An Overview of Recent French Studies of Possible Secondary Side Crevice Environments Causing IGA/IGSCC of Mill Annealed Alloy 600 PWR Steam Generator Tubes

P. M. Scott and F. Vaillant

Heated Crevice Seminar

October 7-11, 2002, ANL, Argonne, Illinois

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Overview of Possible Crevice Environments for IGA/IGSCC in Alloy 600MA

> Introduction

> Background : crevice environments

> Background EDF caustic model

EDF near-neutral sulfates

EDF/FRA/CEA near-neutral complex environments

> Summary

> Discussion of liquid / steam environments

> Future plans

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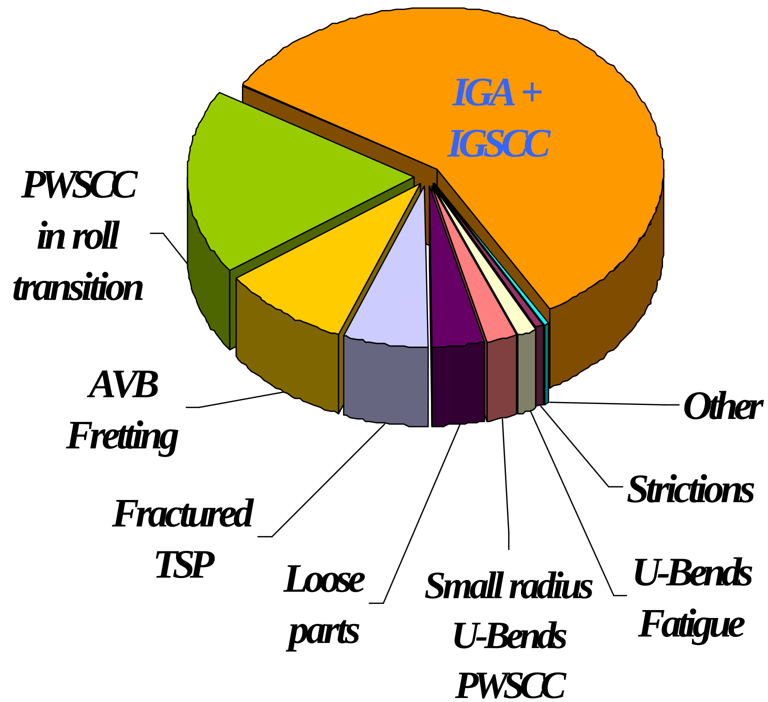
Introduction : Causes of Steam Generator Tube Plugging in France in 1999

·Only Mill Annealed Alloy 600 tubes are affected so far in France but Thermally Treated Alloy 600 has started to crack in the USA

·Secondary water chemistry management is strongly influenced by the tube corrosion issue.

Plugged tubes in France in 1999



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IGA/IGSCC of Alloy 600 SG tubes: Analysis of operating experience 1

> In France, IGA/SCC in plants with 600 MA

- drilled TSPs, one with broached TSPs in C-steel (axial cracks)
- Above the tubesheet TS (small axial cracks) in the sludge pile
- Under the top surface of the TS (circonf. cracks)
- Very limited TGSCC (Pb identified)

> No cracking with 600 TT and 690 TT

> IGA/IGSCC related to hide-out of impurities in crevices under heat transfer conditions in flow-restricted areas

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IGA/IGSCC of Alloy 600 SG tubes: Analysis of operating experience 2

> Inspections of large populations of tubes available for statistical analysis but rather few parametric trends can be discerned

> Strong heat to heat variability

> Some trends with strength and/or carbon content are observed for some tube bundle manufacturers with lower strength materials apparently more susceptible

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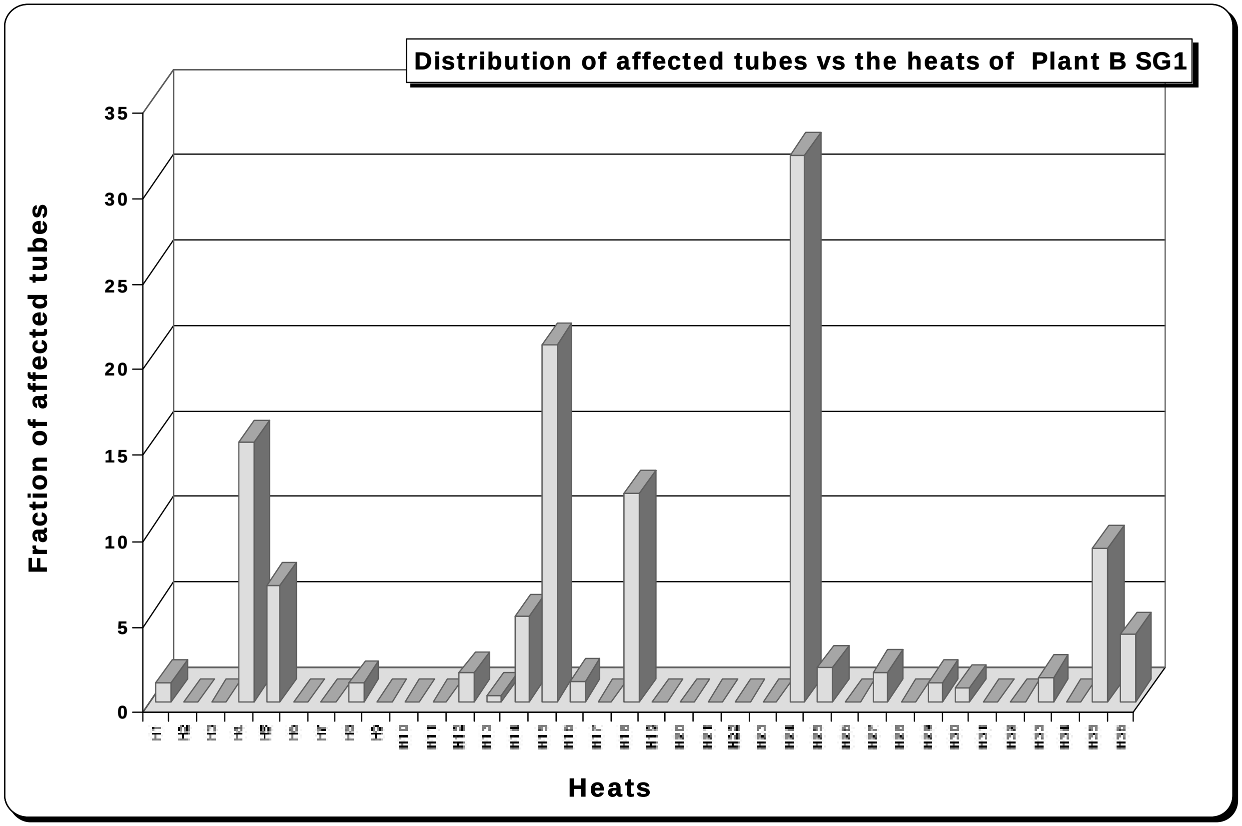
IGA/IGSCC of Alloy 600 SG tubes : Analysis of operating experience 3

Heat to heat variability in a SG tube bundle after ~75,000 h in service



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Background : crevice environments

- Crevice environments poorly characterized
- IGA/SCC traditionally linked to the formation of concentrated caustic or acid sulfate solutions whose boiling point is raised sufficiently to be in equilibrium with the available superheat of up to 30-35°C
- Many investigations in the past in caustic and acid sulfate

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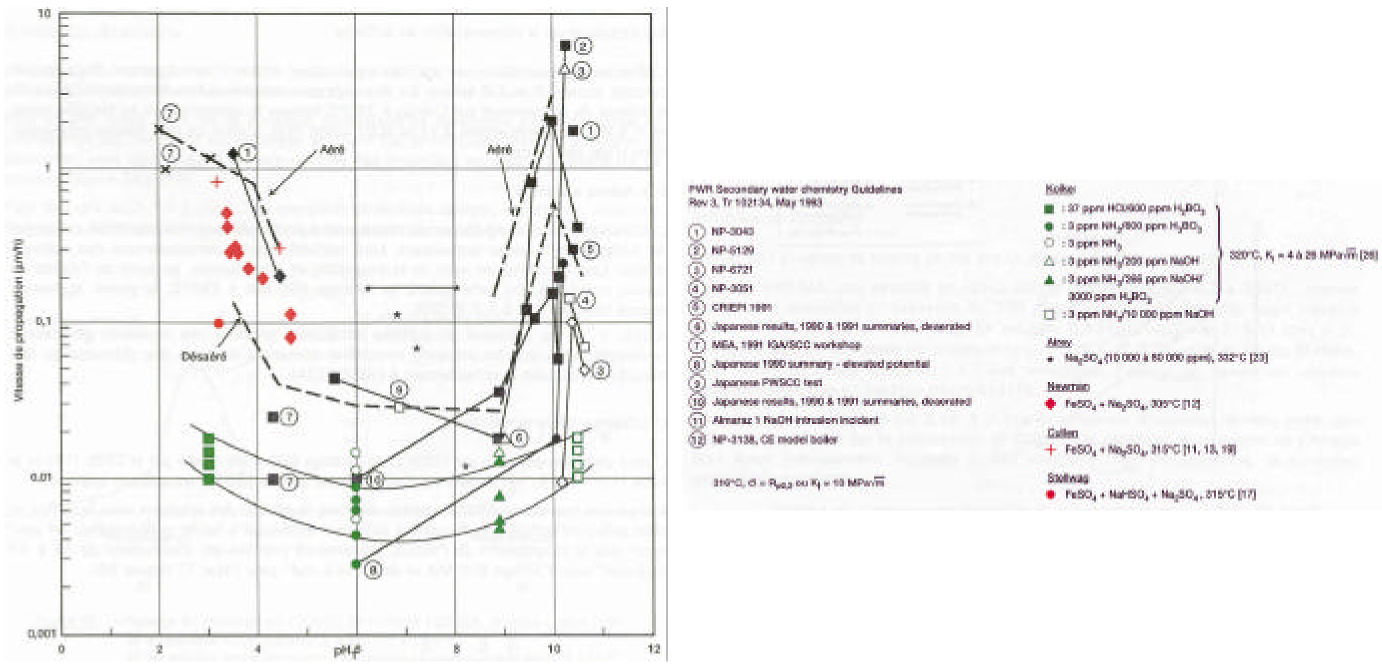
Background : Alloy 600 in Caustic and Acid Sulfate - Laboratory Data



> Only limited data in the range $5 < pH_T < 9.5$ in concentrated solutions (see Airey)

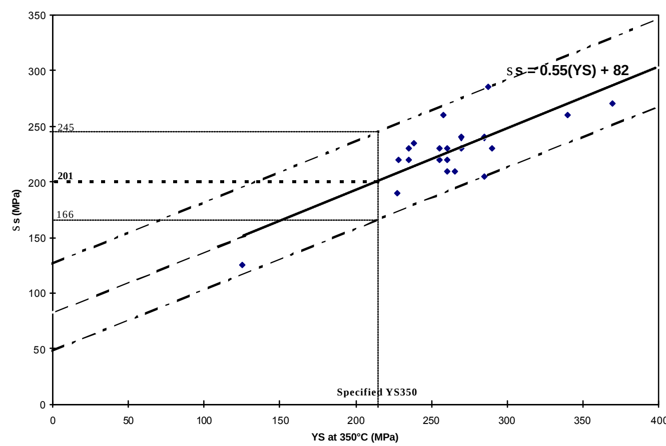
Background : EDF caustic model 1

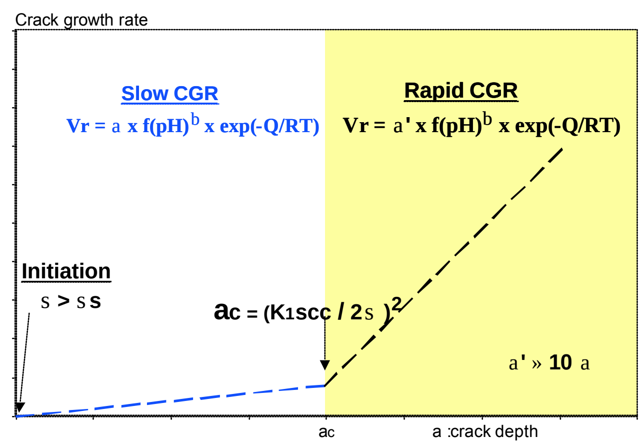
> IGSCC model in laboratory :

Stress threshold for initiation

Propagation

s > 185 MPa





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Background : EDF caustic model 2

> 600 MA :
  - the model explains the main features of the cracking (location, orientation)
  - Slow propagation rate : see next slide
  - No rapid propagation expected

> 600 TT : better behavior predicted, only circonf. cracking possible at the upper surface of the tubesheet

> 690 TT : no cracking expected

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Background : EDF caustic model 3

> **Coupling the corrosion model** with chemistry deduced from hideout return data

- **The calculated (slow) CGRs are consistent with average CGRs from pulled tubes on 8 of the oldest plants (river side) for the first decade of operation**
- **However, they are always lower than the CGRs measured in plants**
- **The model is not applicable to 3 other** (sea side) **plants**

To be improved (reassessment of T_{wall}, sludge porosity)

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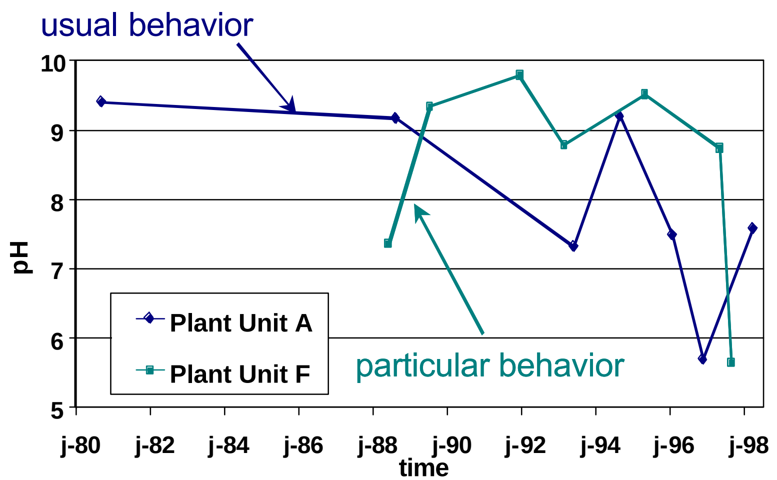
Background : EDF caustic model 4

> Coupling corrosion model (600 MA) with pH deduced with hideout return data

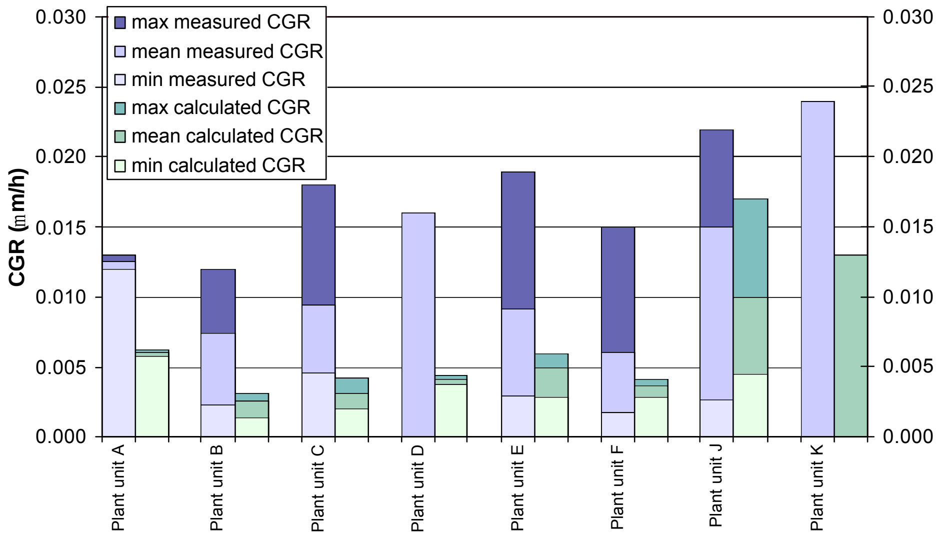


➔ Crevices less and less alkaline with time

Background : EDF caustic model 5

> Coupling corrosion model with pH deduced with hideout return data

- 8 river side plants



- 3 sea side plants : not alkaline

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Neutral to slightly alkaline sulfates 1

> Hideout return data : sulfates are the main pollutants
> Surface analysis : Cr/Ni on pulled tubes consistent with slightly alkaline environment
> Laboratory investigation (EDF)

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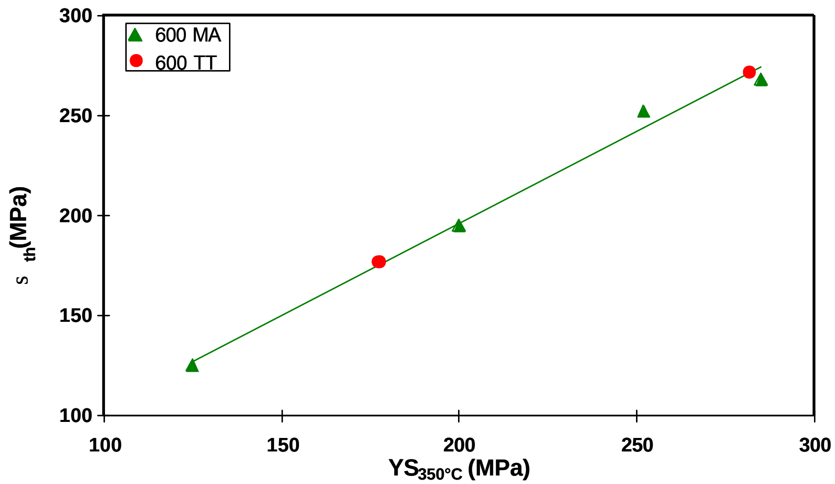
Neutral to slightly alkaline sulfates 2

> Initiation : $\sigma > 215$ MPa (required YS)

$[SO_4] = 0.05$ M, pH = 6.5, T = 320°C, C-rings, 2500 h



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Neutral to slightly alkaline sulfates 3

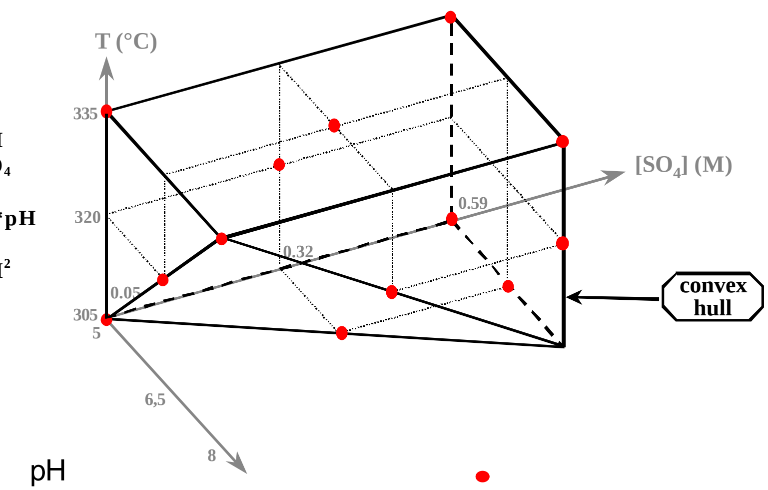
> Slow propagation   Experimental Design

> **slow CGR (MA) = a + b.T + c.[SO_4] - d.pH +e.T.pH- f.T^2 + g.pH^2**

> Pareto diagram :

```
                        |----------o-----------|           pH
                        |-------*-------|                  SO4
           |---------*---------|                            T
        |-------------*-------------|                       T*pH
-------o-------|                                            T2
-------*-------|                                            pH2
```

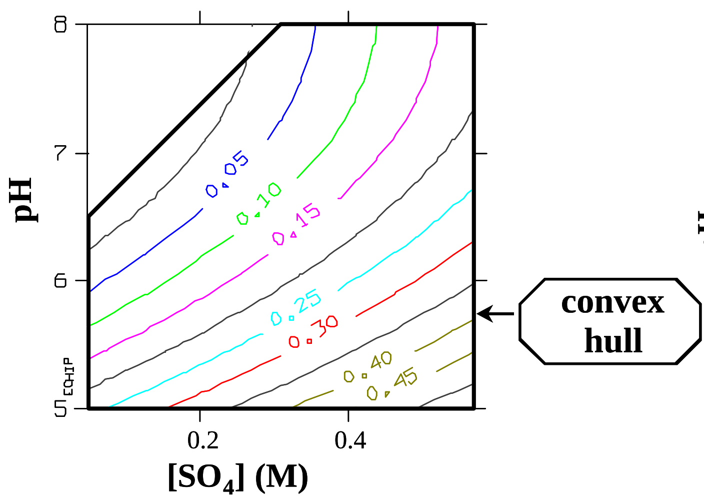
arbirtrary units
* : increasing effect on CGR
o : decreasing effect on CGR

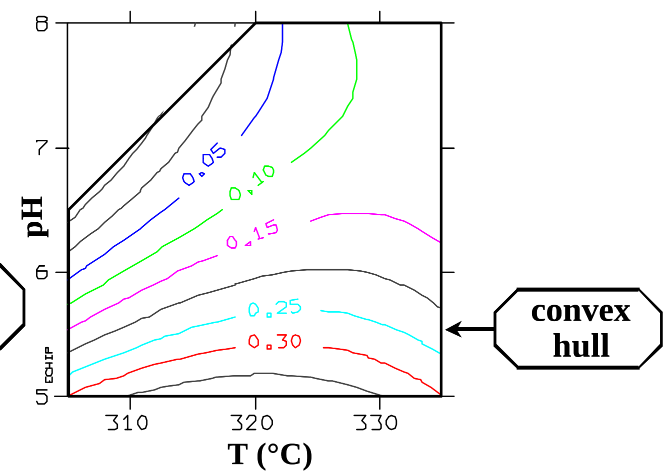


Neutral to slightly alkaline sulfates 4

Effects of pH and $[SO_4]$ for T = 320°C

Effects of pH and T for $[SO_4]$ = 0.32 M





Neutral to slightly alkaline sulfates 5

> 600 MA : the sulfate model

- Consistent with some cracking in plants (location, orientation), but not all
- Provides slow CGRs compatible with plant CGRs at [SO4] > 5000 ppm (pH = 6) or = 31 000 ppm (pH = 8) at 320°C
- Reassessment of true T_{wall} and coupling of the model with HOR data in progress

> 600 TT predicted to be slightly better

> 690 TT immune

Complex environments 1

> Background :

> IGA/IGSCC of mill annealed alloy 600 tubes associated with the presence of **alumino-silicate deposits (zeolites) overlying brittle poorly protective chromium hydroxide films** instead of protective spinel.

> Recent high resolution ATEM work on IGA/IGSCC in alloy 600MA acid formed in acid sulfate or strong caustic do not show the same morphology as observed on those pulled tubes examined to date.

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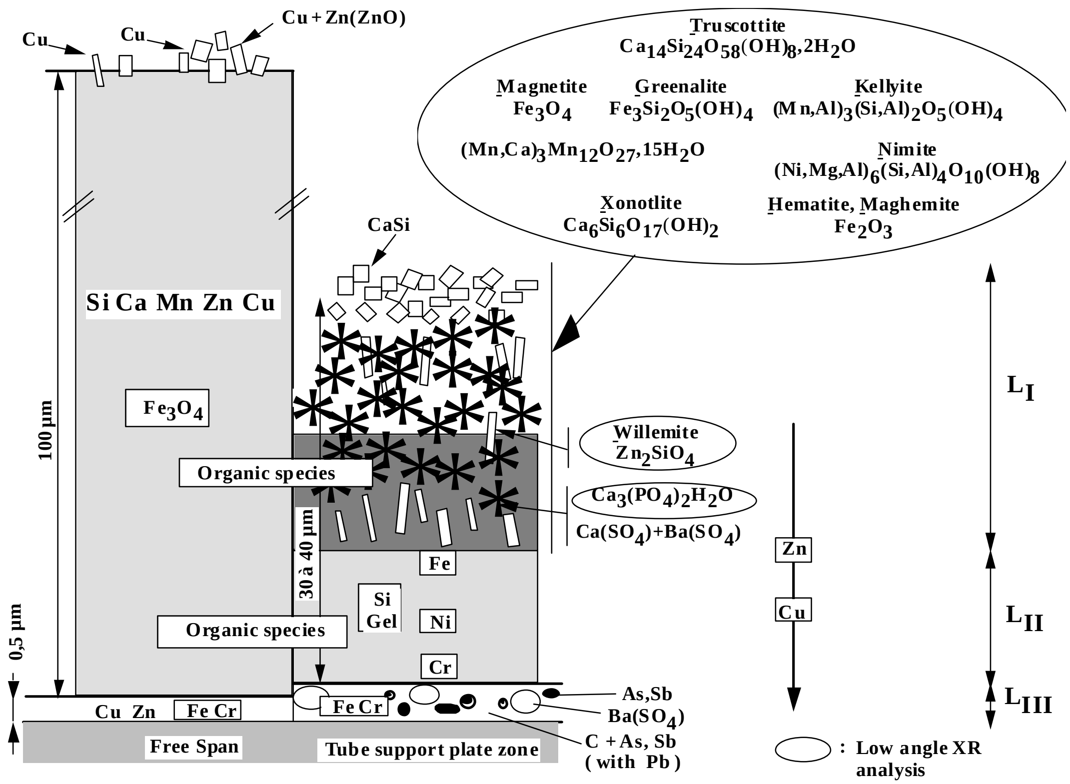
Complex environments 2

> Deposits at TSPs on pulled tubes :



Complex environments : 3

> **Specimens / examination**

- EDF : at least 2 C-rings/environment and metallurgical condition
- CEA : U-bend specimen
  - σ > YS - surface state: as-received (AR)
  - Metallurgical examination on section (max Δa) + SEM / EDS
- Flat coupons, SEM/EDS, GDOS

> **Test facilities**

- EDF: Static SS autoclaves, 1 or 4 liters
- CEA : heated capsules (alloy 600TT) in an autoclave

> **Duration of the tests**

2500 h to 4000 h

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Summary of Recent Results on IGA/IGSCC of Alloy 600 in Complex Mixtures of Impurities

Various combinations of impurities added to **<u>pure water</u>** studied using optimized experimental designs: NaOH, Na_2SO_4, Na_2S, CH_3CO_2H, CO_2, Fe_3O_4, SiO_2, Al_2O_3, CuO, $Ca_3(PO_4)_2$

pH range of the various mixtures at 325°C was 3.3 to 10.3

> Classical detrimental effects:

- pH<5 or pH>10 at temperature
- Presence of SO_4^{--} at pH<5 and HS^-/S^{--} at pH>10
- Presence of Fe_3O_4 & CuO

> Beneficial effects:

- SiO_2 and $Ca_3(PO_4)_2$ as chemical buffers or forming solid barrier deposits
- CuO only in presence of sulfides

One really surprising result where rapid (0.2µm/h) through-wall cracking was observed with CuO+SiO_2+Al_2O_3 but not with CuO alone

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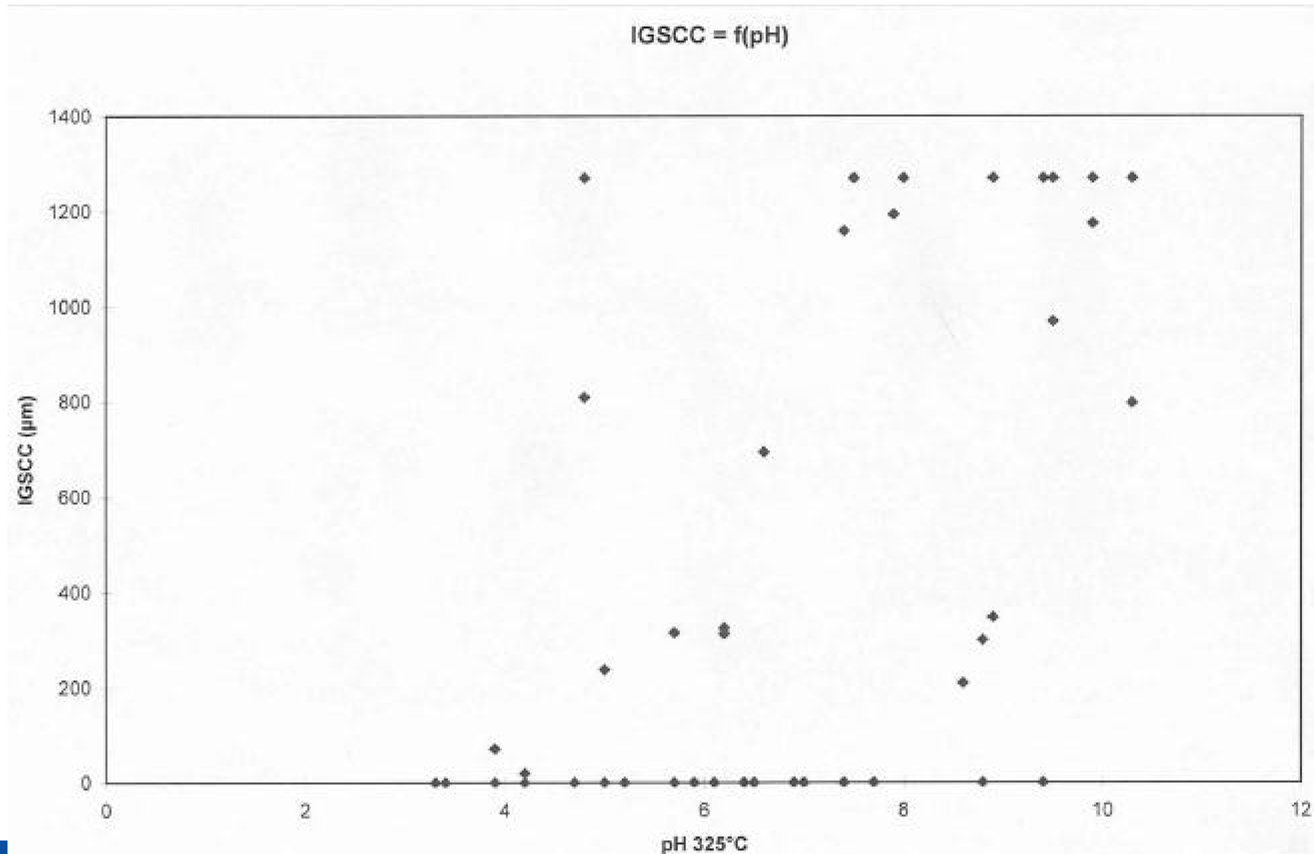
IGSCC of Alloy 600 as a Function of pH in Complex Mixtures of Impurities



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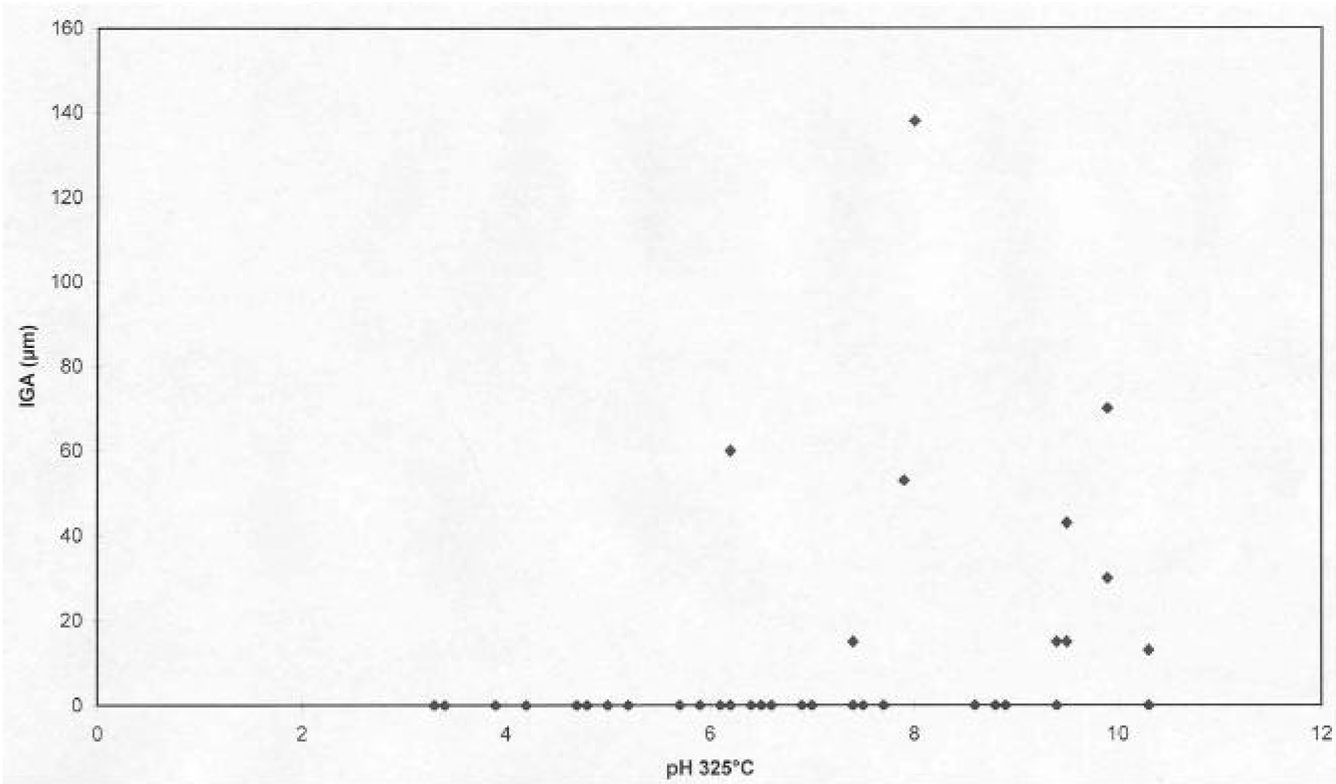
IGA of Alloy 600 as a Function of pH in Complex Mixtures of Impurities



Experimental Plan and Results based on Pulled Tube Deposit Analyses

> Second Experimental Design in AVT environment

Run	Impurities in AVT Secondary Water			pH 325°C	Deepest crack, mm	
	$\frac{Al}{Si}$ (A) -1 level=0.1 +1 level=1.0	CuO (B) -1 level=0 +1 level=0.128M	$Ca_3(PO_4)_2$ + (100ppm CH_3COOH) (C) -1 level=0 +1 level=0.0064M +2 level=0.064M		Heat WF 422	Heat 9861
69*	-1	-1	-1	5.5	0	0
70	+1	-1	-1	5.5	100	150
71	-1	+1	-1	5.9	0	0
72	+1	+1	-1	5.9	0	635
73	-1	-1	+1	5.1	120	120
74	+1	-1	+1	5.1	70	200
75	-1	+1	+1	5.3	0	0
76	+1	+1	+1	5.3	0	0
77	-1	-1	+2	4.8	5	5
78	+1	-1	+2	4.8	100	100
79	-1	+1	+2	5.1	0	0
80	+1	+1	+2	5.1	0	0

* Note: repeated experiment by EDF →15 µm

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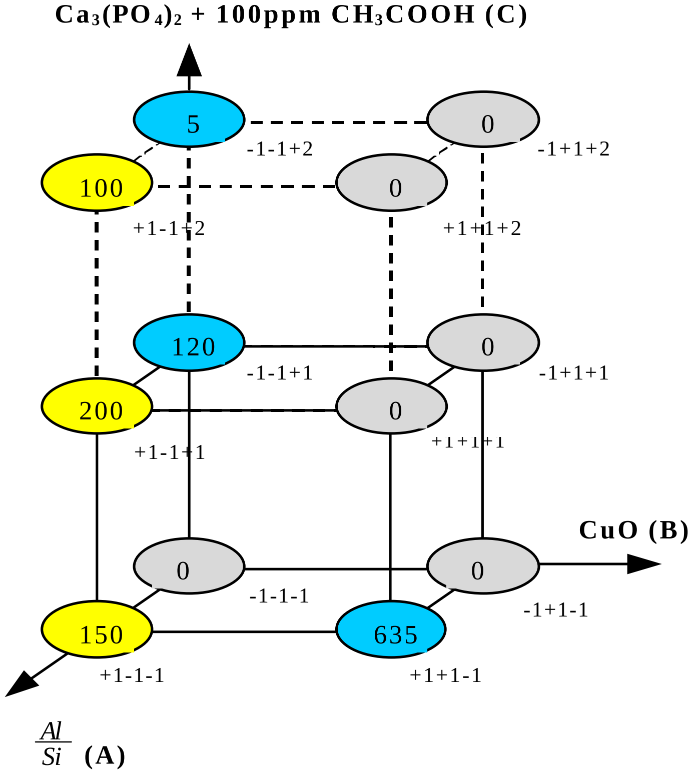
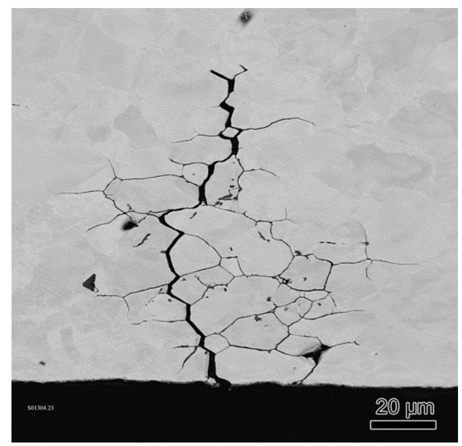
IGA/IGSCC of Alloy 600MA in the presence of alumino-silicates in AVT water





Combination +1-1-1

Note: 1- IGA/IGSCC observed <u>only in AVT water</u> in the absence of CuO

2- Recent EDF tests show that organics are not a necessary condition for cracking

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IGA/IGSCC of Alloy 600MA in the presence of alumino-silicates in AVT water

> Recent EDF data for polluted AVT (de-aerated ammonia solution + 2 ppm hydrazine, pH_{RT} 9.2)

environment parameter	simple	simple without silica		complex			
	Al/Si	w/o alumina	w/o phosph.	reference	amine	w/o organic	amine
Test Environ-ment	AVT + SiO_2 + Al_2O_3	AVT + $Ca_3(PO_4)_2$ + CH_3COOH	AVT + Al_2O_3 + CH_3COOH	AVT + SiO_2 + Al_2O_3 + $Ca_3(PO_4)_2$+ CH_3COOH	**idem** but **morpholine** instead of R	AVT + SiO_2 + Al_2O_3 + $Ca_3(PO_4)_2$	**idem** but **morpholine** instead of R
pH_{320} MulteQ*	5.9	5.2	4.1**	5.2	5.3	5.4	5.2
Test duration(h)	3000	2473	2500	3191	4000	4000	4000
SCC	0.005 µm/h	0.01 µm/h	No Cracking	0.01 µm/h	0.01 µm/h	0.03 µm/h	0.01 µm/h
Deposit	continuous AlSi	no	granular Al	continuous Si	-	-	-
Non protective Cr-rich layer	?	yes <u>Fe,</u> Cr	yes <u>Cr</u>, Fe	yes Cr, Si	-	-	-

* Al_2O_3 not in MulteQ data base : calculated with Al

** CH_3COOH concentration : 10 000 ppm instead of 10 ppm

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Alumino-silicate deposits (Zeolites)

- Very wide range of compositions is possible in which the substitution of species such as aluminum, alkaline earths, phosphate and organic species such as glycols controls their structure and reactivity ('acidity')
- Observed to selectively absorb certain transition metal cations from the passive film on alloy 600 and leave a non-protective chromium hydroxide gel that allows IGA/IGSCC to develop
- Organic ligands can be synthesized in the alumino-silicate deposits and may play a role in the partial breakdown of passivity that is the precursor to IGA/SCC. However, recent EDF tests show that organics are not a necessary condition for cracking.
- Consequences for secondary water chemistry management?!

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Summary 1

- > IGA/IGSCC in some old plants can be explained with the EDF caustic model (reassessment of T_{wall} and influence of porosity in progress)
- > However environmental chemistry associated with impurity hideout complex and still uncertain
- > Local environments (hideout return data and surface analyses) are becoming less and less alkaline - neutral to slightly basic
- > Neutral to slightly basic sulfate environments could be relevant (but can they exist in the liquid state?)

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Summary 2

- Complex (liquid or wet steam) environments including SiO_2, Al_2O_3, organics and phosphate can reproduce IGA/IGSCC and deposits observed on pulled tubes (zeolites, formation of organic ligands to enhance dissolution of nickel)
- Thermally treated alloy 600 is more resistant than mill annealed alloy 600 in all the near neutral environments tested and thermally treated alloy 690 is immune.

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IGA/IGSCC of Alloy 600 SG Tubes: Do such concentrated liquids really form?

> **Concentrations of dissolved species must be ~ 8 M to ensure a liquid phase with up to 30-35°C of superheat**

- Recent tests show that only NaOH is sufficiently soluble to ensure a liquid phase at the SG pressure and >25 °C superheat
- Concentrated NaCl, for example, can only support 25°C of superheat before precipitating
- Impurity concentrations in SGs are probably only sufficient to form droplets or a liquid film at most

> **Crevice mouths fouled with very low porosity (<10%) deposits**

- Possibility of local steam blanketing (polluted and/or hydrogenated steam?)

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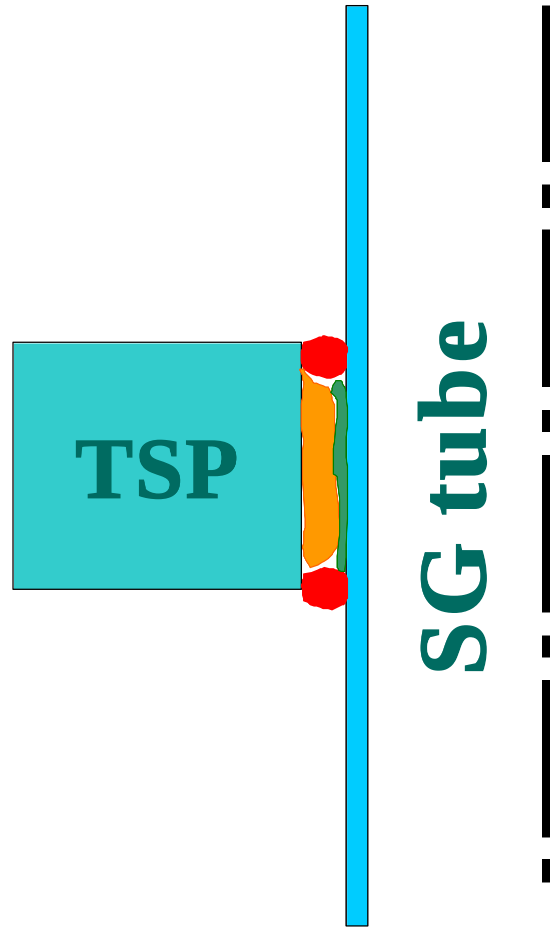
Typical Fouled Tube/Drilled Tube Support Plate Crevices

High density magnetite rich in silica.
High porosity magnetite and complex silicate deposits, which remain on pulled tubes



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IGA/IGSCC in Steam or Aqueous Phase: Does it matter?

> Nano-porous (1 to 2 nm diameter with ATEM) deposits allow certain impurities, notably lead, copper and sulfur, to diffuse to the crack tip

> Liquid water and steam in a 2 nm diameter tube are unlikely to be distinguishable and transport to the crack tip is probably by surface diffusion

> Kelvin's equation (which allows the vapor pressure of extremely small droplets to be calculated) shows that the boiling point of pure water can be elevated by as much as 15°C (because of surface tension in very small diameter pores)

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Current and future R&D

> Further assessments in (neutral) sulfates and complex environments

> Test program (FRA Owners' Group) in progress to test hypothesis of IGASCC in polluted superheated steam in plugged crevices

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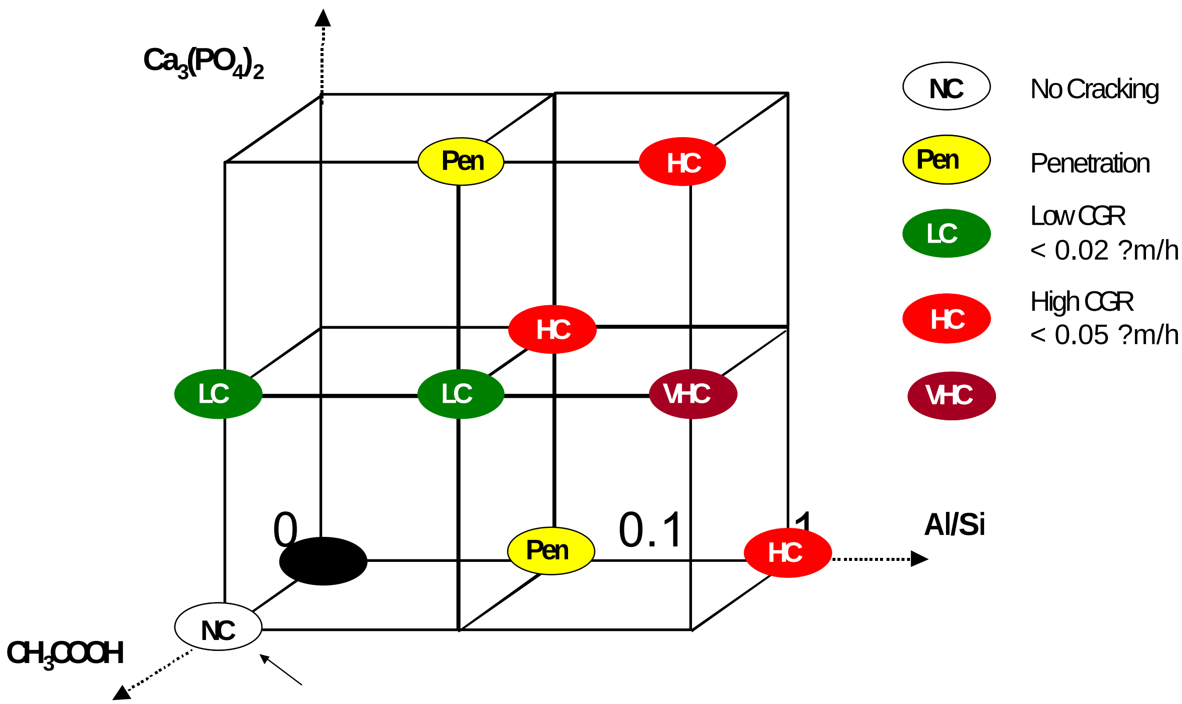
IGA/IGSCC of Alloy 600MA in the presence of alumino-silicates in AVT water



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- P. COMBRADE (Framatome-ANP)
- T. TRAN (CEA)

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APPROACH TO PREDICTING CORROSION OF SG TUBES BASED ON QUANTIFYING SUBMODES OF SCC IN A STATISTICAL FRAMEWORK

Roger W. Staehle

Adjunct Professor
University of Minnesota

Presented at Joint EPRI-ANL Meeting
Argonne National Laboratory

October 8-11, 2002

PRIMARY OBJECTIVE OF THE MEETING:

Predict Corrosion of Tubes in Modern SGs.

REQUIRED TO PREDICT CORROSION

- **Dependencies of submodes of corrosion on primary variables: pH, potential, species, alloy composition, alloy structure, temperature, stress**
- **Definition of local environment immediately adjacent to tube surface.**
- **Statistical framework.**

MAIN COMPONENTS OF PREDICTING THE CORROSION BEHAVIOR OF STEAM GENERATOR TUBING IN MODERN PLANTS:

- **Alloys 600TT and 690TT**
- **Line contact crevices and TTS**
- **High purity water**

PROBLEMS IN PREDICTION FOR MODERN PLANTS

- Few failures of tubes

- No chemical, physical, nor phase definitions of line contact crevices: i.e. the environment that produces corrosion

- Lack of definition for possible serious SCC submodes including S^{-y}SCC, AcSCC, complex environments, and PbSCC

- Lack of data and theory for interaction of SCC species with immobilizing species, e.g. Pb with sulfate.

PROBLEMS IN CARRYING FORWARD DRILLED HOLE EXPERIENCE

- Little direct evidence for causative chemistries.

- Little agreement on the presence of steam phase.

- Few data on corrosion in steam phase

- Few data on corrosion in complex environments.

- Large variability of corrosion response for constant conditions, i.e. Scott study.

- No (semi)-quantitative theory for local chemistry.

MY APPROACH

- **Objective: Predict first crack on secondary side before detection by NDE.**

- **Scope: Alloy 600MA, drilled hole,**

- **Basis: Use existing data from Alloy 600MA failures to calibrate and develop theory.**

- **Approach:**

  - **Integrate statistical framework with physical descriptions of the submodes from plant and laboratory data for describing SCC.**

  - **Evaluate integrated descriptions of submodes with chemistry of drilled hole crevices.**

- **Validation: Compare integrated theory with known behavior of Alloy 600MA in drilled hole crevices.**

- **Apply: Present plants still with drilled holes and Alloy 600.**

- **Modify: Apply methodology to modern plants**

STEPWISE DEVELOPMENT

1. Assess the statistical nature of SCC in SGs and related applications and environments. [Done]. Conclude:

   • Weibull format models SG data well and provides a good format for prediction

   • Space parameter , θ, and location parameter, t_o, of Weibull follow same patterns as mean values of experimental data

   • Shape parameter, β, difficult to interpret and model.

2. Identify submodes of SCC (submodes depend differently on the primary variables of pH, potential, species, alloy composition, alloy structure, temperature, stress). [Done]. Conclude:

   • Sufficient data (more would be desirable) for modeling the primary variables for: AkSCC, LPSCC, AcSCC, PbSCC

   • Need data for S^{y-}SCC

   • Treating complex chemical environments not clear

   • Presence and signficance of steam phase not clear.

3. Survey dependencies of submodes on primary variables. [Done]

4. More detailed study of PbSCC. [One short report done. Detailed report almost done]

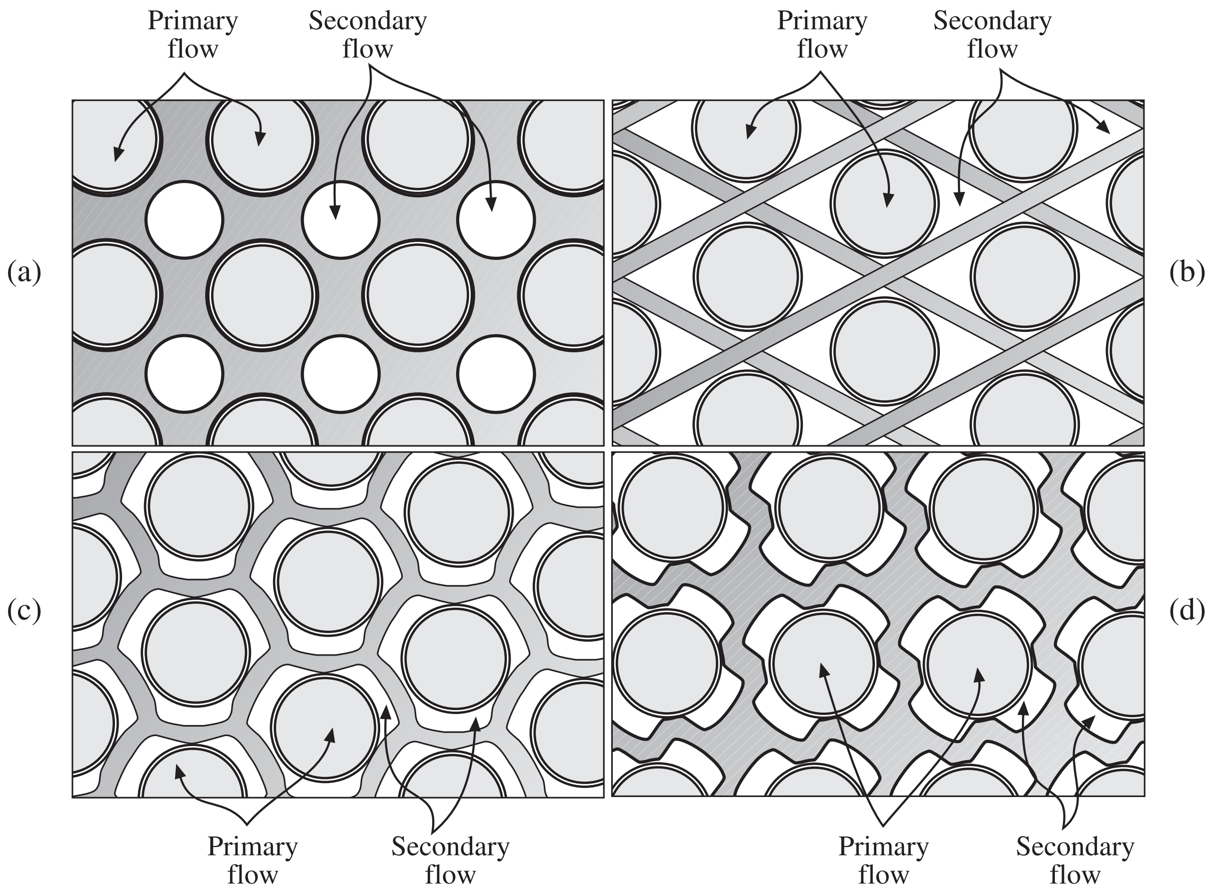
5. More detailed study of oxidized sulfur and other acidic species. [Next project]

6. More detailed study of reduced sulfur, S^{y-}SCC. [The next after #5.]

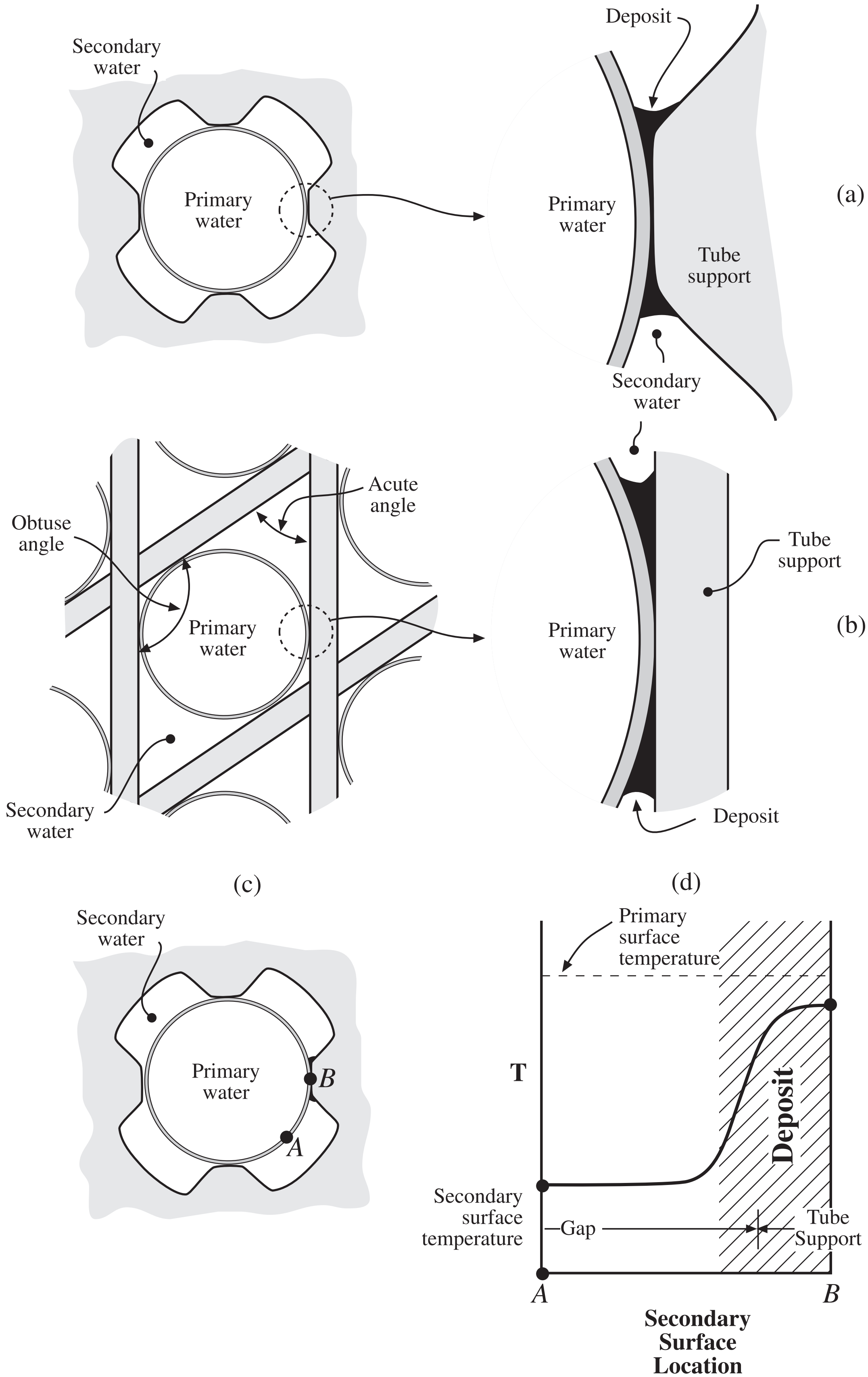
7. Detailed study of chemistry of crevices using data from: model boilers, pulled tubes, collars (pieces of deposit from intersection of tube and tube supports), hideout return. Use "machine thermodynamics" for analyzing data (evaluate MULTEQ, geochemist work bench, OLI) [Next]

8. Integrate all submodes using product of reliabilities. [Next]

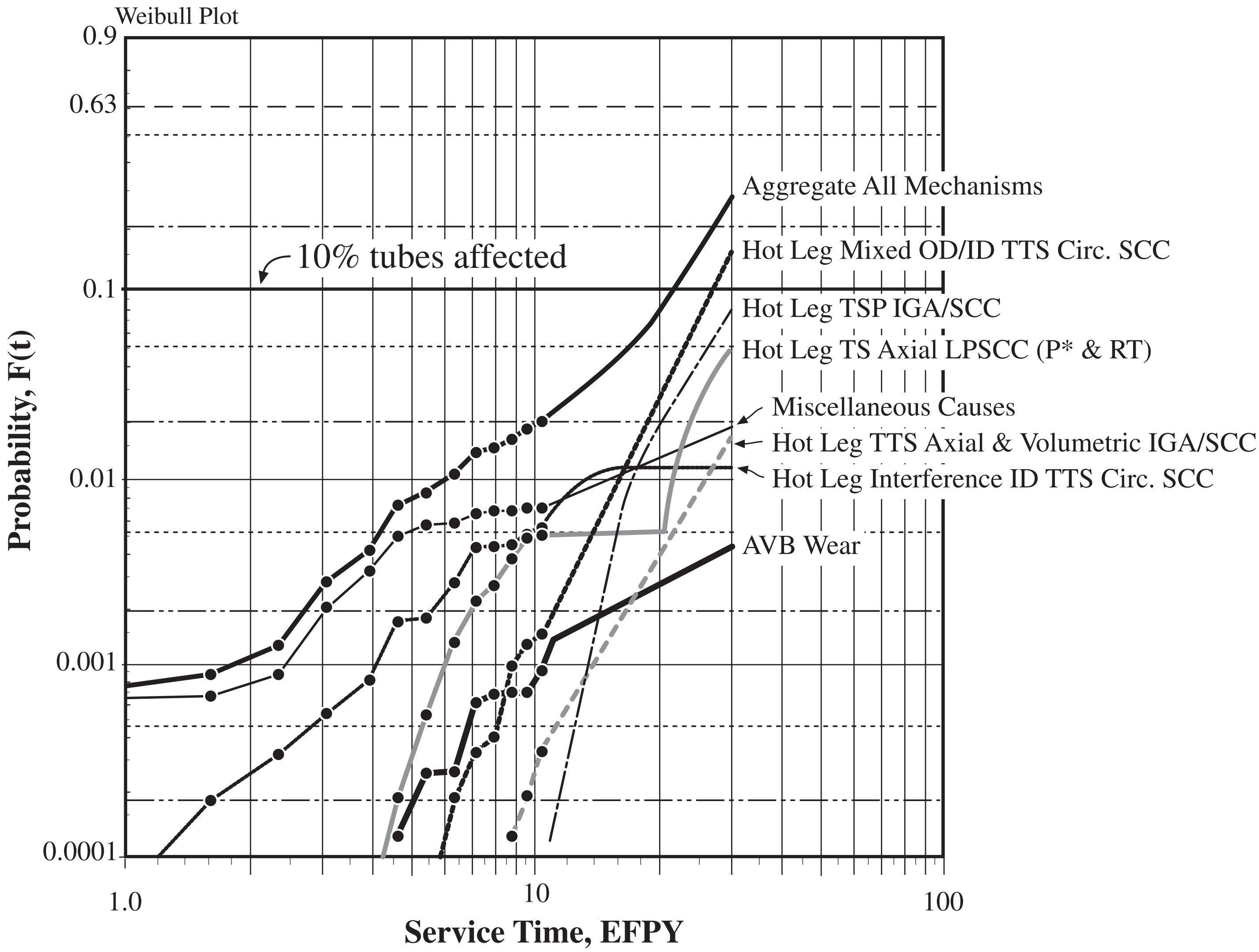
9. Integrate dependencies of submodes with chemistry of crevices. [Final]



Geometries of tube supports: (a) Drilled hole typical of early Westinghouse designs; (b) egg crate typical of siemens and Combustion Engineering; (c) broached trefoil typical of Babcock and Wilcox; (d) broached quatrefoil typical of later Westinghouse designs.



Schematic view of accumulation of deposits at line contact crevices associated with (a) broached holes and (b) egg crates. Example (c) of different temperatures (d) at open area and at deposit-filled contact area.



Probability vs. equivalent full power years (EFPY) for failures of tubing from a set of SGs in the Ringhals 4 PWR. Designations: TTS = “top of tube sheet.” TS = “tubesheet.” Circ. SCC = “circumferential SCC.” P* = special location where SCC is not serious. RT = “roll transition.” AVB = “antivibration bars.” From Bjornkvist and Gorman.

$$f(t)=\left[\frac{\beta}{(\theta-t_o)^{\beta}}\right](t-t_o)^{\beta-1}\exp\left[-\left(\frac{t-t_o}{\theta-t_o}\right)^{\beta}\right],\ t>t_o \tag{1}$$

$$\ln\left[\ln\left(\frac{1}{1-F(t)}\right)\right]=\beta\left[\ln(t-t_o)-\ln(\theta-t_o)\right] \tag{2}$$

$$h(t)=\frac{f(t)}{1-F(t)}$$

(3)

$$h(t)=\left(\frac{\beta}{\theta-t_o}\right)\left(\frac{t-t_o}{\theta-t_o}\right)^{\beta-1}=\frac{\beta}{(\theta-t_o)^{\beta}}(t-t_o)^{\beta-1}$$

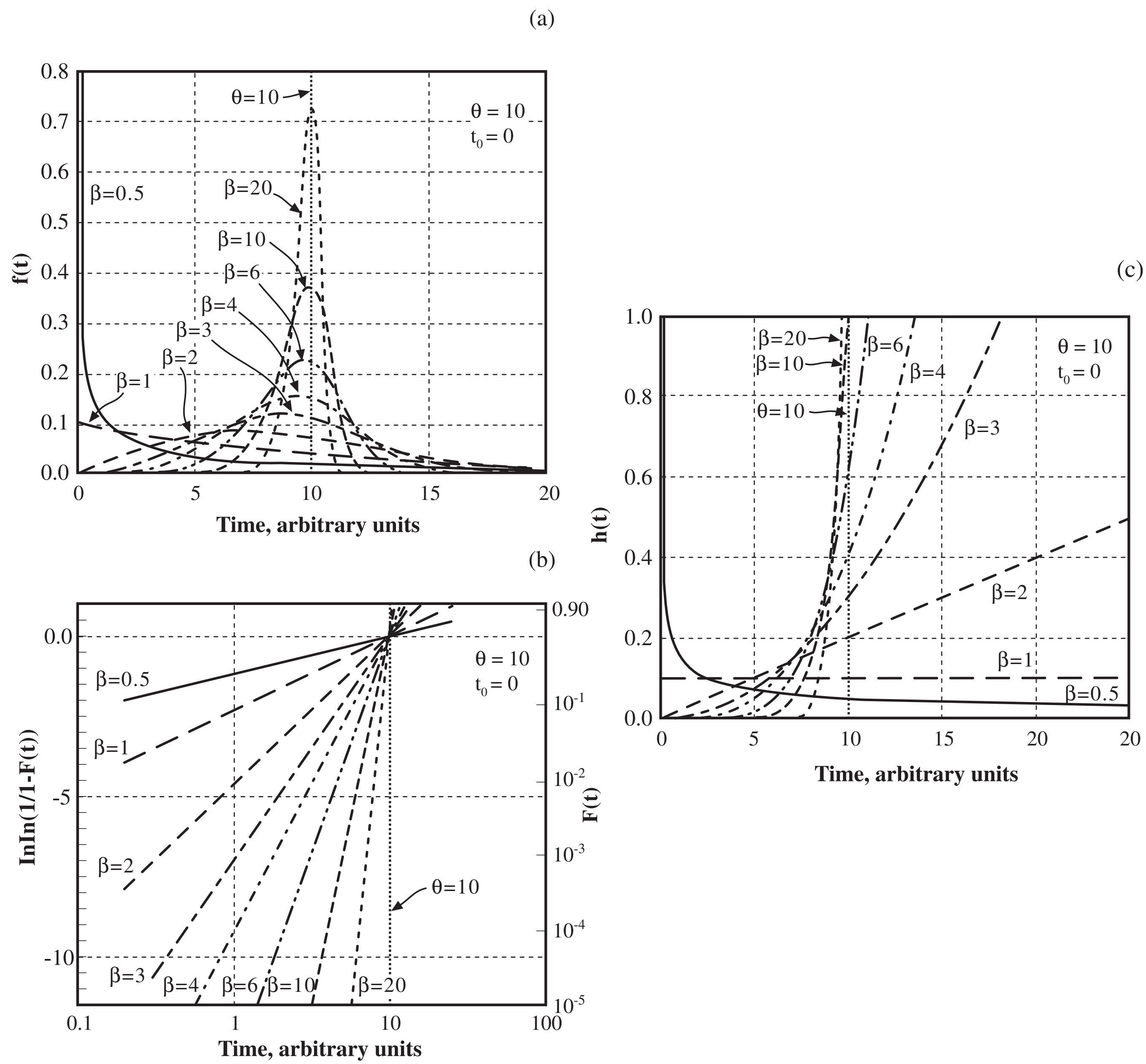
where:

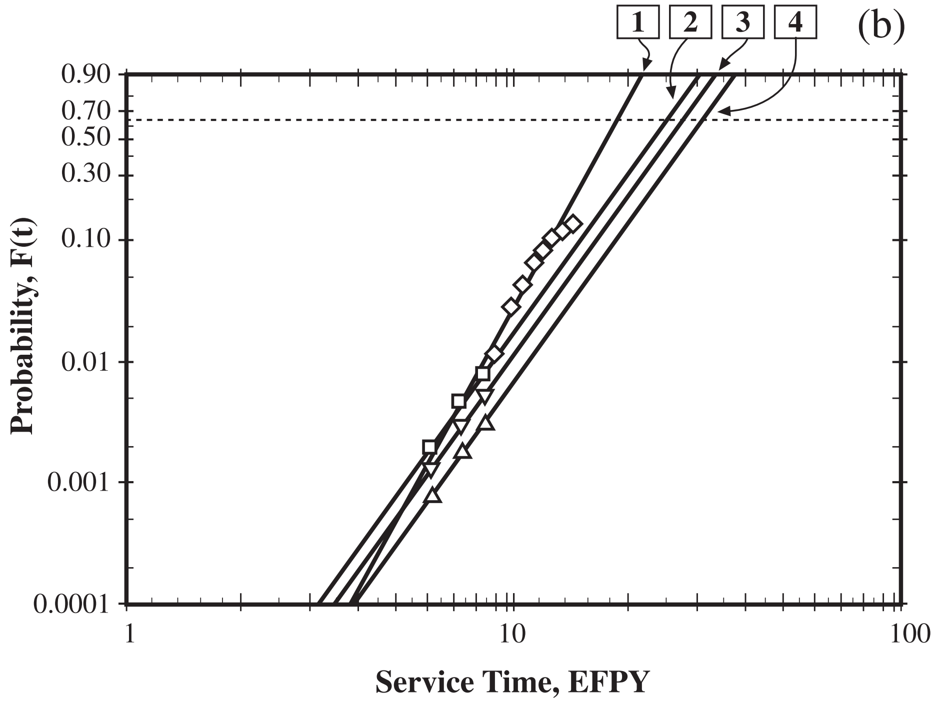
θ = Space parameter or Weibull characteristic

t_o = Location papameter

β = Shape parameter

t = Time


(a)
f(t)
Time, arbitrary units
θ=10
θ = 10
t_0 = 0
β=0.5
β=20
β=10
β=6
β=4
β=3
β=2
β=1
(b)
lnln(1/1-F(t))
F(t)
Time, arbitrary units
θ = 10
t_0 = 0
β=0.5
β=1
β=2
β=3
β=4
β=6
β=10
β=20
θ=10
(c)
h(t)
Time, arbitrary units
β=20
β=10
θ=10
β=6
β=4
β=3
β=2
β=1
β=0.5
θ = 10
t_0 = 0

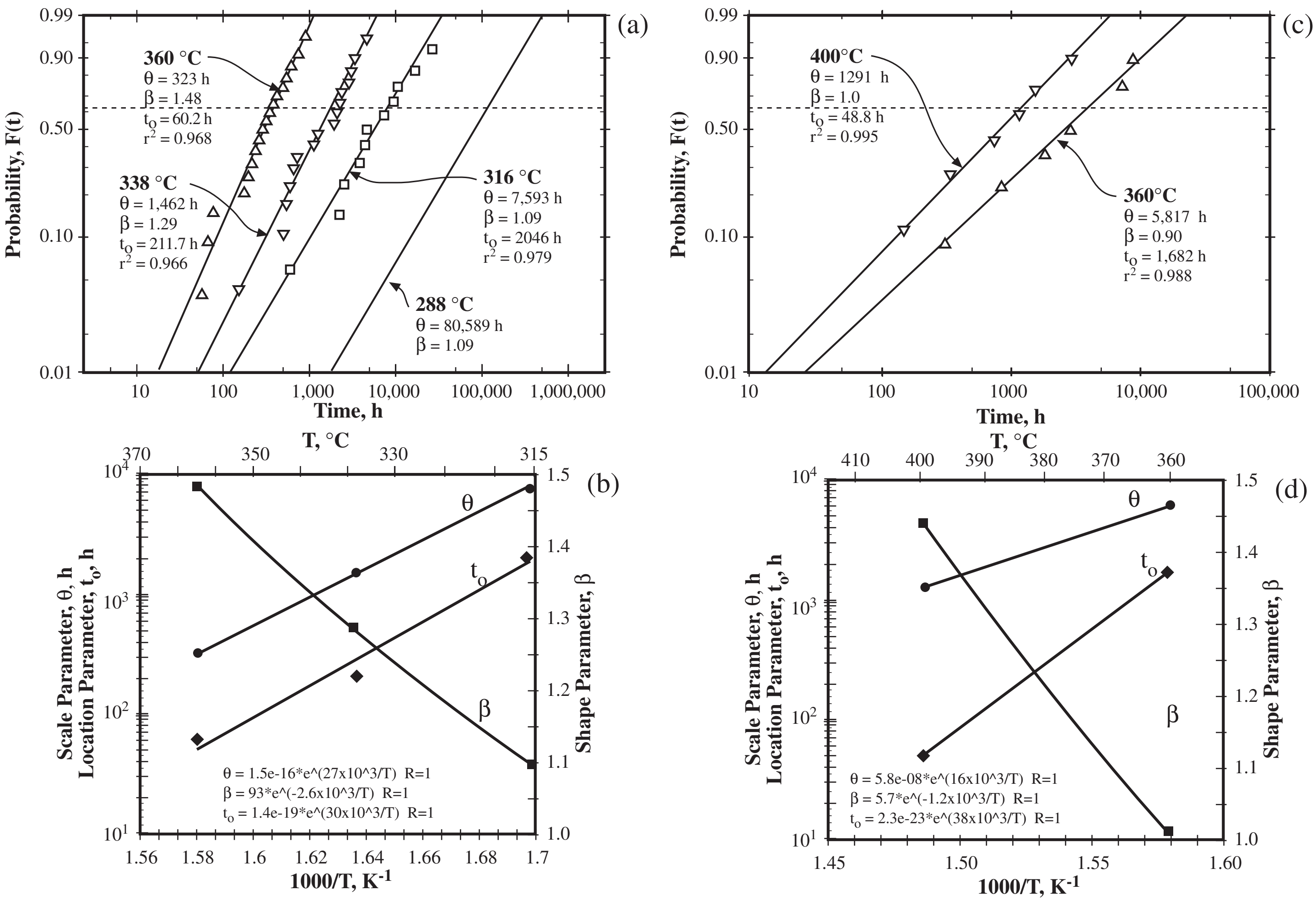


1. Cold Leg Sludge Pile, HTMA Tubing
θ = 30.24 EFPY
β = 4.49
r^2 = 0.975

2. Hot Leg Sludge Pile, HTMA Tubing
θ = 26.69 EFPY
β = 4.48
r^2 = 0.971

3. Hot Leg Eggcrate Tube Supports, HTMA Tubing
θ = 24.4 EFPY
β = 4.45
r^2 = 0.963

4. SCC and IGC on the Secondary Side in Tube Sheet Crevices
θ = 18.57 EFPY
β = 5.86
r^2 = 0.892

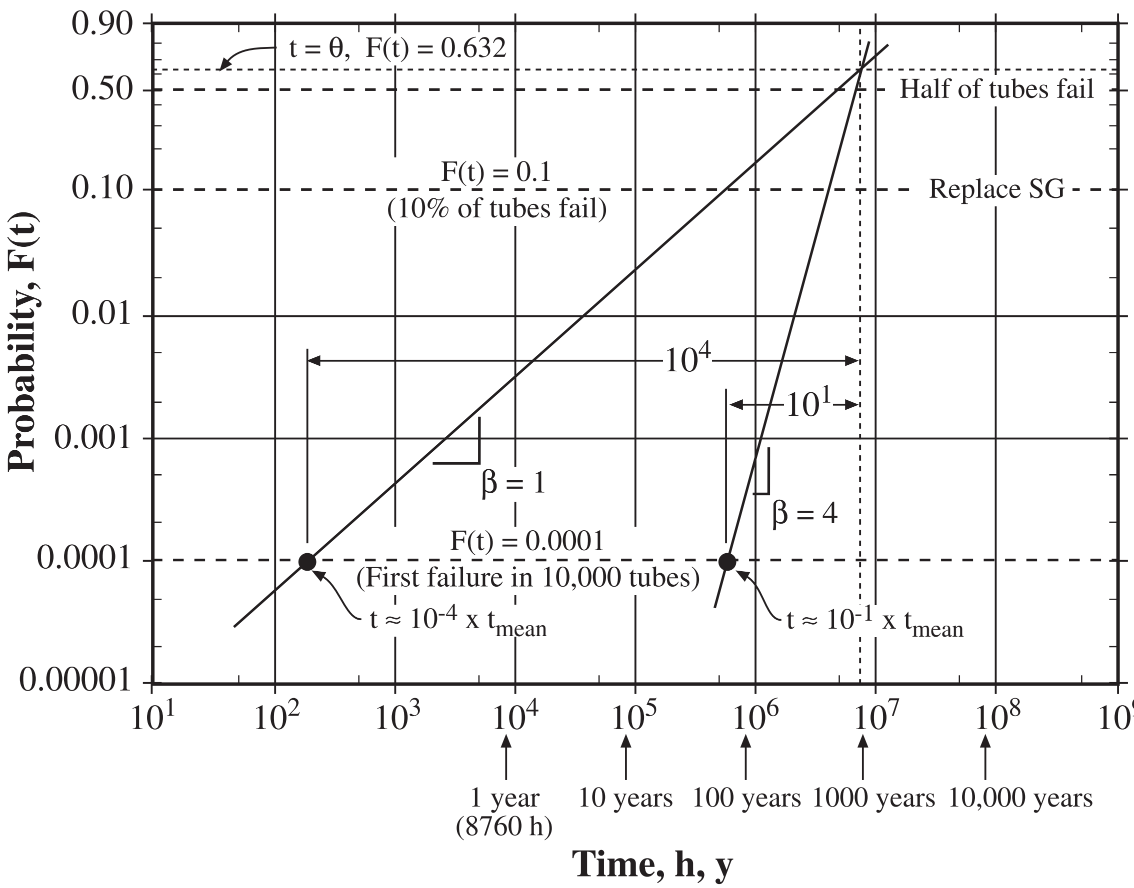


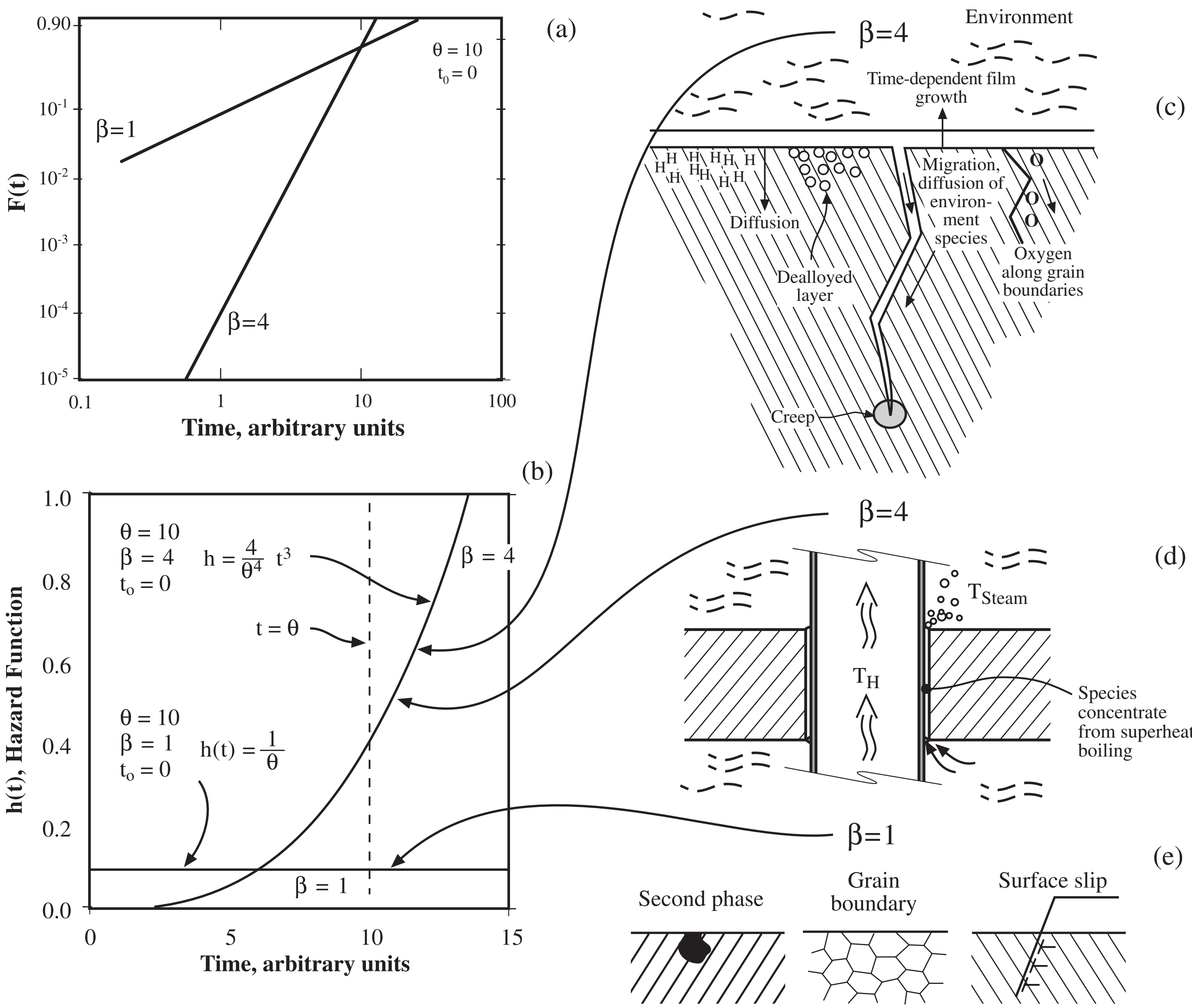
LPSCC of Alloy 600MA. (a) Probability vs. time to fail by LPSCC for a temperature range of 288 to 360°C for testing in high-purity deoxygenated water containing a hydrogen concentration of 10-60 cc H_2/kg H_2O. From Webb. (b) Correlation of data in (a) for θ, β, t_o vs. 1/T. (c) Probability vs. time to fail by LPSCC in high-purity water and steam for 360°C water and 400°C steam with 1 psia hydrogen in the former and 11 psia steam in the latter. From Jacko. (d) Correlation of data in (c) for θ, β, t_o vs. 1/T.

Cumulative Distribution Function
(correlation without physical foundation)

$$F(t) = 1 - \exp\left[-\left(\frac{t - t_o}{\theta - t_o}\right)^{\beta}\right]$$

$$\ln\left[\ln\left(\frac{1}{1 - F(t)}\right)\right] = \beta\left[\ln(t - t_o) - \ln(\theta - t_o)\right]$$





(a) Probability vs. time for *b*=1.0 and *b*=4.0. (b) Hazard function vs. time for *b*=1.0 and 4.0. (c) Examples of physical processes that produce *b*=1.0. (d) Examples of a heated crevice where accumulation processes occur before SCC can initiate. (e) Examples of accumulation processes that occur within metals and inside SCC.

Problem with β

(Dispersion $\alpha \frac{1}{\beta}$)

1. Stressor dependence

Stressors: T, σ, X, E, pH

- $\beta \; \alpha$ stressor

or

- $\beta \; \alpha \; \frac{1}{\text{stressor}}$

2. Dependence on physical processes

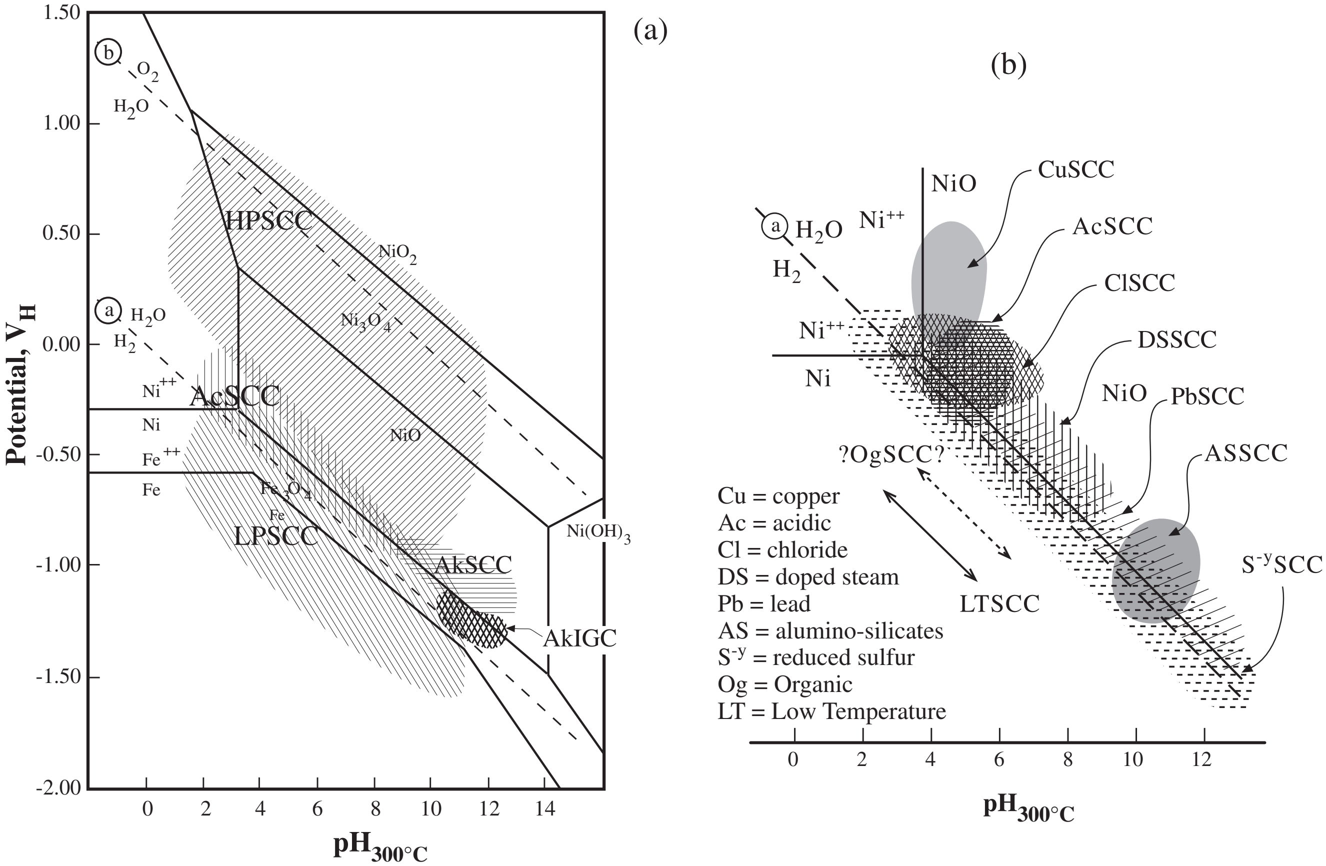
- $\beta = 1$ for surface processes (pitting, grain boundary, initiation of SCC)
- $\beta > 1$, e.g., $\beta = 4$ for accumulation at surface or inside metal

3. Initiation and propagation mixed

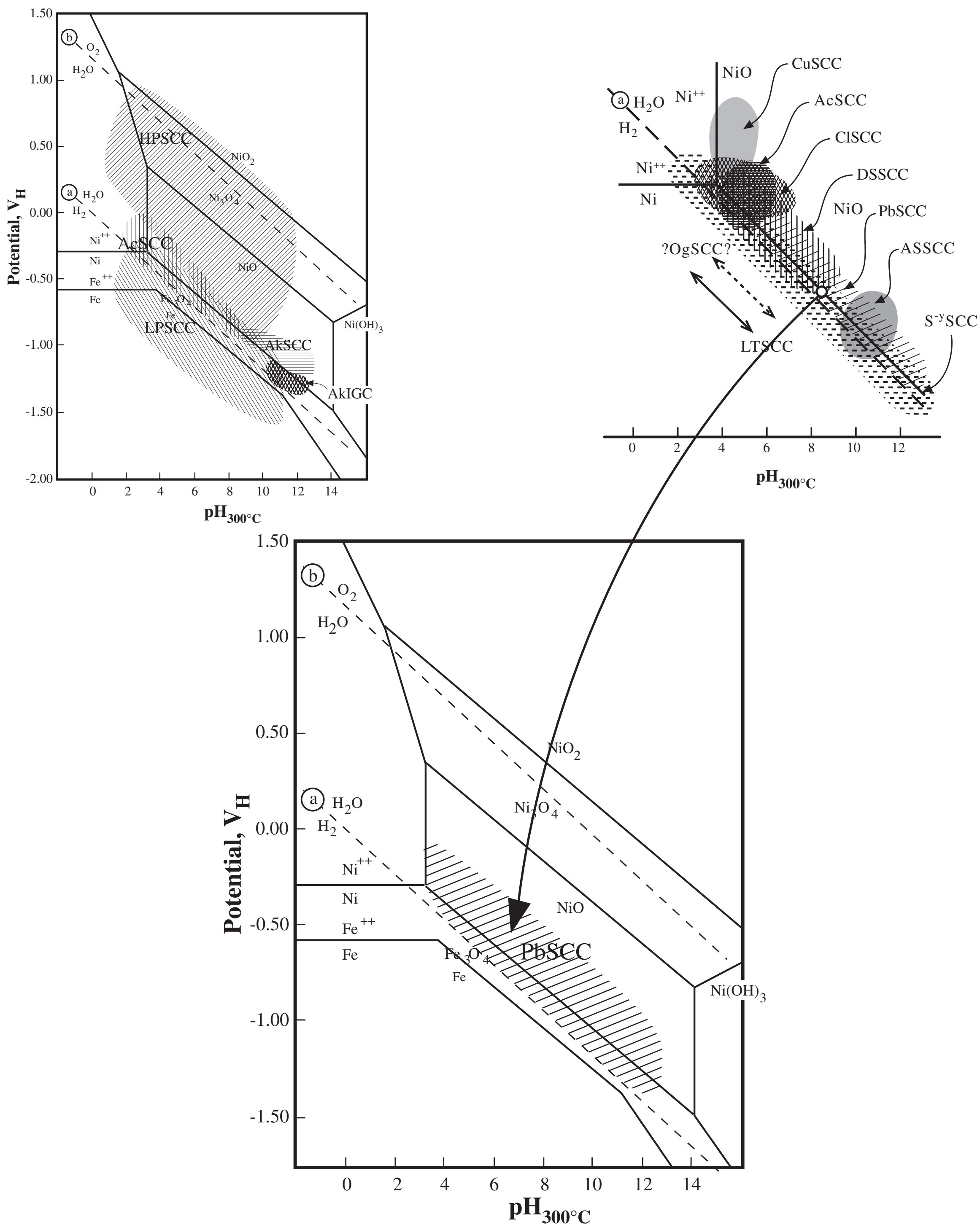
- $\beta = 1$ for initiation
- $\beta > 1$ for propagation

4. Aggregate data reduces β

5. Testing near boundaries of SCC submode reduces β



(a) Major submodes of SCC plotted with respect to coordinates of potential and pH for significant reactions of Ni and Fe at 350°C. Potential-pH relationships from Chen. Extent of the submodes based on experience from laboratory testing and reasonable interpolation and extrapolations. Submodes are applicable to Alloy 600 MA in the range of 300 to 350°C. (b) minor submodes of SCC for Alloy 600MA plotted with respect mainly to the NiO/Ni half-cell equilibrium at 300°C.


Potential, V_H
$pH_{300°C}$
HPSCC
AcSCC
LPSCC
AkSCC
AkIGC
NiO_2
Ni_3O_4
NiO
$Ni(OH)_3$
Ni^{++}
Ni
Fe^{++}
Fe
Fe_3O_4
O_2
H_2O
H_2
CuSCC
ClSCC
DSSCC
PbSCC
ASSCC
$S^{-y}SCC$
?OgSCC?
LTSCC

Depth of SCC Penetration

2. pH

3. Environmental Species

1. Electrochemical Potential

6. Alloy Composition and Environment

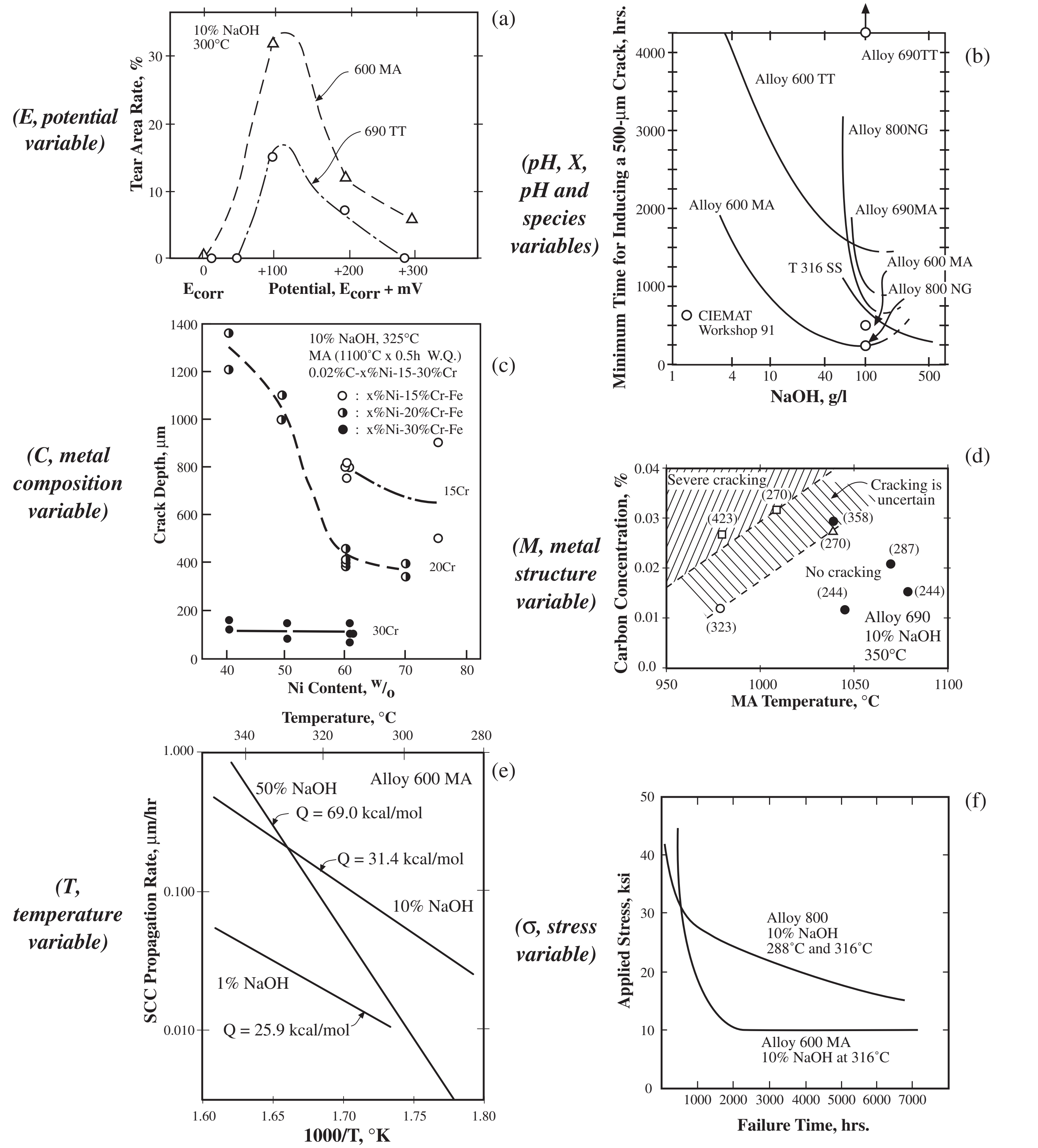
5. Temperature

$$\mathbf{x} = \mathbf{A}\,[\,\mathbf{H}^{+}]^{n}\,[\,\boldsymbol{x}\,]^{p}\,\sigma^{m}\,\mathbf{e}^{\frac{E-E_o}{b}}\;\mathbf{e}^{\frac{Q}{RT}}\;\mathbf{t}^{q}$$

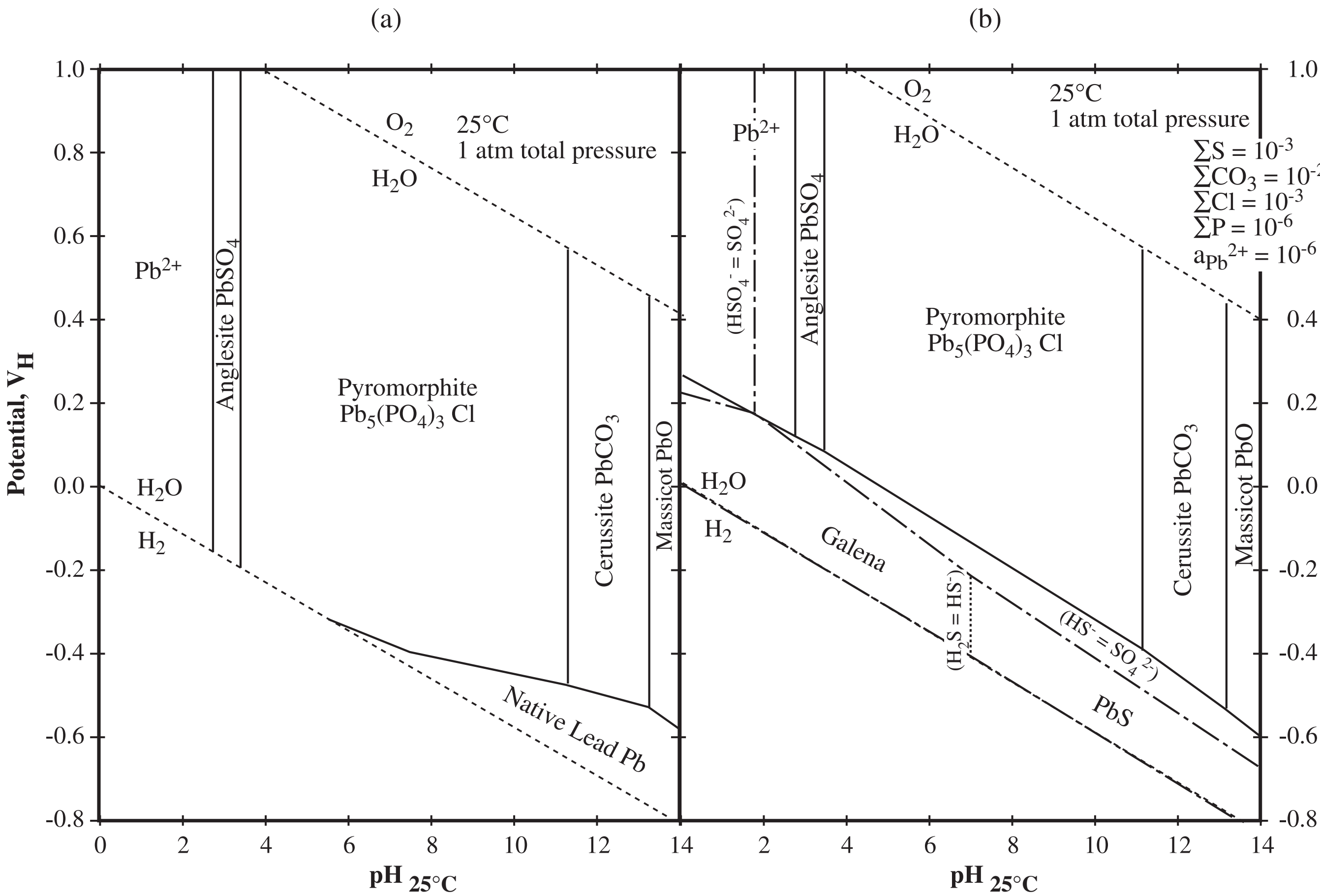
6. Alloy Composition

7. Alloy Structure

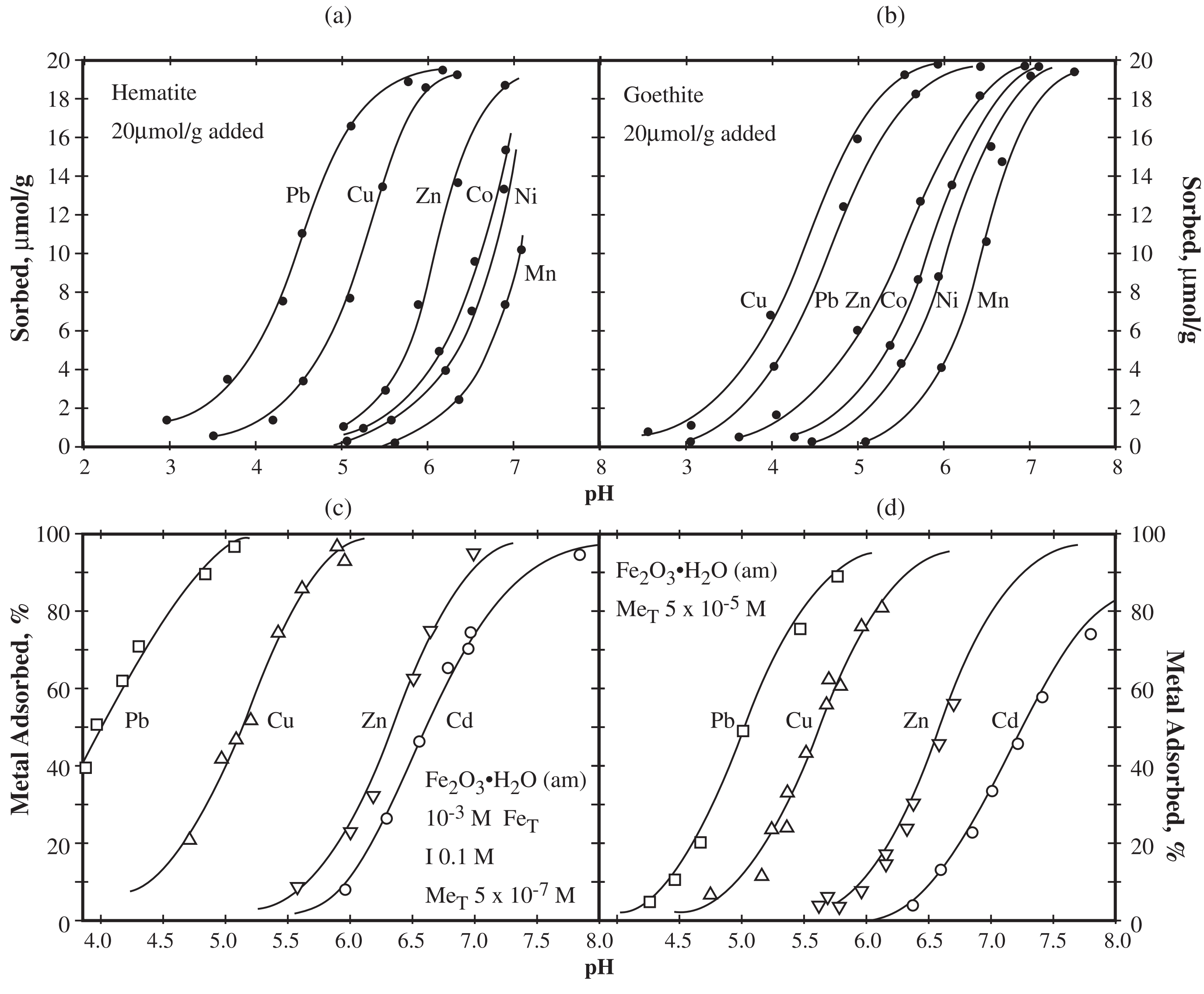
4. Stress



Dependencies of AkSCC on the primary variables. (a) Tear area ratio vs. potential for Alloy 600MA and 690TT on 10% NaOH at 300°C. From Suzuki. (b) Minimum time for inducing a crack in smooth surface specimens vs. concentration of NaOH for various Fe-Cr-Ni alloys. Specimens are C-rings stressed to approximately the yield stress. The original curves of Berge and Donati were redrawn, and data were added by McIlree. Data points added by McIlree were C-rings with 2% strain tested at 10% NaOH. testing at 350°C. (c) Crack depth vs. Ni concentration for Ni-Cr-Fe alloys +0.02%C exposed to deaerated 10% NaOH solution at 325°C for 200 hours as single U-bends. Speciments are mill annealed. From Nagano et al. (d) IGSCC sensitivity of TT (700°C) Alloy 690 vs. MA, temperature and C constant in 10% NaOH, 350°C. From Valliant et al. (e) SCC propagation rate vs. 1000/T for Alloy 600 MA in various concentrations of NaOH. From Jacko. (f) Stress vs. time for Alloy 600 in 10% NaOH at 288 and 316°C for Alloys 600 and 800. From Wilson et al.



Potential vs. pH at 25°C for the H_2O, S, C, P, Cl system (a) without galena and (b) with galena. From Nriagu. [NRI-74]

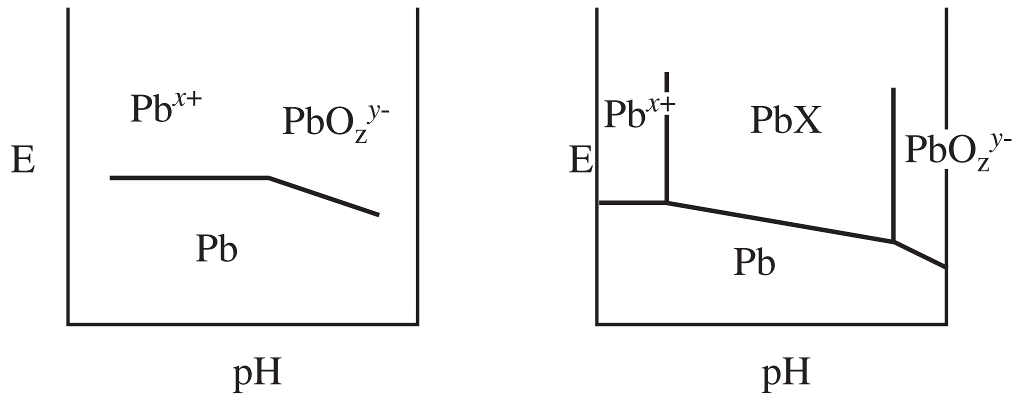


Quantity absorbed vs. pH at RT of Pb, Cu, Zn, Co, Ni and MN on (a) menatite and (b) goethite. From McKenzie. [McK-80] (c) Precent metal, Pb, Cu, Zn, Cd, adsorbed vs. pH at RT on amorphous $Fe_2O_3 \cdot H_2O$. (c) added metal $5x10^{-7}$ M. (d) added metal $5x10^{-5}$ M. From Benjamin and Leckie3. [BEN-81]

The Immobilization of Pb

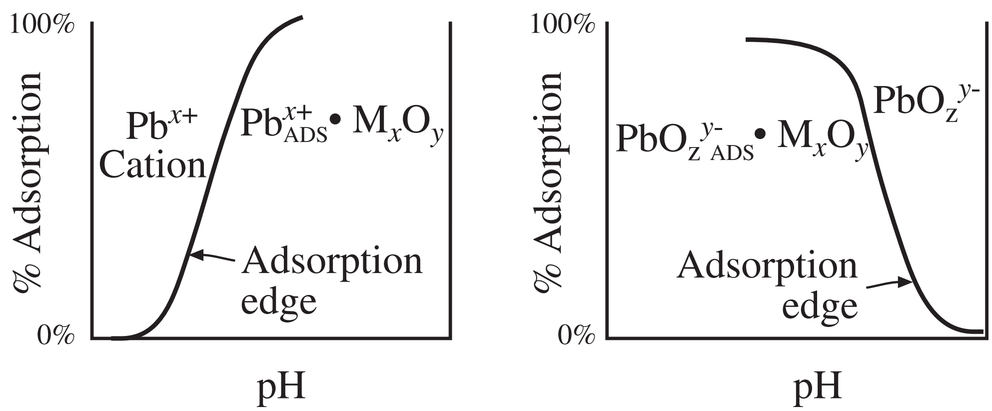
Formation of Soluble Compounds

$$Pb + X \Rightarrow PbX$$



Adsorption

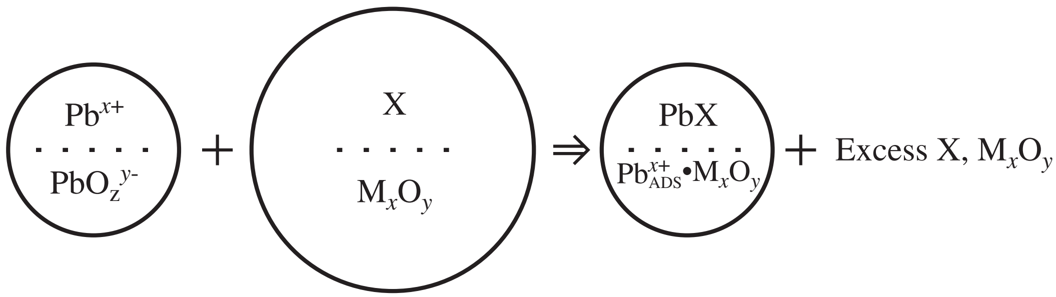
$$\left.\begin{matrix} Pb^{x+} \\ PbO_z^{y-} \end{matrix}\right\} + M_xO_y \Rightarrow \left.\begin{matrix} Pb^{x+}_{ADS} \\ PbO_{z\,ADS}^{y-} \end{matrix}\right\} \bullet M_xO_y$$



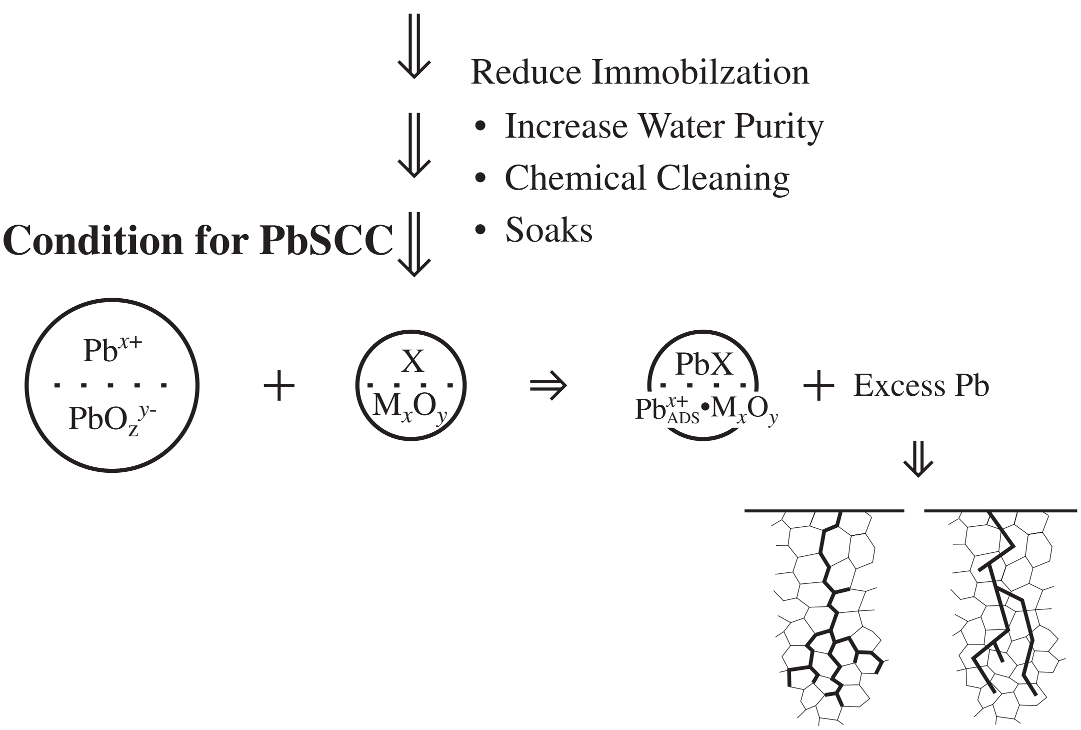
Schematic view of options for immobilizing and mobilizing Pb in SG deposits. Roles of compound formation and adsorption in immobilizing Pb.

The Immobilization of Pb (cont.)

Condition for No PbSCC

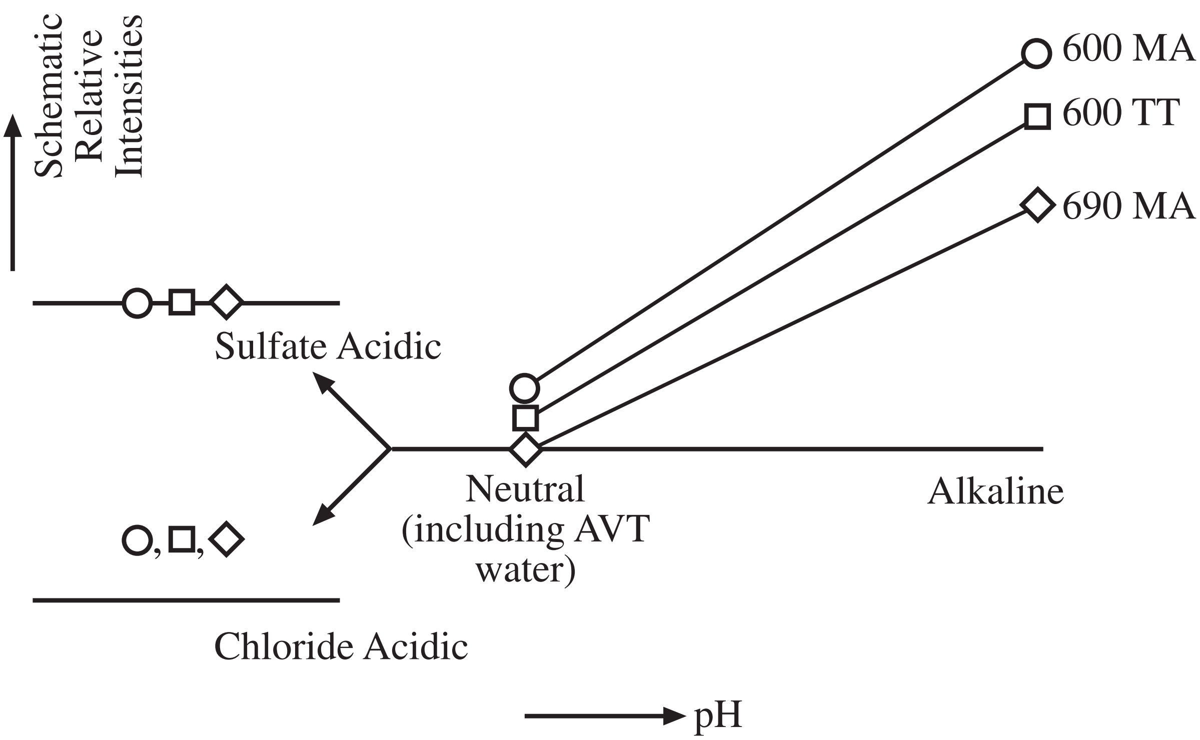


Condition for PbSCC



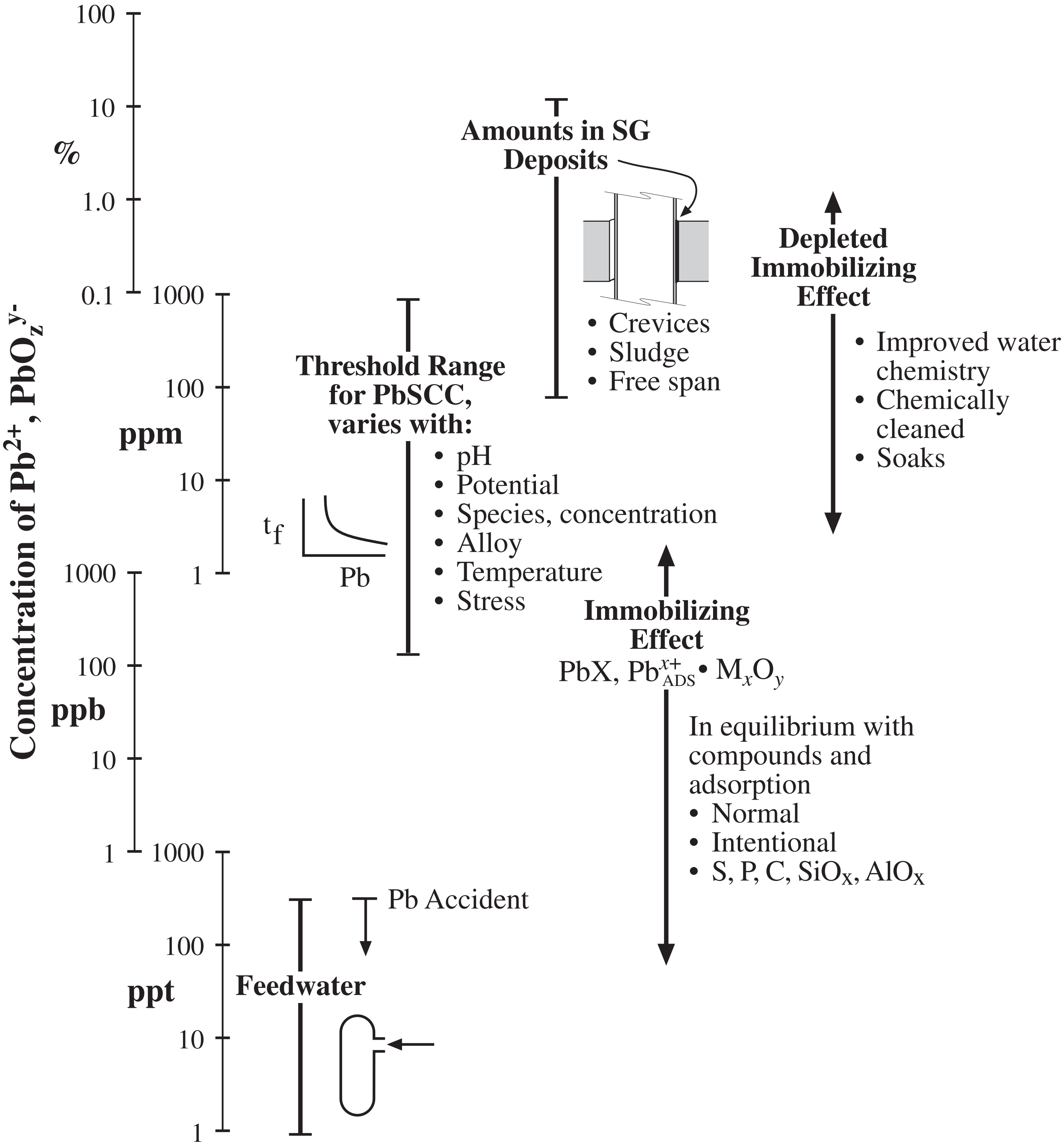
Schematic view of options for immobilizing and mobilizing Pb in SG deposits. Conditions for avoiding PbSCC.

Schematic Relative Intensity of PbSCC in SG Temperature Range



Schematic view of dependence of PbSCC for Alloys 600MA, 600TT, and 690TT on pH in the alkaline, neutral and acidic regions. Horizontal reference lines are for zero PbSCC.

Schematic Effect of Pb Concentrations as They Affect SGs



pH	pH
Potential	E
Identity and concentration of species	X
Alloy composition	C
Alloy structure	M
Temperature	T
Stress	σ

$$\rightarrow \left\{ \begin{matrix} \theta \\ \beta \\ t_o \end{matrix} \right.$$

$$F_i(t) = F_i(\theta, \beta, t_o)$$

$$\theta_i, \beta_i, t_{o_i} = \theta_i, \beta_i, t_{o_i} (E, pH, X, C, M, T, \sigma)$$

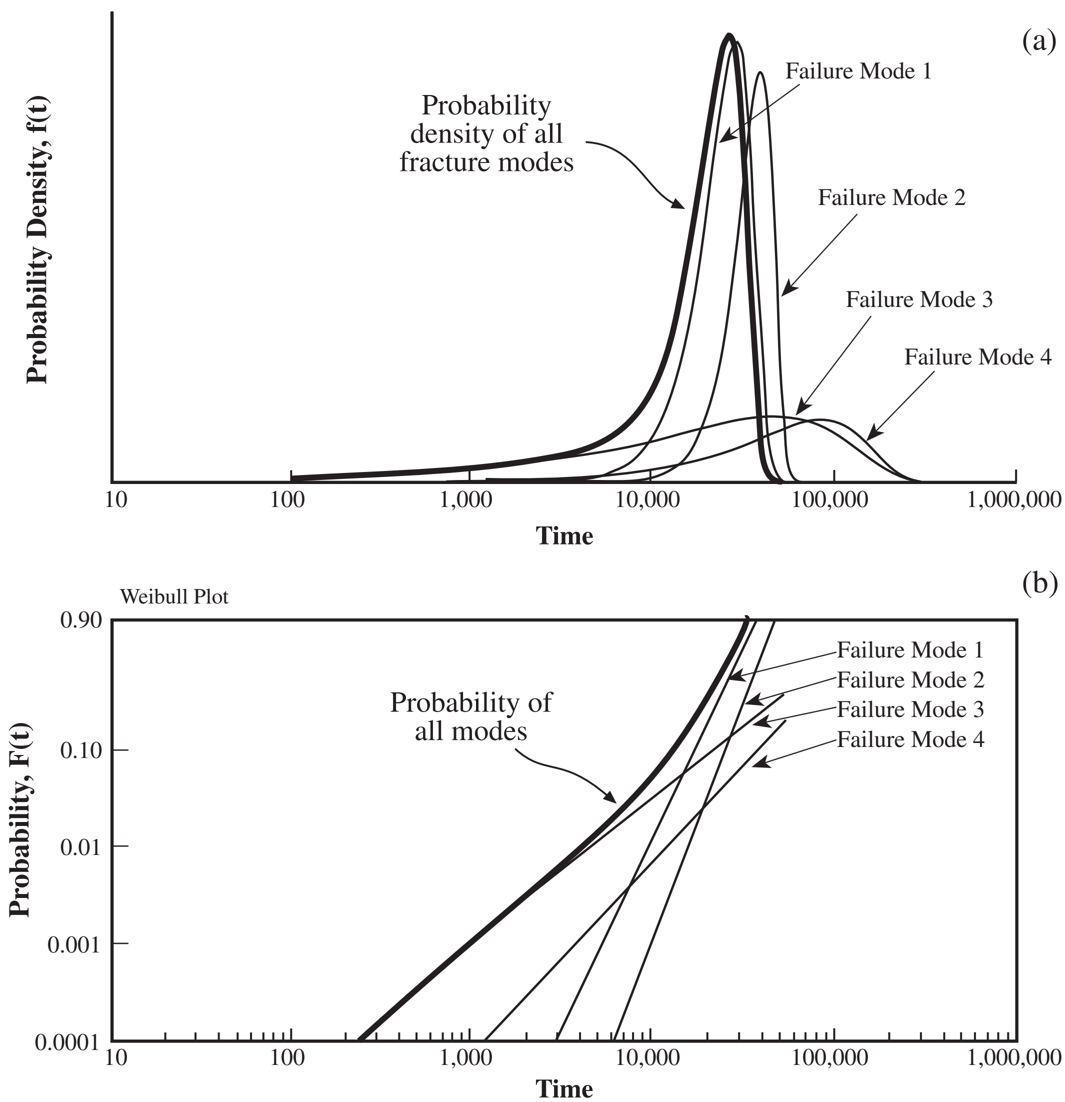
where i = AkSCC, LPSCC, AcSCC, PbSCC, S^{y-}SCC

Application of primary variables to statistical parameters.

$$F_T(t) = 1 - [1 - F_1(t)][1 - F_2(t)] \bullet\bullet\bullet [1 - F_n(t)]$$

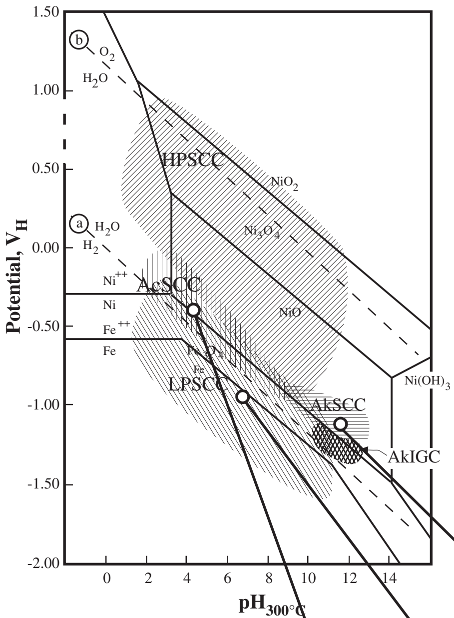
Where:

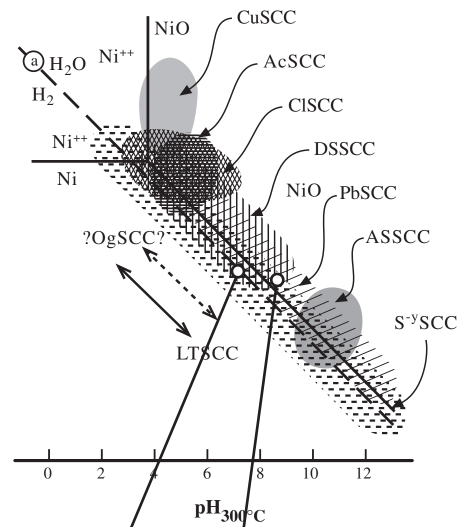
F_T = Total probability, and where the subscripts refer respectively to AkSCC, LPSCC, PbSCC and S^{y-}SCC



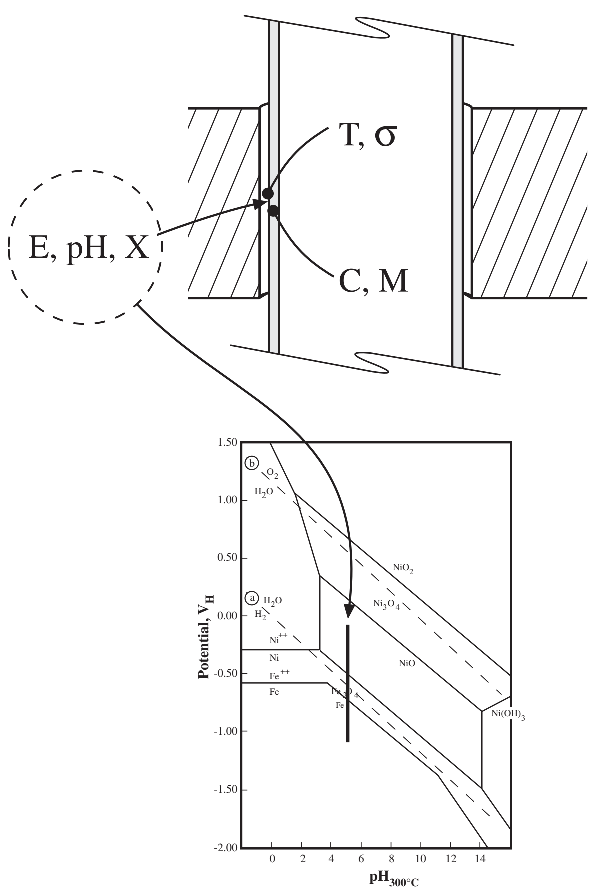
(a) pdfs for four separate failure modes occurring in the same subcomponent. Total pdf shown aggregating data from four. (b) cdf for the four cases in (a) and the aggregate distribution is shown based on Eqn. (36).

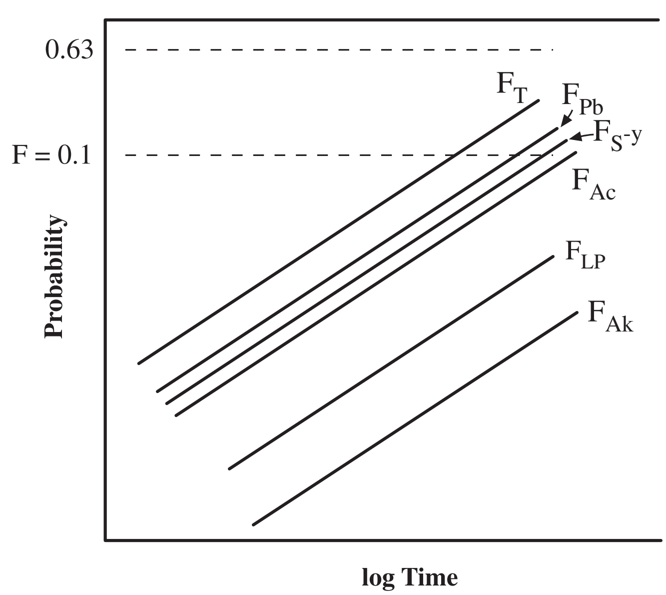
Overall Expression

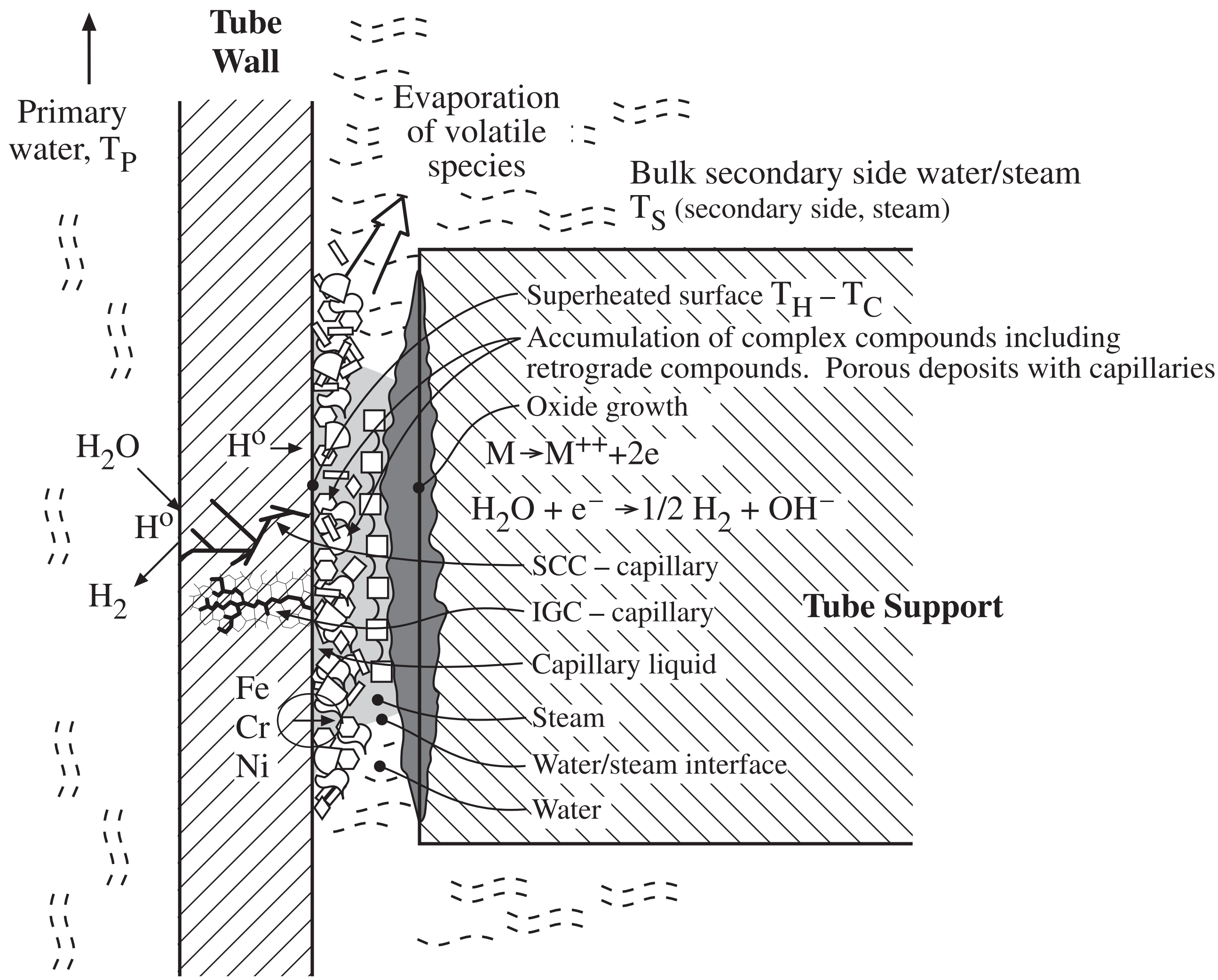




$$F_T(t) = 1 - (1 - F_{Ac})(1 - F_{LP})(1 - F_{Ak})(1 - F_{S^{-y}})(1 - F_{Pb})]$$

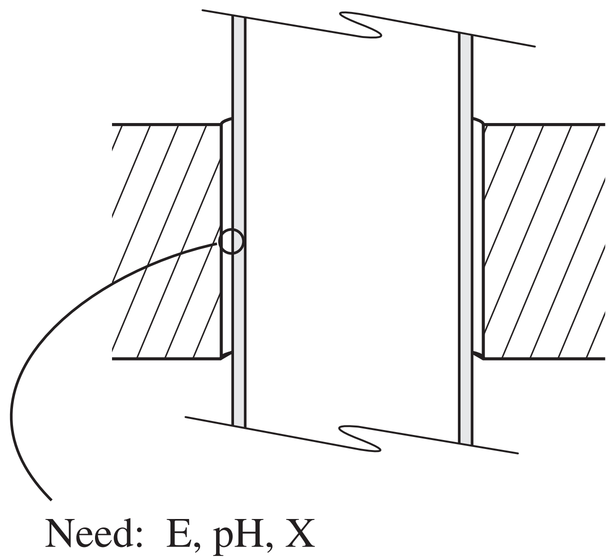






Schematic view of heat transfer crevice at a tube support.

Defining the Local Environment



Sources:

- Morphology of deposits
- Chemistry of deposits
- Hideout return
- Blowdown chemistry
- Concentration relative to bulk
- Analysis
- Laboratory experiments

Data from:

- EPRI Reports
- Direct measurements of collars
- Utility reports
- Published literature
- Experiments