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# FUNDAMENTALS ON CORROSION AND STRESS CORROSION CRACKING

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# CONTENT

- Why corrosion?
  - Definition (ISO 8044)
  - Thermodynamics / Pourbaix diagrams
  - Kinetics stability diagrams
- Electrochemistry and water corrosion
  - Anodic and cathodic reactions
  - Current-potential curves
- Localised corrosion: Stress corrosion cracking
  - Phenomena
  - Key parameters
  - Historical background
- References

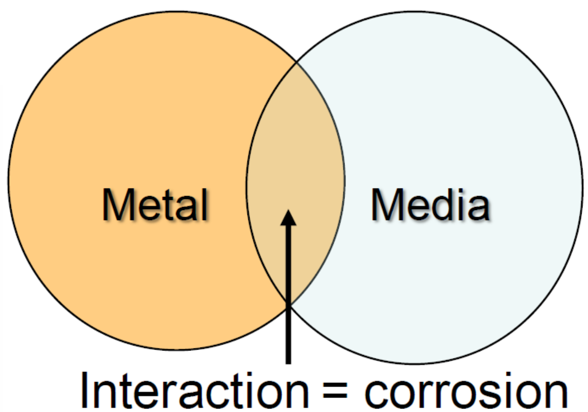
# Definition

**Corrosion** (ISO 8044, April 2000)

"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.

- NOTE This interaction is often of an electrochemical nature."

Minneapolis, USA, 2007



# Why Corrosion ?

- Industrial alloys are not thermodynamically stable in their environment
- Thermodynamic stability diagrams
- In water : E-pH diagrams
- Marcel Pourbaix, « Atlas d'équilibres électrochimiques », Gauthier-Villars, Paris, 1963

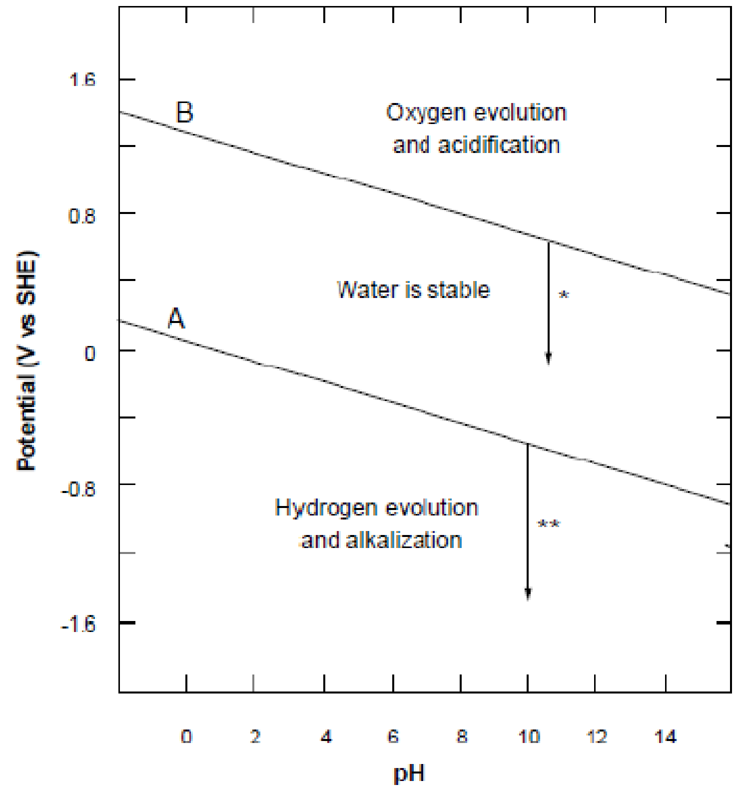
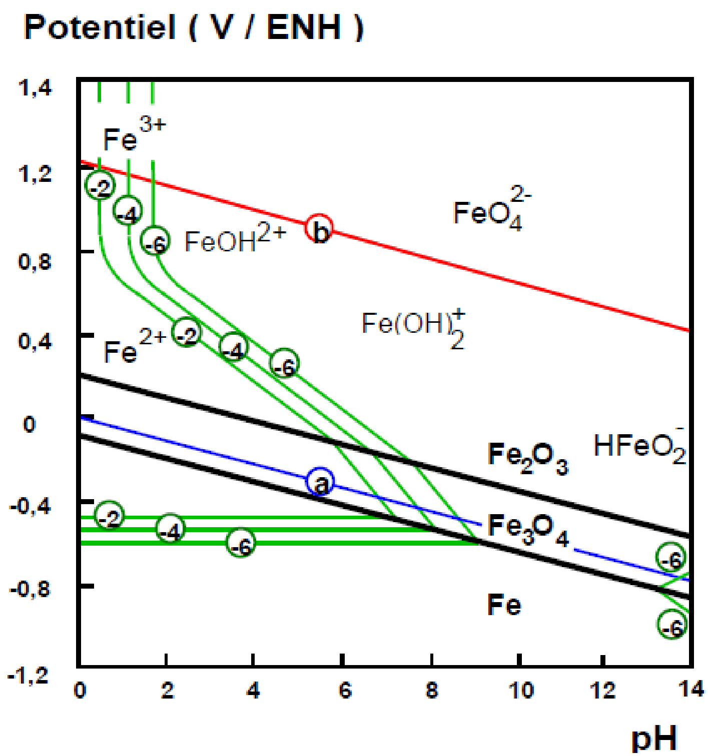
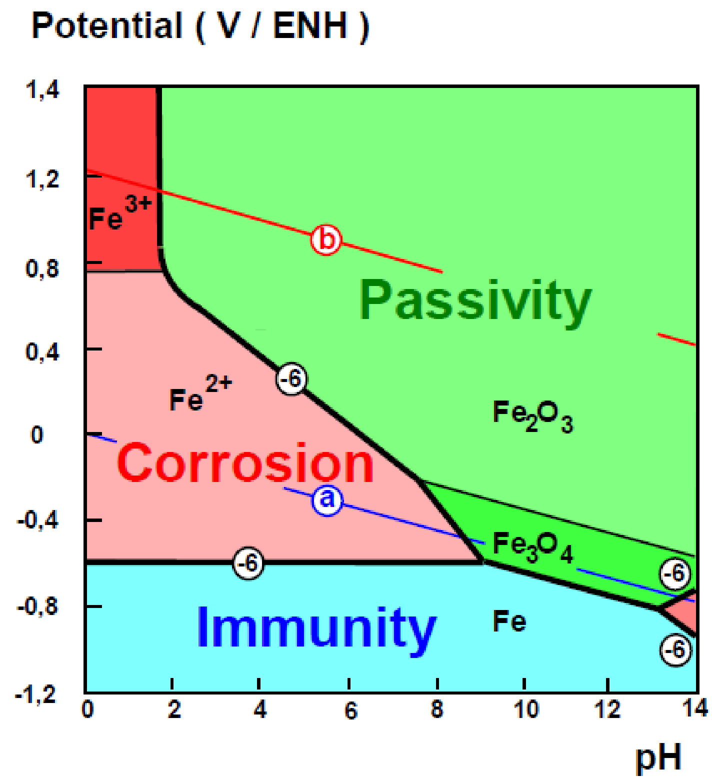



Figure 1.3 Thermodynamic stability of water, oxygen, and hydrogen. (A is the equilibrium line for the reaction: $H_2 = 2H^+ + 2e^-$. B is the equilibrium line for the reaction: $2H_2O = O_2 + 4H^+ + 4e^-$. * indicates increasing thermodynamic driving force for cathodic oxygen reduction, as the potential falls below line B. ** indicates increasing thermodynamic driving force for cathodic hydrogen evolution, as the potential falls below line A.)

## Potential-pH diagrams / "Pourbaix diagrams"




a) Solubility diagram

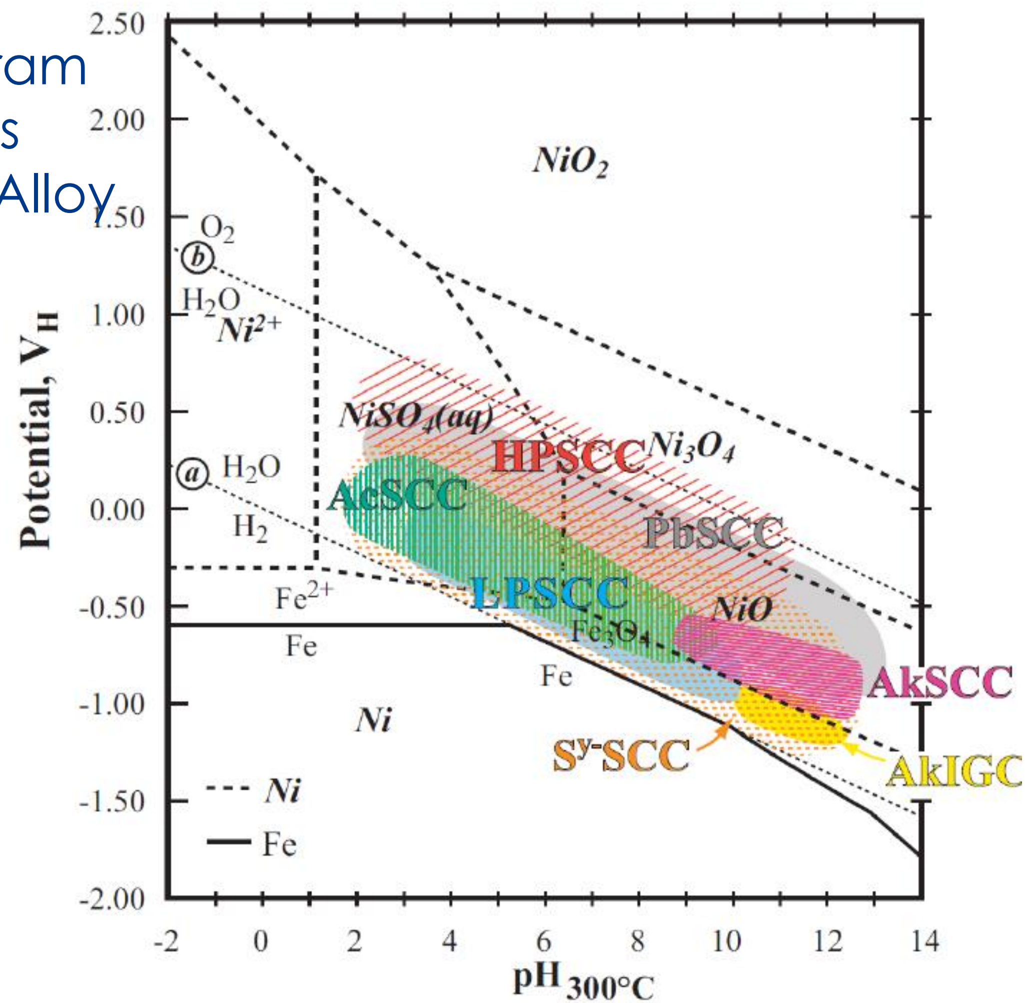



b) Corrosion diagram

# Corrosion & Thermodynamics

Regions of potential - pH diagram where different modes of Stress Corrosion Cracking occur for Alloy 600 at (300°C)

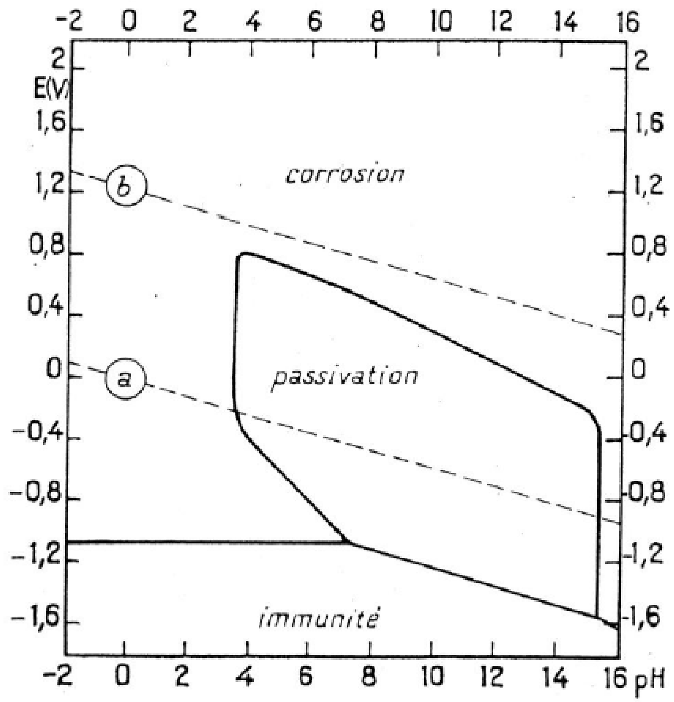
- **LPSCC**: low potential SCC
- **HPSCC**: high potential SCC
- **AkSCC**: Alkaline SCC
- **AcSCC**: Acid SCC
- **AkIGC**: Alkaline IGC
- **Pb SCC**: lead SCC
- **Sy- SCC**: Sulfur SCC




from Roger Staehle

# Corrosion & Kinetics

## Thermodynamics # Kinetics




*a.* Figure établie en considérant Cr $(OH)_3$.

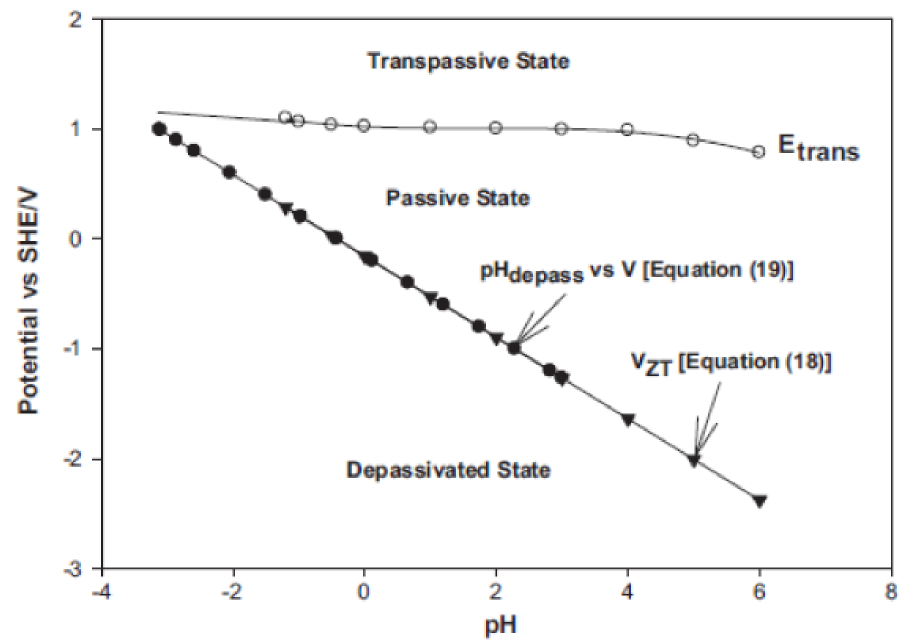



**Fig. 9.** Primitive Kinetic Stability Diagram (KSD) for Alloy X in 6.256 m NaCl at 50 °C.

Chromium Pourbaix diagram

Kinetic stability diagram (KSD)
Chromium oxide passive layer
(Digby MacDonald)

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  - Passivation
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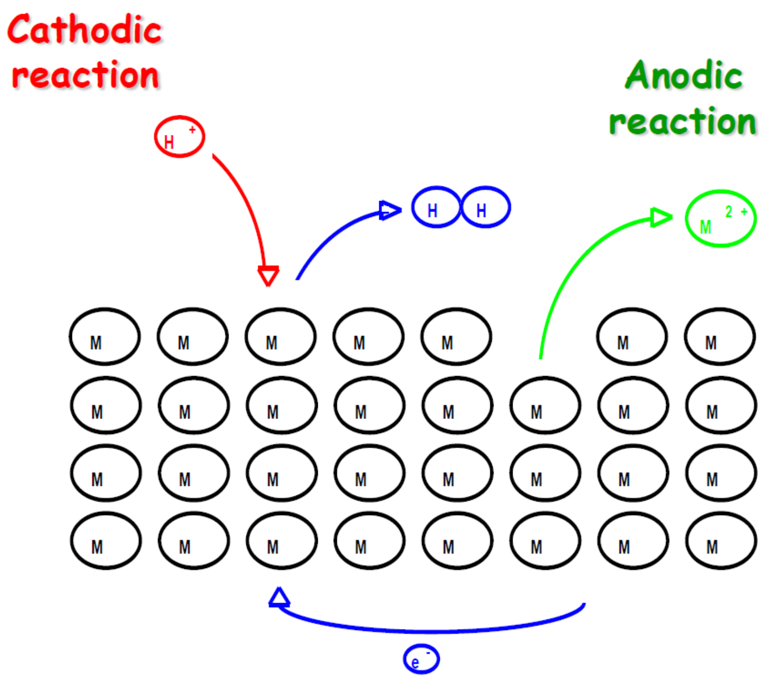
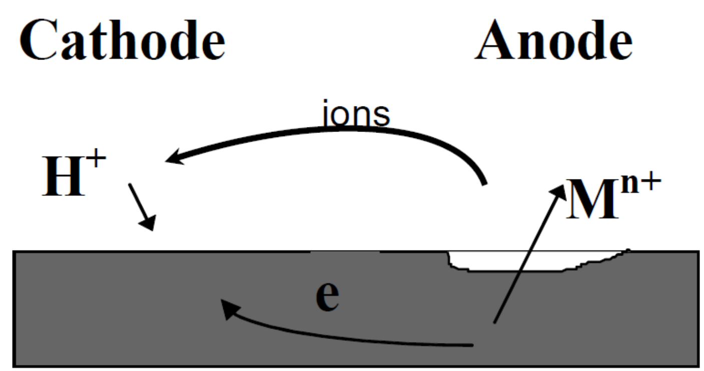
# Anodic & cathodic reactions

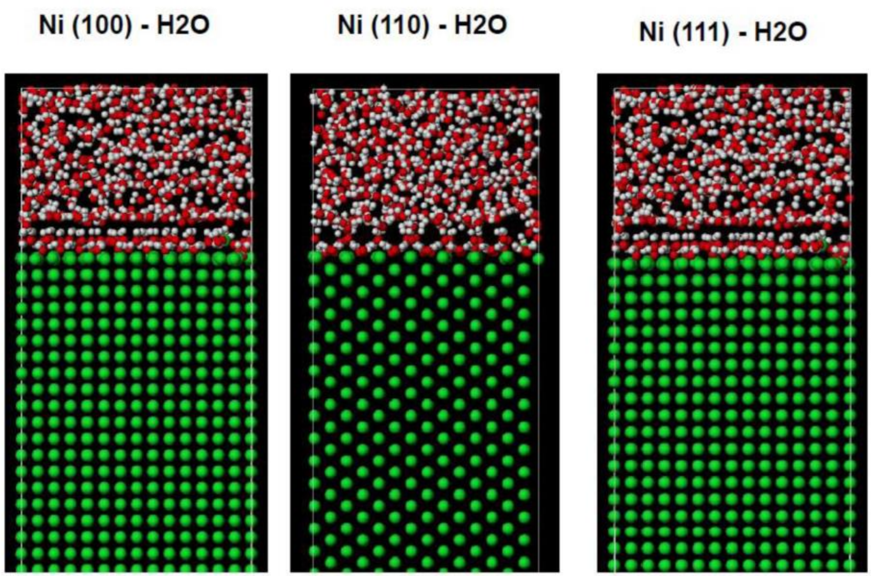
**Electrochemical corrosion:** "corrosion involving at least one anodic reaction and one cathodic reaction"



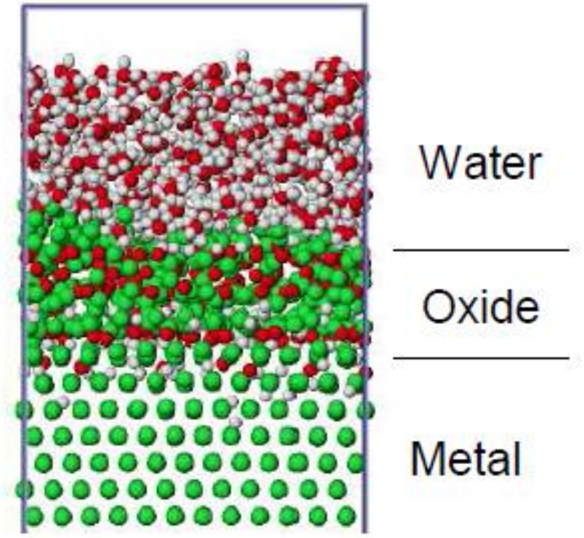




**Aqueous corrosion (corrosion in LWRs) is an electrochemical corrosion**

# Atomistic simulations



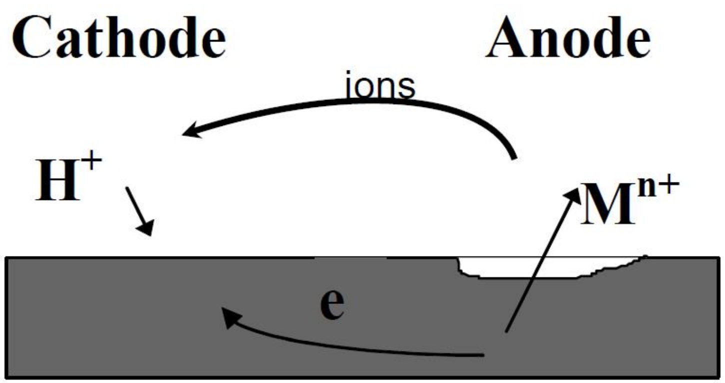

From B. Diawara & Al., 2012-2014

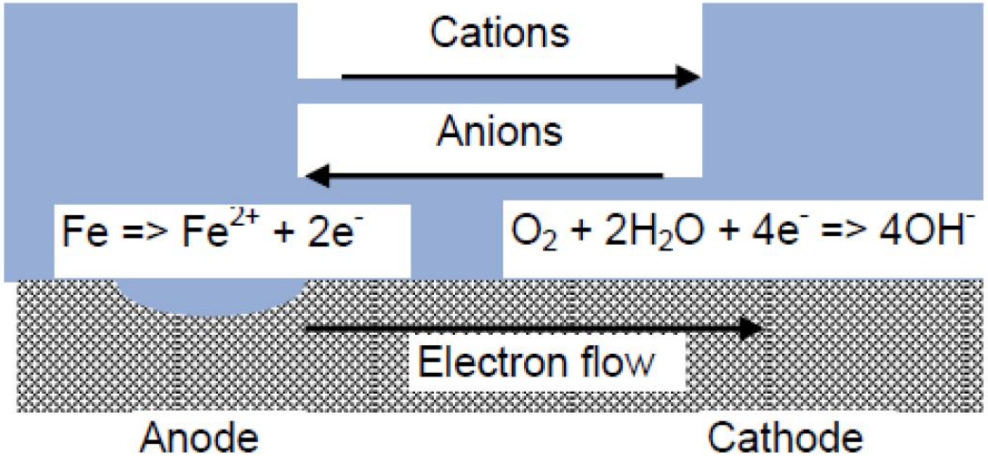



Molecular dynamics

- Surface reactivities
- Continuous oxide layer
- Hydrogen in the metal

# Corrosion current



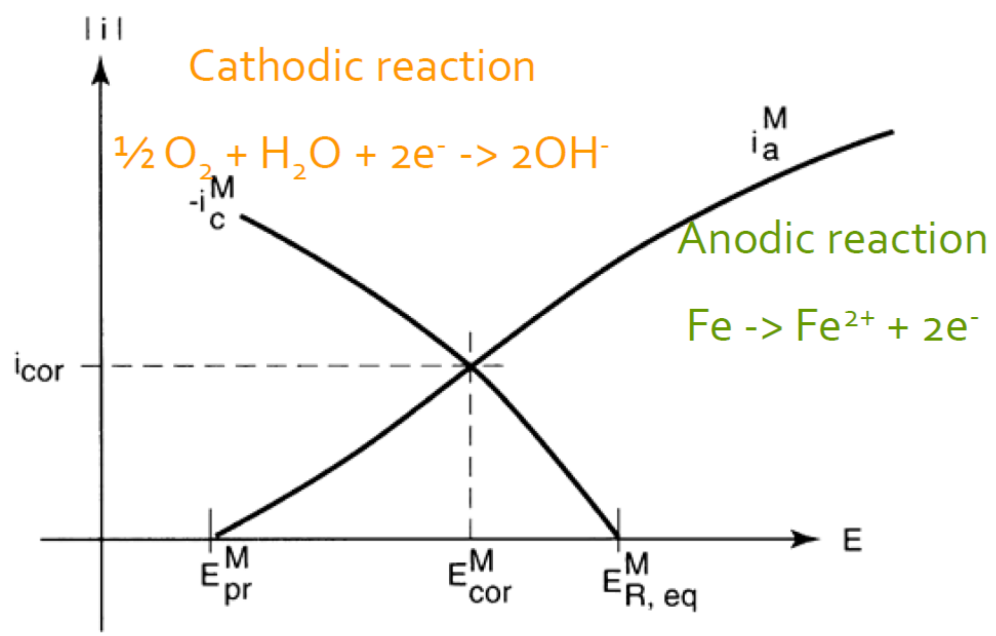

- Main cathodic reactions in aqueous media
  - $2H^+ + 2e^- \rightarrow H_2$ (acid environment – fast)
  - $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
  - $H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (slow – idem first one)

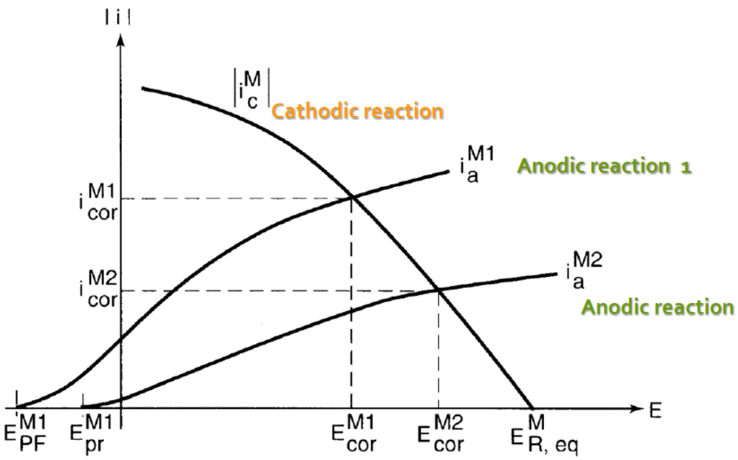
$$\text{Mass loss} = \frac{I \times t \times M}{z \times F}$$

*I* is the current , *t* is the time, *M* is the molar mass of the metal, *z* is the number of electrons involved in the reaction and *F* is Faraday's constant

# Anodic & cathodic curves

- Anodic current is positive / Cathodic current is negative




If the cathodic reaction rate is constant, free corrosion potential decreases when corrosion rate increase

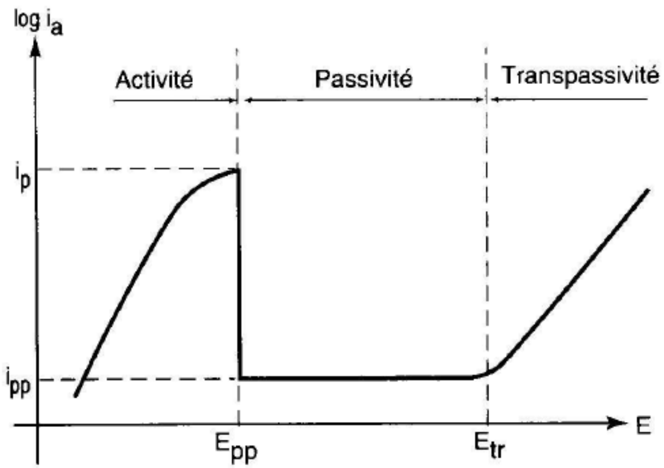
# Corrosion & passivation

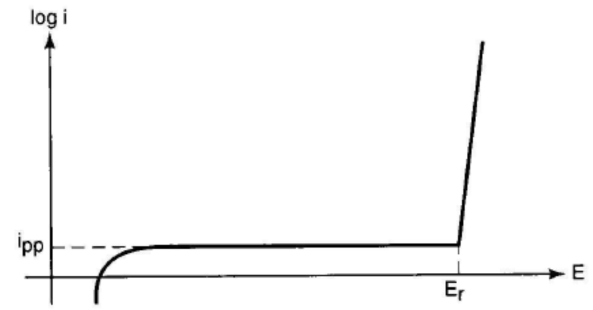
**Passivation**: "decrease of corrosion rate by a passivation layer

NOTE Incomplete passivation may lead to localized corrosion"

**Passivation layer:** "passive layer thin, adherent, protective layer formed or a metal surface through reaction between metal and environment"

**Anodic curves of a passive material**




In neutral media, no activation peak

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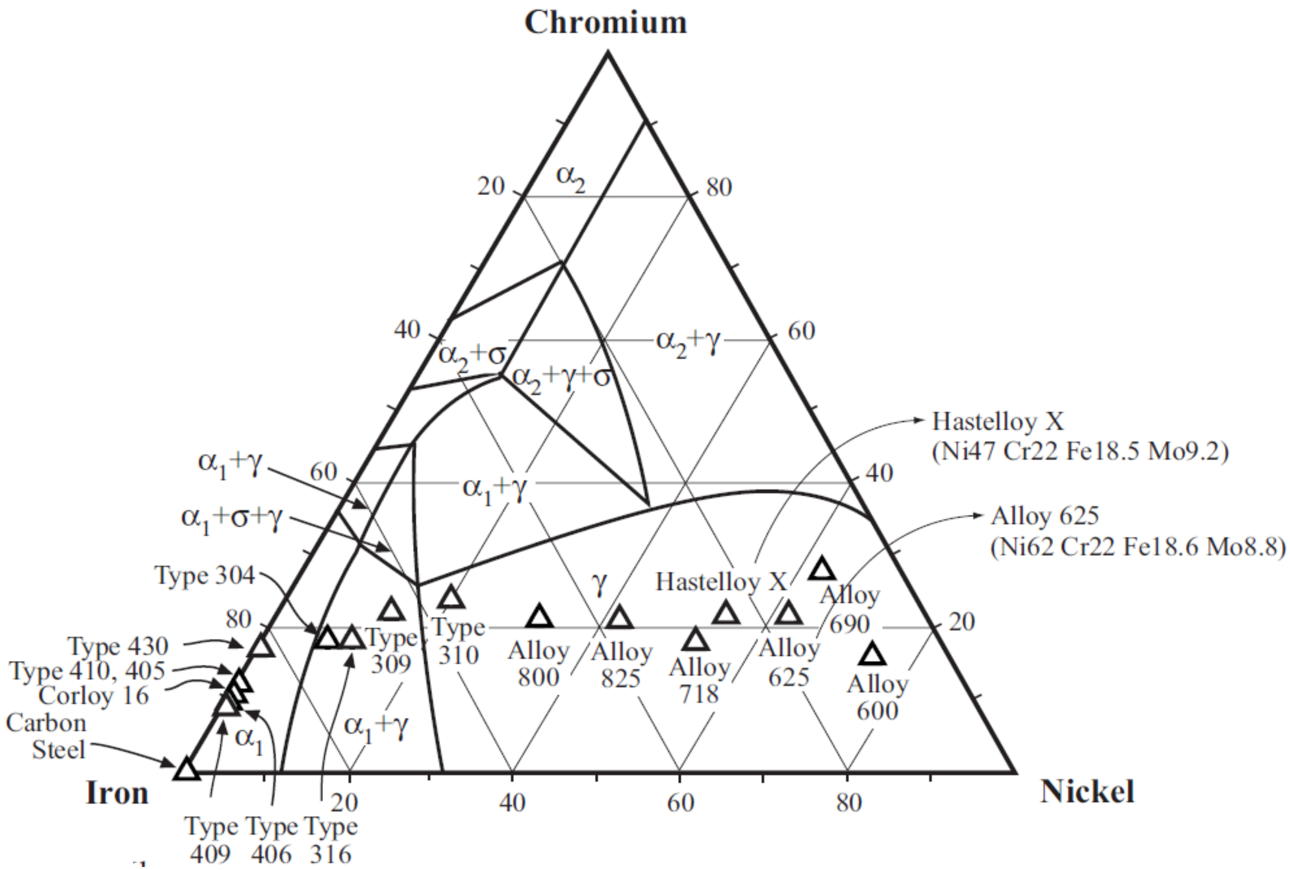
# EAC & SCC

- Environmental Assisted Cracking (EAC) covers different degradation modes
  - Stress corrosion cracking (SCC): cracking of a metal under the combined effects of constant stress and a specific environment
  - Corrosion fatigue (CF) takes place under cyclic stresses
  - Strain induced corrosion cracking (SICC): cracking under increasing strain

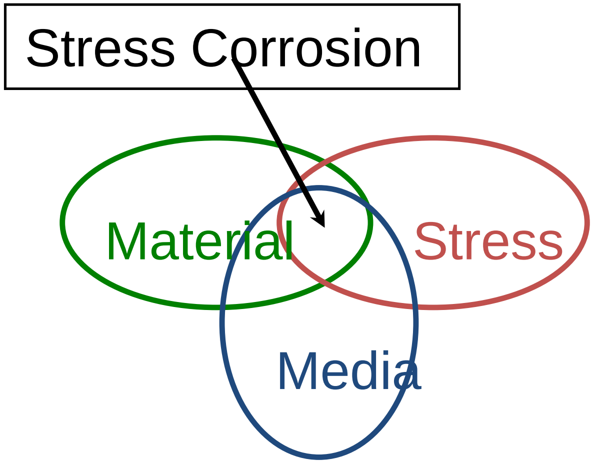
- Materials susceptible to SCC in LWR conditions
  - Austenitic stainless steels (300 type)
  - Nickel base alloys (Alloy 600, weld Alloys 82 & 182, Alloy X-750)
  - Low alloy & carbon steels
  - others

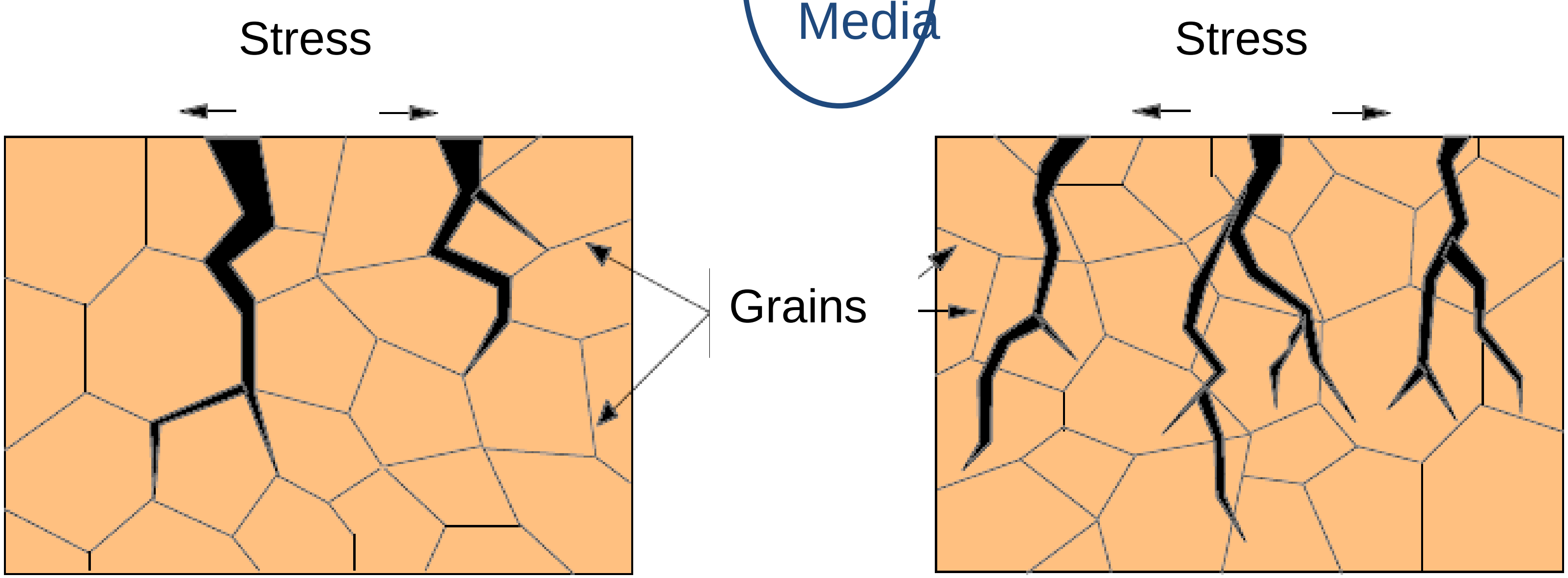
# SCC and allloys

- Main alloys in LWRs



# Morphology of SCC

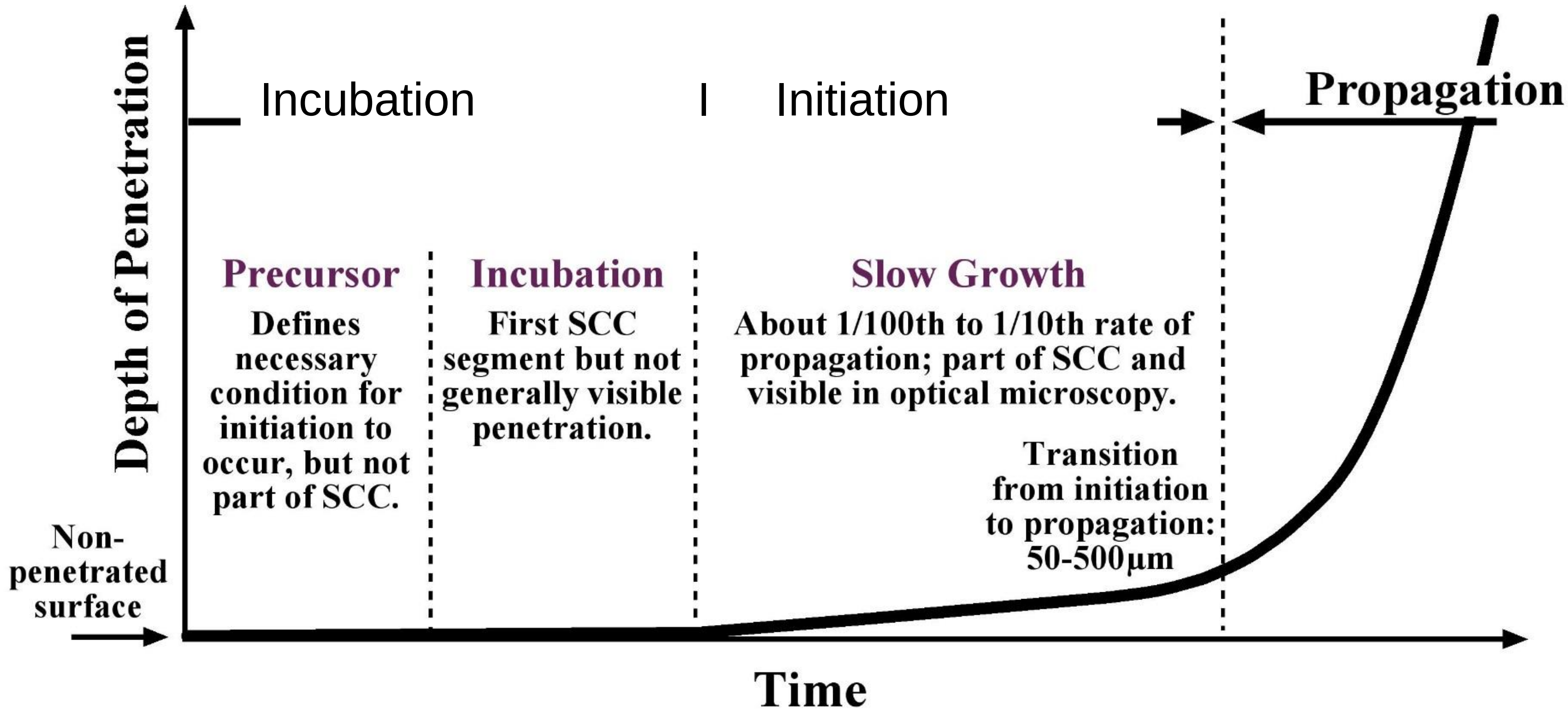



Intergranular cracks

Transgranular cracks

# SCC phases

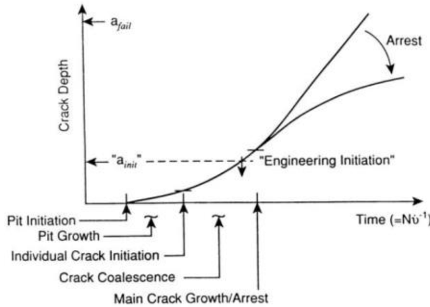



From R. Staehle

**Incubation:** Passive film formation and evolution

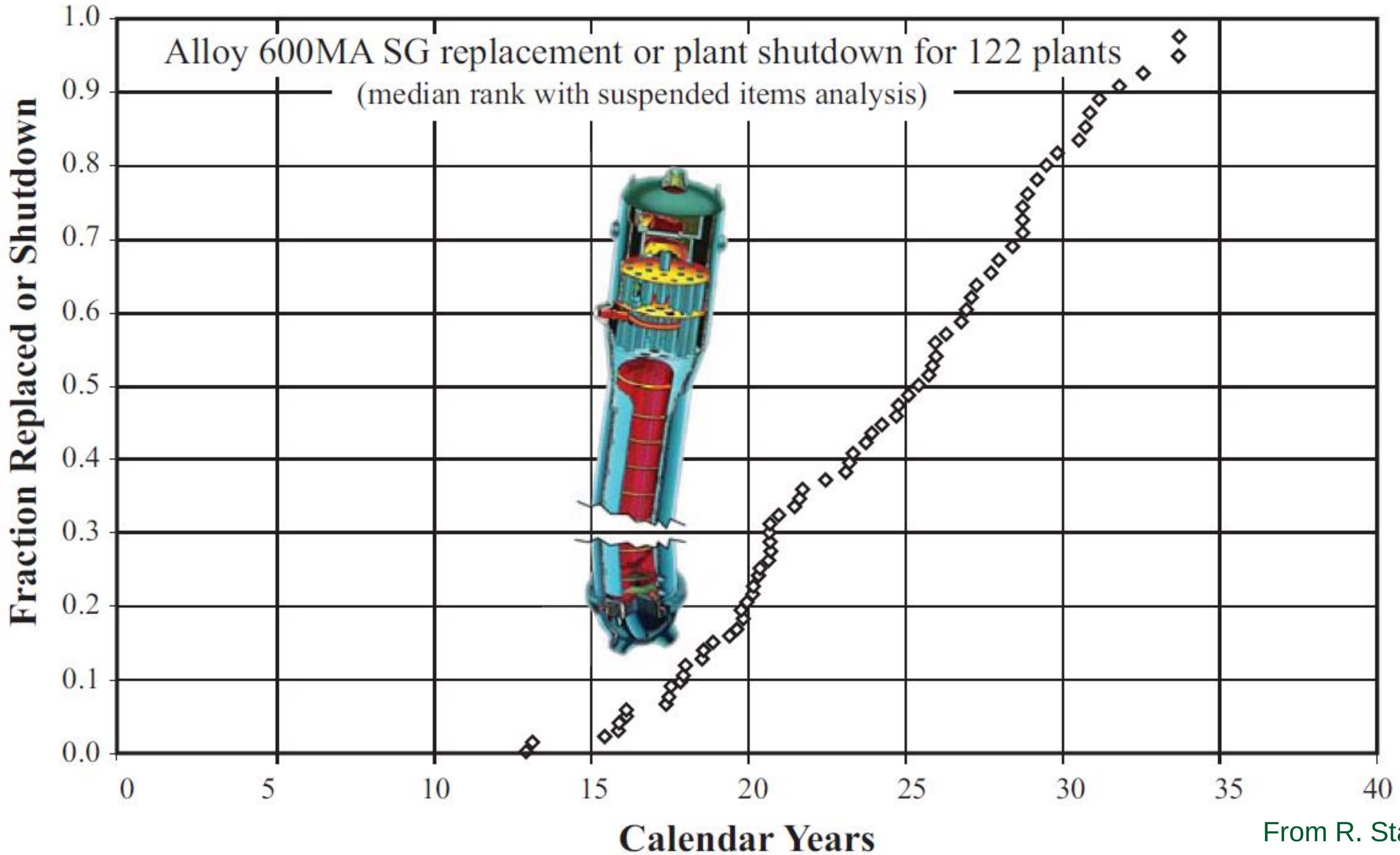
**Initiation:** Film rupture & Intergranular oxidation

**Propagation:** Internal oxidation & Hydrogen



# SCC of Alloy 600

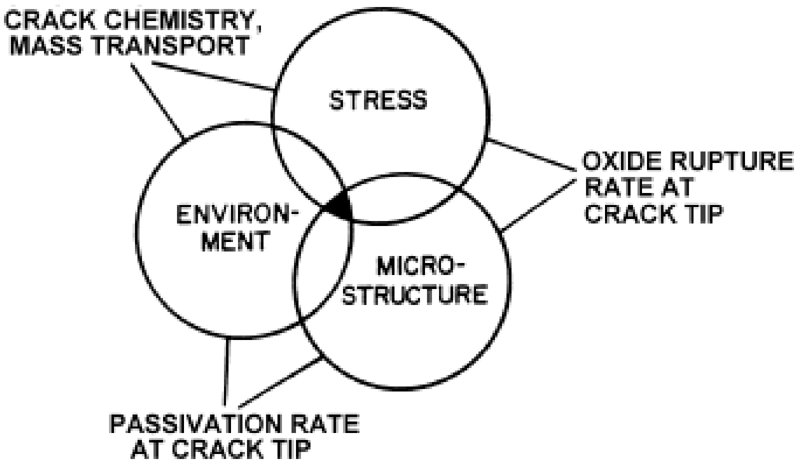
- Long initiation time




From R. Staehle

# SCC Key Parameters

- The complexity of SCC is reflected in the large number of influential variables (from Peter L. Andresen)



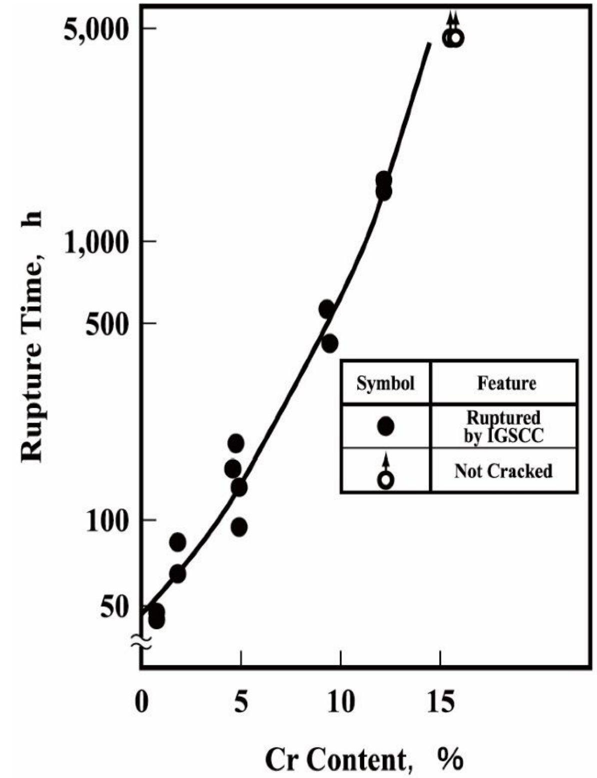

Crack depth vs. time = f ( Material, Stress, Environment )

| Material | Stress | Environment |
|---|---|---|
| Chromium | Primary | Corrosion Potential |
| % Cold Work | Static | Oxidizing Species |
| Neutron Fluence | Dynamic | Anionic Species |
| Silicon | Residual | Type |
| Nickel | Crack Depth | Activity |
| Sulfur | Neutron Fluence | Temperature |
| Phosphorus | Relaxation | Flow Rate |
| Carbon | Thermal | Neutron flux |
| Weld heat input | Radiation | Crack Depth |

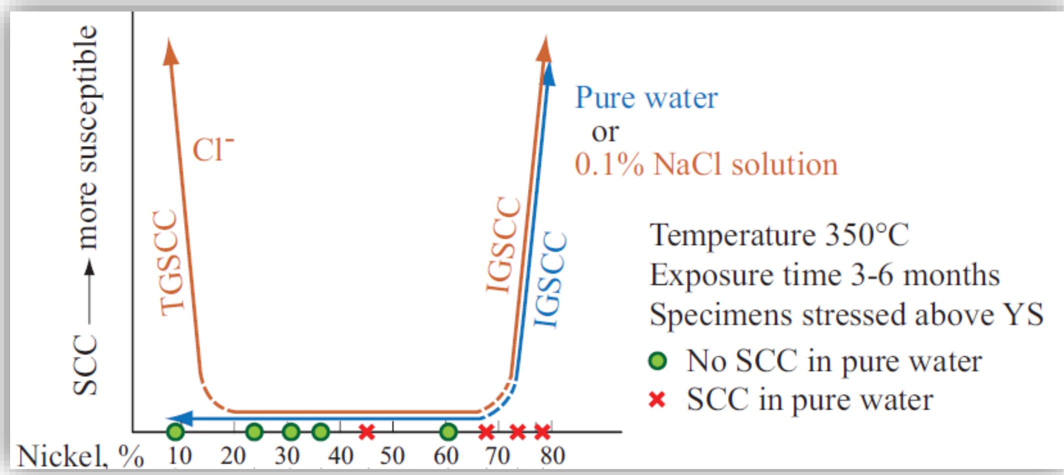
# SCC main parameters

From T. Yonezawa

- Eight principal variables (from R. Staehle)
  - **Temperature**
  - **Stress**
  - **Alloy composition**
  - Alloy structure (cold work)
  - **Electrochemical potential**
  - Species (pollutants)
  - pH
  - Irradiation




Influence of the alloy composition: 10% Fe-Cr-Ni alloys with various Cr contents




Influence of the alloy composition: Fe-18%Cr-Ni alloys with various Ni contents

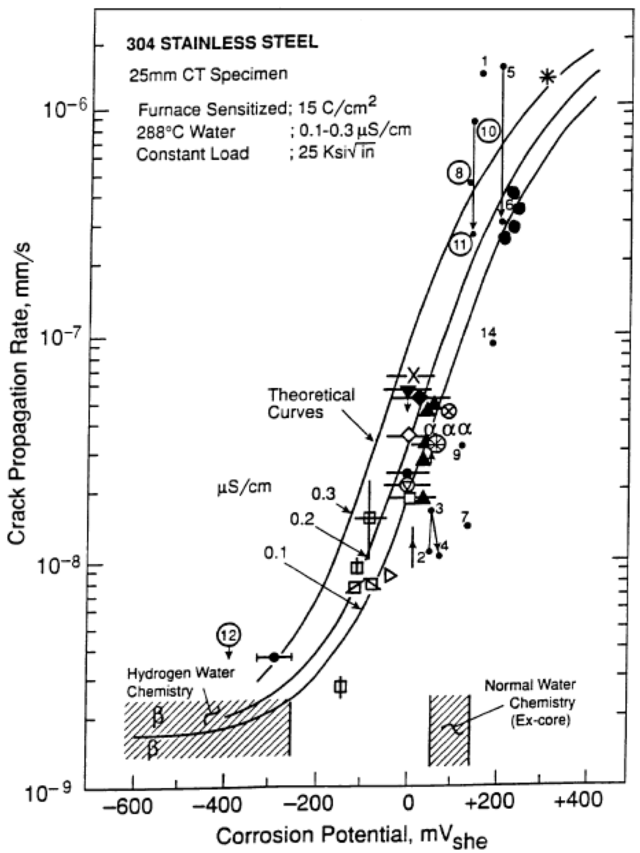


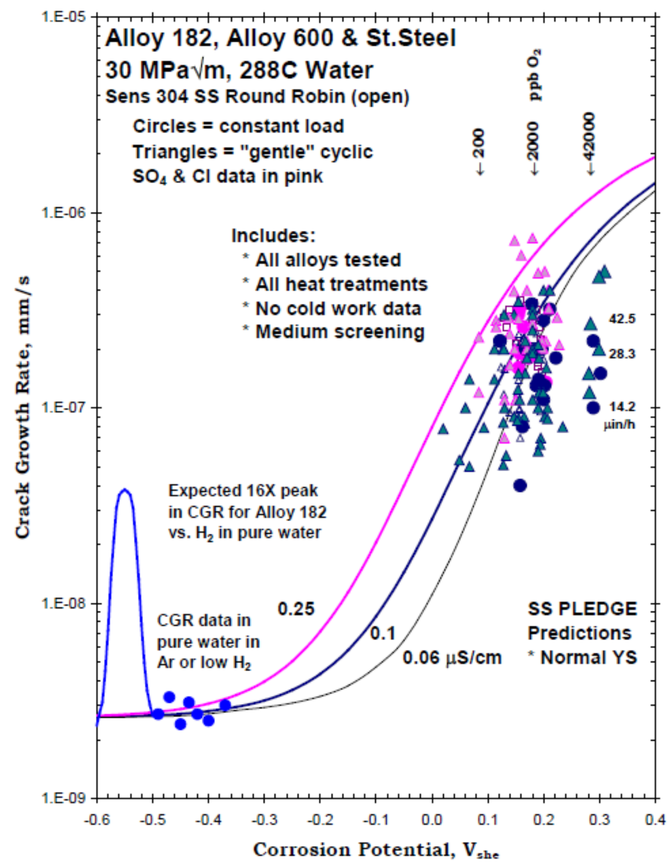
From H. Coriou

# SCC and corrosion potential

- Stainless steels

Nickel base alloy

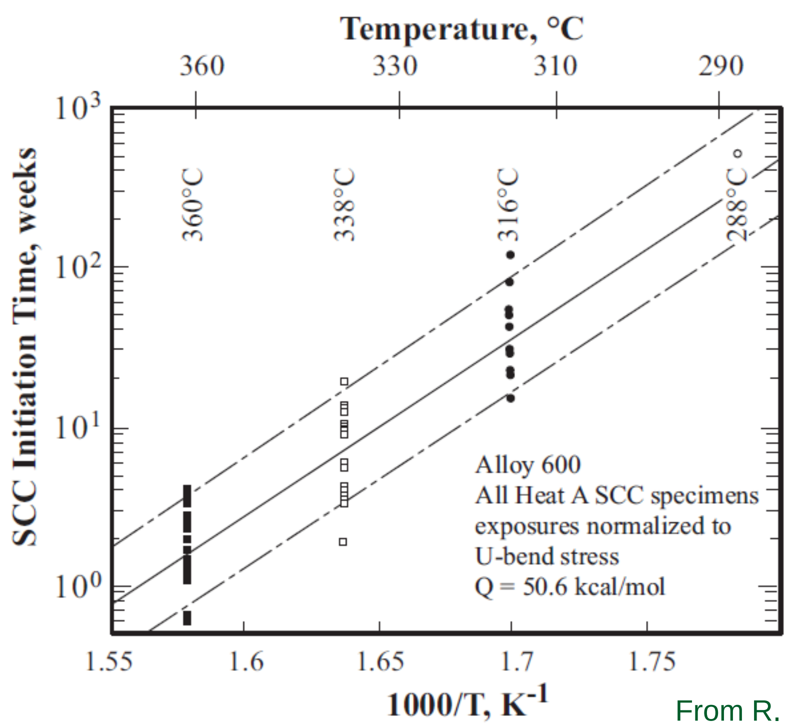


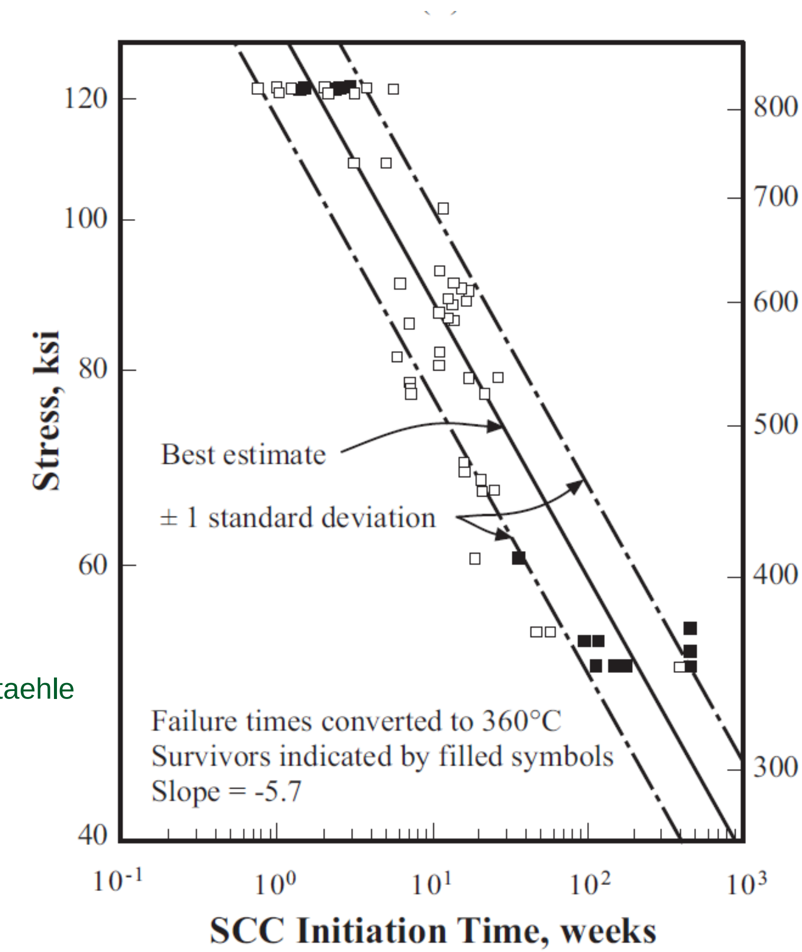




From P. Andresen

# SCC initiation (Alloy 600)

- Influence of temperature



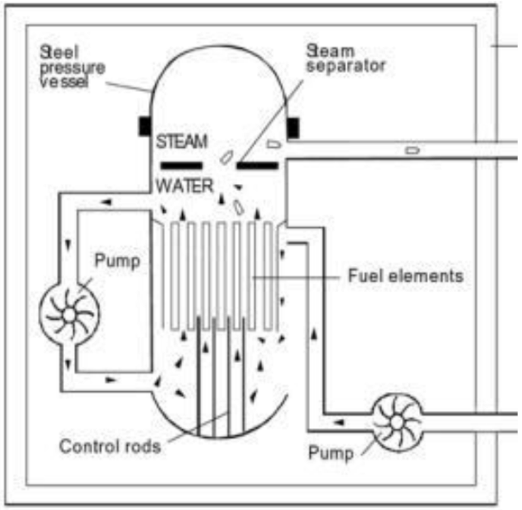

From R. Staehle

- Influence of stress

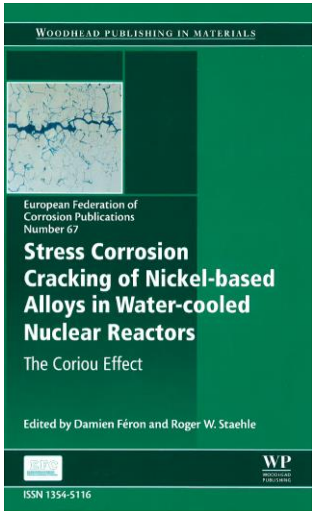
# Historical background - BWRs

***Austenitic stainless steels and nickel base alloys are susceptible to IGSCC in BWR conditions***

- ✓Stainless Steels Fuel Cladding Late 1950s and Early 1960s
- ✓304 during Construction Late 1960s
- ✓ Furnace Sensitized Type 304 during Operation Late1960s
- ✓ Welded Small Diameter Stainless Steel Piping Mid1970s
- ✓ Large Diameter 304 Piping Late 1970s
- ✓ Alloy X750 Jet Pump Beam Late 1970s
- ✓ Alloy 182/600 in Creviced Nozzles w/sulfate Late 1970s
- ✓ Crevice-induced Cracking of Type 304L/316L Mid 1980s
- ✓ Localized Cold Work Initiates IGSCC in Resistant Material 1980s



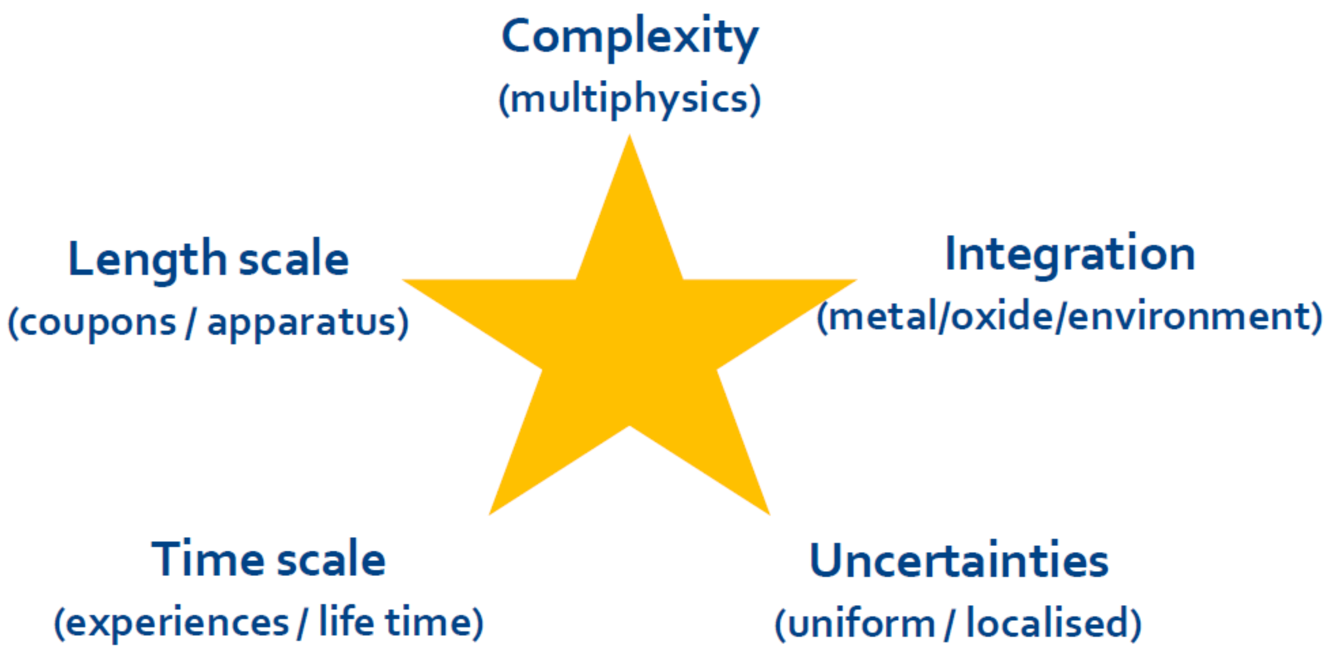
# SCC of Alloy 600 in PWRs or the « Coriou effect »




- ✓1957: Copson et al. (Inco, USA) proposed Alloy 600 (resistant to SCC cracking in boiling $MgCl_2$)
- ✓1959: *Coriou et al.* published that Alloy 600 is susceptible to SCC in pure water at 350°C.
- ✓1959-1975: Controversy between laboratory results in US and in France
- ✓1975-1985: Confirmation of the phenomena in pure water and in PWR primary water, named also "PWSCC" for Pure *or Primary* Water Stress Corrosion Cracking".
- ✓1985 – 1990s: generic phenomena occurring on Alloy 600 components and particularly on SG tubes.
- ✓1991 (in France) – 2002 (US, then Japan …): cracking of vessel head penetrations (Alloy 600 tubes, Weld made of Alloy 18 or 82).

# To conclude

- Corrosion accuracy



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