce activity

- ▶ Up to now most actions have been reactive i.e. undertaken in response to critical events
- ▶ Trend is presently to try to have more proactive approach in order to adopt counter measures before significant damage has occurred



- ▶ But proactive management requires life prediction capabilities, i.e.
 - ◆ Identifying and understanding degradation processes
 - ◆ Developing reliable, quantified, models, preferably based on a knowledge of mechanisms, in order to ensure reliable extrapolations outside of the existing databases