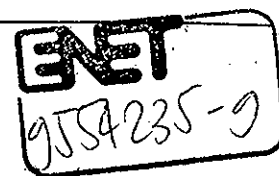


SCC of Low Alloy Reactor Pressure Vessel Steels in Oxygenated High Temperature Water

H.P. Seifert, J. Heldt



Paul Scherrer Institut
Laboratory for Safety and Accident Research
Component Safety
CH-5232 Villigen PSI

Tel: ++41 56 310 44 02 Fax: ++41 56 310 21 99 E-mail: hans-peter.seifert@psi.ch

Presented at ICG-EAC Meeting, May 17 - 21, 1999, Turku, Finland

04.05.99/C:\eigene dateien\vortrag\icg\icg98\titleblatt.doc

Outline

- **Introduction**
- **Materials and experimental set-up**
- **Results and discussion**
 - Effect of water chemistry conditions
 - Effect of loading conditions
 - Overview on standard tests
 - Tests under constant deformation
 - Tests under constant active external loading
 - Effect of initial loading rate and hold time under subsequent static loading
 - Effect of environmental and material parameters on SCC/SICC
- **Summary and conclusions**

14.05.99/C:\eigene dateien\vortrag\icg\icg98\outline.doc

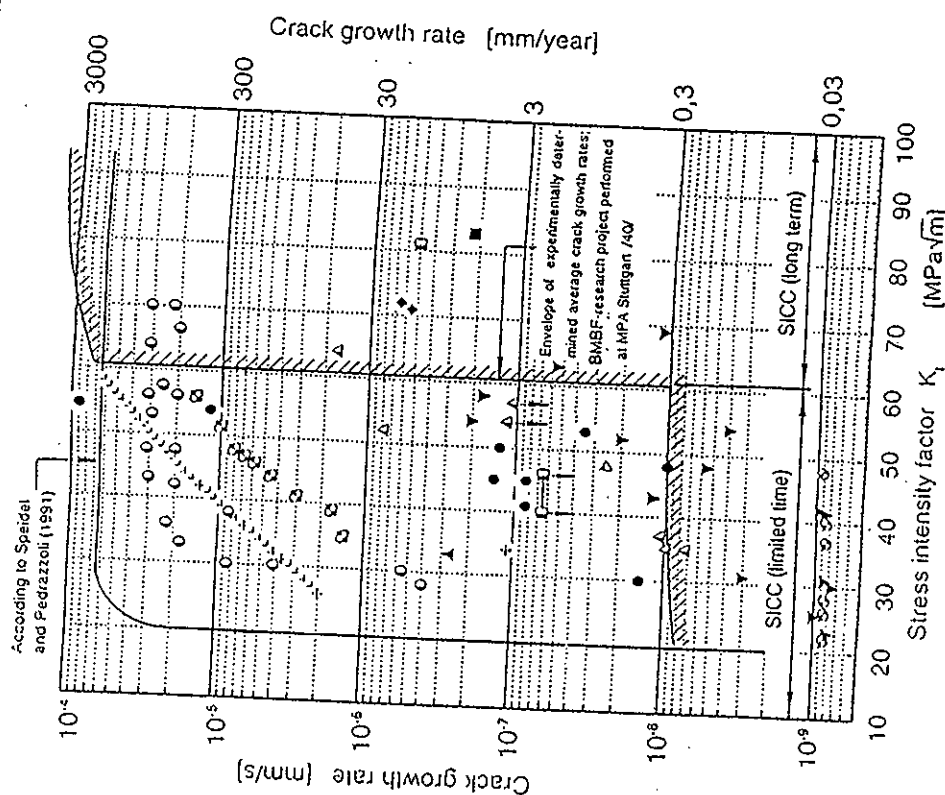
Environmentally-Assisted Cracking of RPV Steels

mechanism	EAC		
	SCC	SICC	CF
	stress corrosion cracking	strain-induced corrosion cracking	corrosion fatigue
type of loading	static	dynamic slow monotonically rising or very low cycle (VLCF)	cyclic low cycle high cycle
data	K_{ISCC} , da/dt	da/dt, N_f , da/dN	N_f , da/dN, $K_{I,th}$
LWR operation condition	steady state power operation	start-up/shut-down thermal stratification	thermal fatigue
quantitative characterisation	-	-	ASME III and XI

10.05.99/C:\eigene dateien\vortrag\cgcg99\leac

CGR Literature Data (up to 1995)

Low alloy steels in oxygenated high temperature water:



V. L  ppl  , "Untersuchungen zum korrosionsgest  tzten Risswachstum ferritischer St  hle in sauerstoffhaltigem Hochtemperaturwasser", Tech. wiss. Ber. MPA Stuttgart, 1996, Heft 96(02).

F.P. Ford, P.L. Andresen, "Stress Corrosion Cracking of Low Alloy Steels in 288   C Water", Corrosion-89, Paper No. 498, pp.498/1 - 498/19, New Orleans 1989, Publ.: NACE, Houston, Texas.

M.O. Speidel, R.M. Magdowski, "Stress Corrosion Cracking of Nuclear Reactor Pressure Vessel and Piping Steels", J. Pres. Ves. & Piping, 34 (1988), pp. 119 - 142.

14.04.99/C:\eigene dateien\vortrag\cgcg99\literatdata.doc

Investigated Materials

Material	Code / Standard	Sulphur content [wt.%]	Similar to
20 MnMoNi 5 5	KTA 3201.1	0.004, 0.009, 0.010	SA 508 Cl. 3 SA 533 B Cl.1
SA 508 Cl. 2	ASME	0.004	22 NiMoCr 3 7
SA 533 B Cl. 1	ASME	0.018	20 MnMoNi 5 5

Overview on investigated low alloy RPV steels

Alloy	Heat treatment
20 MnMoNi 5 5	as received
20 MnMoNi 5 5	910 °C - 920 °C / 6 h / WQ / 640 °C - 650 °C / 9.5 h / FC
20 MnMoNi 5 5	910 °C - 920 °C / 6 h / WQ / 640 °C - 650 °C / 9.5 h / Air
SA 533 B Cl.1	915 °C / 12 h / 860 °C / 12 h / WQ / 635 °C / 12 h / FC
20 MnMoNi 5 5	910 °C - 920 °C / 4.5 h / WQ / 640 °C - 645 °C / 9 h / FC
SA 508 Cl.2	as received

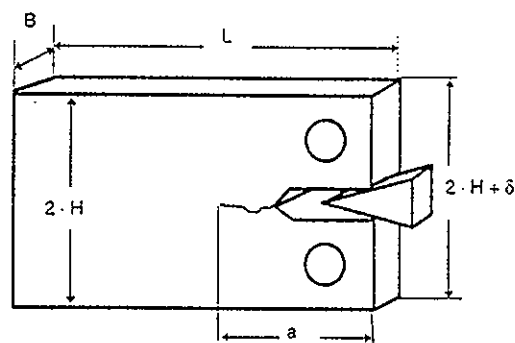
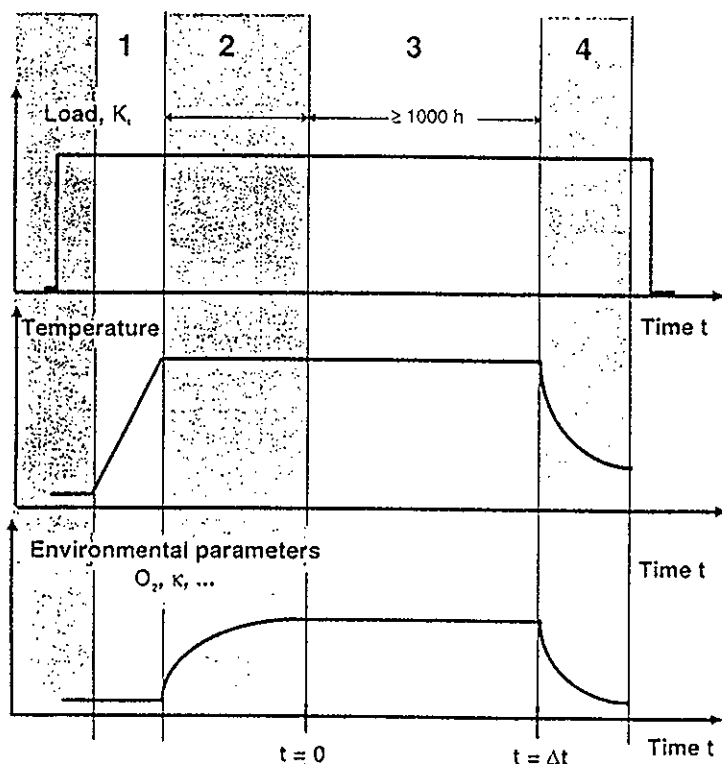
Heat treatment (Q+T WQ: Water quenched FC: Furnace cooled)

Alloy	C	Si	Mn	P	S	Cr	Mo	Ni	V	Al	Cu
20 MnMoNi 5 5	0.15	0.29	1.40	0.005	0.005	0.14	0.51	0.65	0.007	0.036	-
20 MnMoNi 5 5	0.21	0.25	1.26	0.004	0.004	0.15	0.5	0.77	0.008	0.013	0.06
20 MnMoNi 5 5	0.19	0.2	1.39	0.008	0.010	0.14	0.53	0.53	0.009	0.04	0.08
SA 533 B Cl.1	0.25	0.24	1.42	0.006	0.018	0.12	0.54	0.62	0.007	0.03	0.15
20 MnMoNi 5 5	0.20	0.16	1.24	0.008	0.009	0.09	0.50	0.78	0.010	0.01	0.06
SA 508 Cl. 2	0.21	0.27	0.69	0.005	0.004	0.38	0.63	0.78	0.006	0.015	0.16

Chemical composition

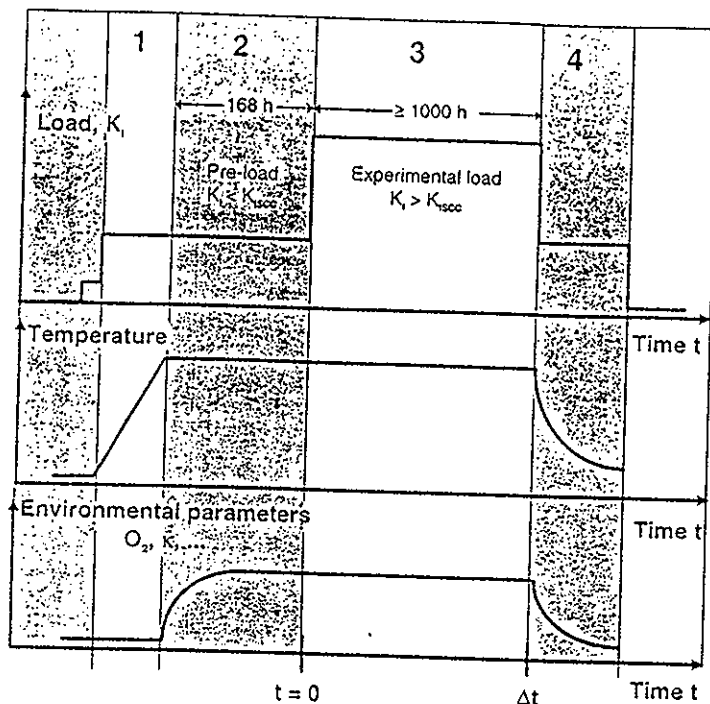
Alloy	Room temperature				288 °C
	R _{0.2} [MPa]	R _m [MPa]	A ₅ [%]	Z [%]	R _{0.2} [MPa]
20 MnMoNi 5 5	553	669	22.3	74.5	-
20 MnMoNi 5 5	485	648	19.3	72.1	418
20 MnMoNi 5 5	565	684	19.6	73.5	-
SA 533 B Cl.1	468	616	21.0	43.0	411
20 MnMoNi 5 5	475	619	22.7	63.6	444
SA 508 Cl.2	448	611	17.9	71.0	396

Mechanical tensile properties (DIN 50145, B5X50)



$$K_I = E \cdot H \cdot \delta \cdot f(a, H)$$

$$f(a, H) = \frac{[3 \cdot H \cdot (a + 0.6 \cdot H)^2 + H^3]^{1/2}}{4 \cdot [(a + 0.6 \cdot H)^3 + H^2 \cdot a]}$$



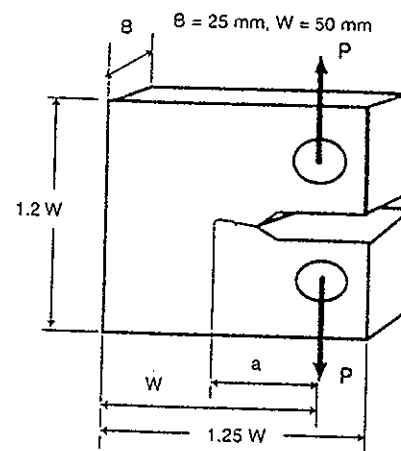
1: Heating phase 2: Conditioning phase 3: Experimental phase 4: Cooling phase

Conditioning phase:

- formation of an uniform oxide film
- stable and constant environmental parameters

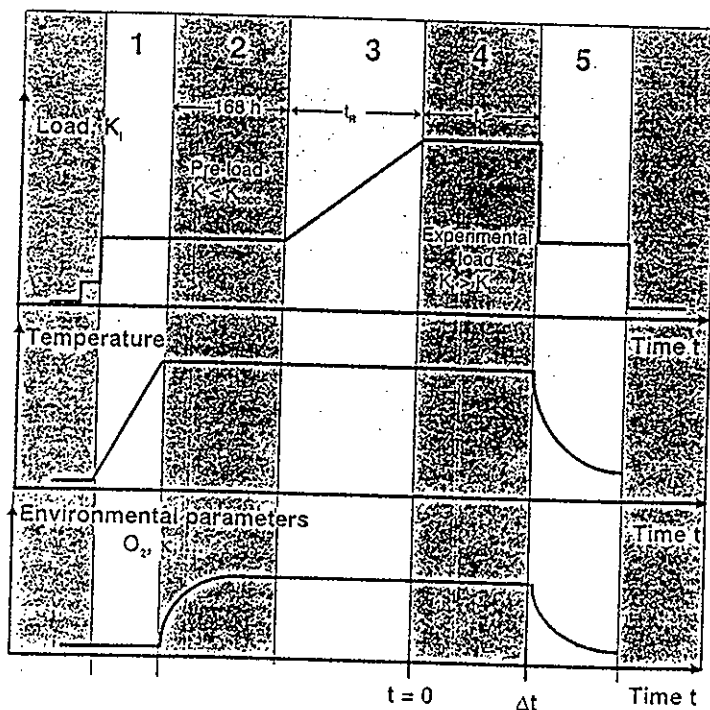
Experimental phase:

- SCC test in a well controlled environment
- Δt : experimental load is reached - start unloading
- $\dot{a} = \Delta a / \Delta t$



$$K_I = \frac{P}{B \cdot \sqrt{W}} \cdot f\left(\frac{a}{W}\right)$$

$$f\left(\frac{a}{W}\right) = \frac{\left[2 + \frac{a}{W}\right] \cdot \left[0.886 + 4.64 \cdot \left(\frac{a}{W}\right) - 13.32 \cdot \left(\frac{a}{W}\right)^2 + 14.72 \cdot \left(\frac{a}{W}\right)^3 - 5.6 \cdot \left(\frac{a}{W}\right)^4\right]}{\left[1 - \frac{a}{W}\right]^{1.5}}$$



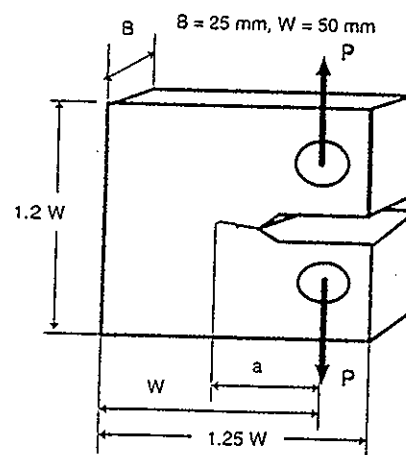
1: Heating phase 2: Conditioning phase 3: Slow rising displacement phase (t_r)
4: Constant load phase (t_h) 5: Cooling phase

Conditioning phase:

- formation of an uniform oxide film
- stable and constant environmental parameters

Experimental phase 3 + 4:

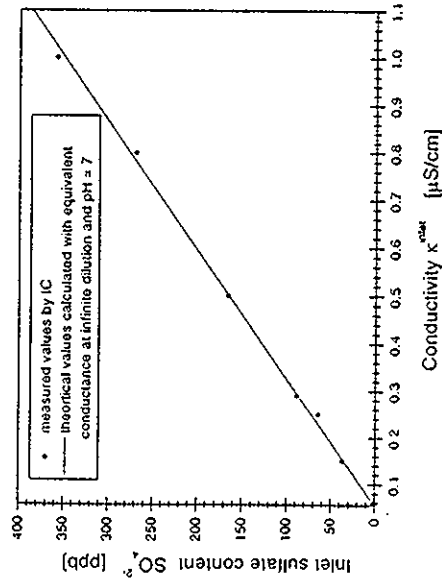
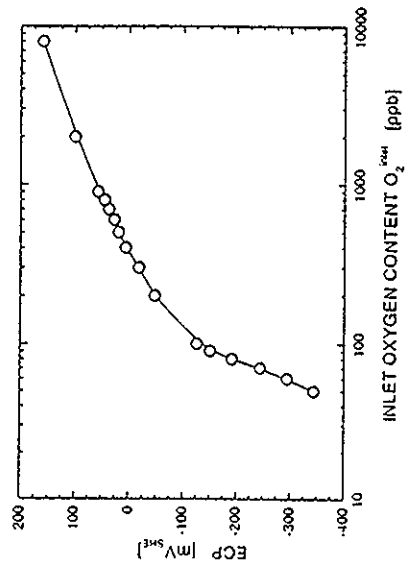
- SCC test in a well controlled environment
- systematic variation of initial loading rate and subsequent hold time under constant load



$$K_I = \frac{P}{B \cdot \sqrt{W}} \cdot f\left(\frac{a}{W}\right)$$

$$f\left(\frac{a}{W}\right) = \frac{\left[2 + \frac{a}{W}\right] \cdot \left[0.886 + 4.64 \cdot \left(\frac{a}{W}\right) - 13.32 \cdot \left(\frac{a}{W}\right)^2 + 14.72 \cdot \left(\frac{a}{W}\right)^3 - 5.6 \cdot \left(\frac{a}{W}\right)^4\right]}{\left[1 - \frac{a}{W}\right]^{1.5}}$$

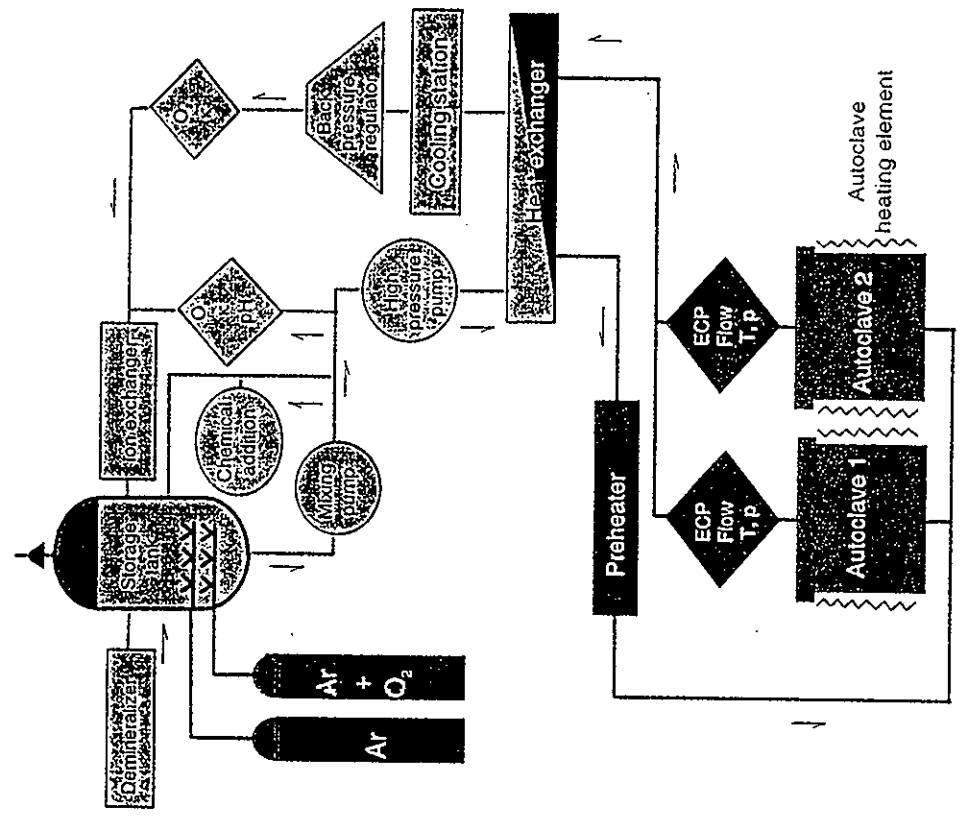
Electrochemical and Water Chemistry Conditions



Ion chromatography							ICP-AES								
[ppb]							[ppb]								
	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻	F ⁻	PO ₄ ³⁻	SiO ₂ ²⁻	Si _{tot}	K _{tot}	Na _{tot}	Cu _{tot}	Fe _{tot}	Cr _{tot}	Ni _{tot}	Co _{tot}	Zn _{tot}
Inlet	<1-2	<1-2	<1-2	<1	<1	10-20	2-3	<1	<1	<0.5	<0.5-1	<1	<0.1	<0.8	0.3
Outlet	<1-2	<1-2	<1-2	<1	<1	10-20	3-6	<1	<1	<0.5	<0.5-1	1-4	0.5	<0.8	0.5

Typical water chemistry analysis for tests with an inlet conductivity ≤ 0.06 μS/cm. Tests with higher inlet conductivity (by addition of Na₂SO₄) only differ from this analysis in higher SO₄²⁻ and Na⁺ contents (according to the figure above).

Simplified Scheme of Recirculation Loops



Mechanical validity criteria and limits for SCC tests:

ASTM E 399	$B, W-a, a > 2.5 \cdot (K_{Ic} / \sigma_{ys})^2$
ASTM E 647	$W-a > (4/\pi) \cdot (K_{Ic} / \sigma_{ys})^2$
Size of plastic zone $<< B, W-a, a$	$r_p = (1/(\alpha \cdot \pi)) \cdot (K_{Ic} / \sigma_{ys})^2 < 0.1 \cdot B, 0.1 \cdot W-a$ $\alpha = 1$ (plane stress) or 3 (plane strain)

σ_{ys} or $(\sigma_{ys} + \sigma_{ts})/2$ if $(\sigma_{ys} / \sigma_{ts}) > 1.3$
 σ_{ts} : yield stress σ_{ts} : tensile strength both at test temperature

	ASTM E 399	ASTM E 647	$r_p \leq 0.1 \cdot B$ plane strain $\alpha = 3$	$r_p \leq 0.1 \cdot B$ plane stress $\alpha = 1$
$K_{Ic,lim}$ 1T-CT	42 MPa $\sqrt{m}$	59 MPa $\sqrt{m}$	66 MPa $\sqrt{m}$	37 MPa $\sqrt{m}$
$K_{Ic,lim}$ DCB	27 MPa $\sqrt{m}$	95 MPa $\sqrt{m}$	41 MPa $\sqrt{m}$	24 MPa $\sqrt{m}$
Mechanical crack tip conditions	plane strain linear elastic	linear elastic		
Threshold for EAC	K_{EAC}	$K_{EAC} = f(B)$		

1T-CT: $a/W = 0.5, B = 25$ mm DCB: $a = 35$ mm, $W-a = 65$ mm, $B = 10$ mm $\sigma_{ts}(288^\circ C) = 420$ MPa

Crack growth rate resolution limits for used methods:

Method	Detection limit	Crack growth rate resolution limits for different test periods		
		100 h	1000 h	1 a
SEM	50 μm	1.4 E-10 m/s	1.4 E-11 m/s	1.6 E-12 m/s
SM	100 μm	2.8 E-10 m/s	2.8 E-11 m/s	3.2 E-12 m/s
DCPD	20 μm	5.6 E-11 m/s	5.6 E-12 m/s	6.3 E-13 m/s
CMOD/Compliance	100 μm	2.8 E-10 m/s	2.8 E-11 m/s	3.2 E-12 m/s

Metallurgical periodicity criteria Criteria for reliable CCR measurements	Required min. Δa_{EAC}	Resulting crack growth rate limits $\Delta a_{EAC}/\Delta t$ for different test periods Δt		
		100 h	1000 h	1 a
10 x mean grain size	200 μm	5.6 E-10 m/s	5.6 E-11 m/s	6.3 E-12 m/s
10 x mean distance between MnS	> 1000 μm	> 2.8 E-9 m/s	> 2.8 E-10 m/s	> 3.2 E-11 m/s
DCPD: 10 X resolution limit	200 μm	5.6 E-10 m/s	5.6 E-11 m/s	6.3 E-12 m/s
CMOD/Compliance: 10 x resolution limit	1000 μm	2.8 E-9 m/s	2.8 E-10 m/s	3.2 E-11 m/s

EPRI BWR/NWC Water Chemistry Guidelines for the Recirculation Water („Reactor Water“) for BWR/NWC Steady State Power Operation

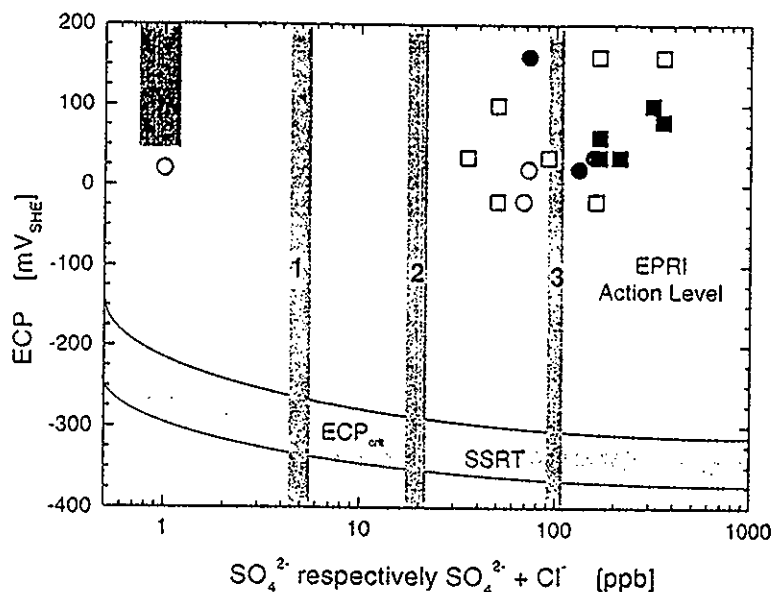
Diagnostic parameter	Achievable	Action level		
		1	2	3
Conductivity [$\mu S/cm$]	≈ 0.1	> 0.3	> 1.0	> 5.0
Sulfate [ppb]	≈ 1	> 5	> 20	> 100
Chloride [ppb]	≈ 2	> 5	> 20	> 100

Comparison of Reactor Water with Range of Tested Loop Conditions

	T [$^\circ C$]	κ [$\mu S/cm$]	$O_2^{eff.}$ [ppb]	ECP [mV _{SHE}]	Flow rate
Reactor water BWR/NWC	270 - 290	0.1	300 - 400	+ 150** - + 200**	turbulent m/s
Loop	288	0.06 - 1.0	200 - 8000	- 50 + 150	laminar mm/s

* $O_2^{eff} = (O_2 + 1/2 H_2O_2)$ **on stainless steel cladding

Effect of Water Chemistry



Open symbols:

no SCC

Solid symbols:

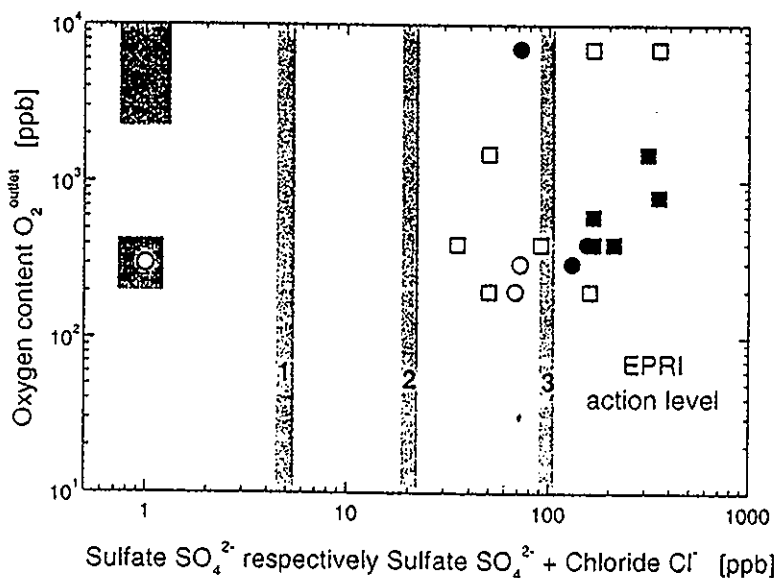
SCC in at least one specimen

○: Standard tests under constant active external load with 1T-CT specimens

□: Tests under constant deformation with WOL DCB specimens

11.05.99/C:\eigene dateien\vortrag\cvg\cvg99\ecpsulfat

Effect of Water Chemistry



Open symbols:

no SCC

Solid symbols:

SCC in at least one specimen

○: Standard tests under constant active external load with 1T-CT specimens

□: Tests under constant deformation with WOL DCB specimens

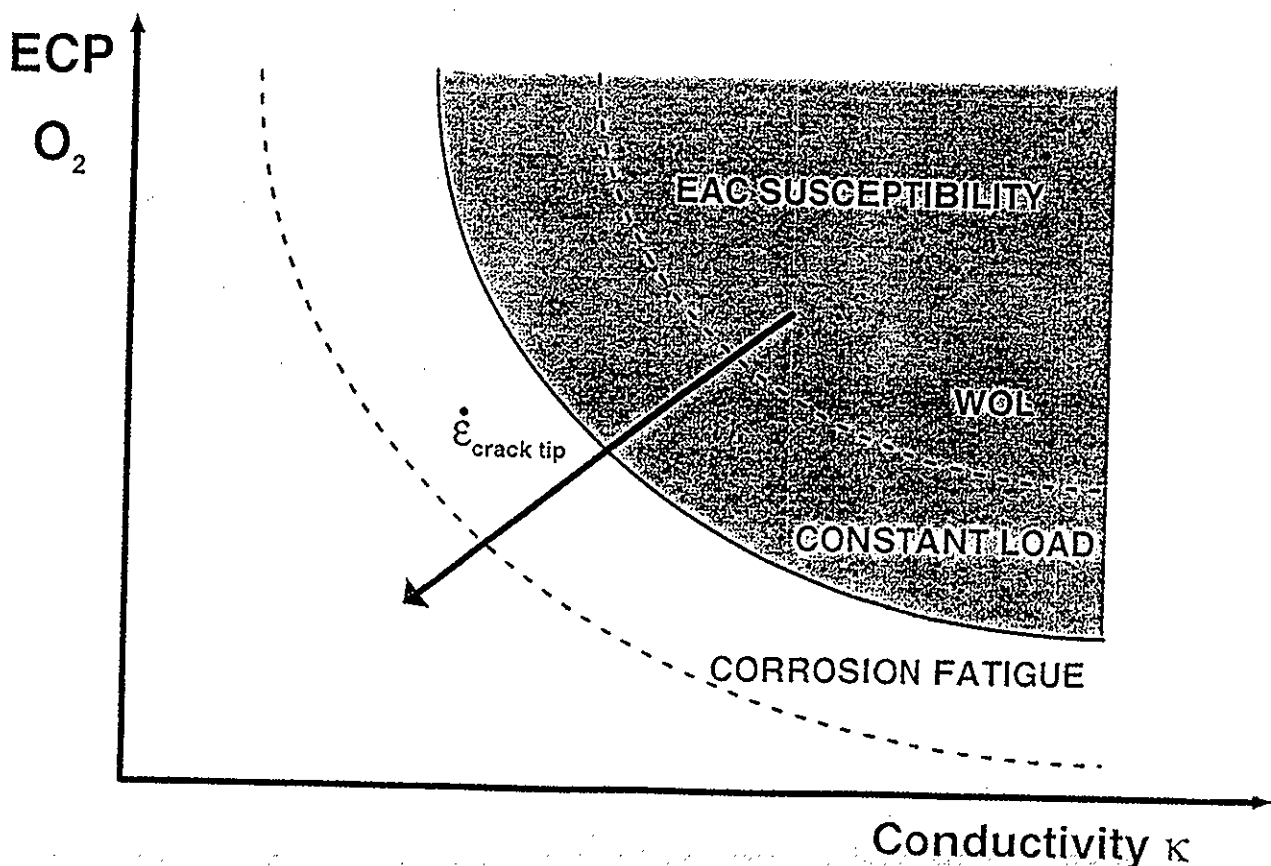
11.05.99/C:\eigene dateien\vortrag\cvg\cvg99\ecpsulfat

Environmental Margins for SCC Crack Growth

The following environmental margins for SCC crack growth under static load can be established for the LAS investigated:

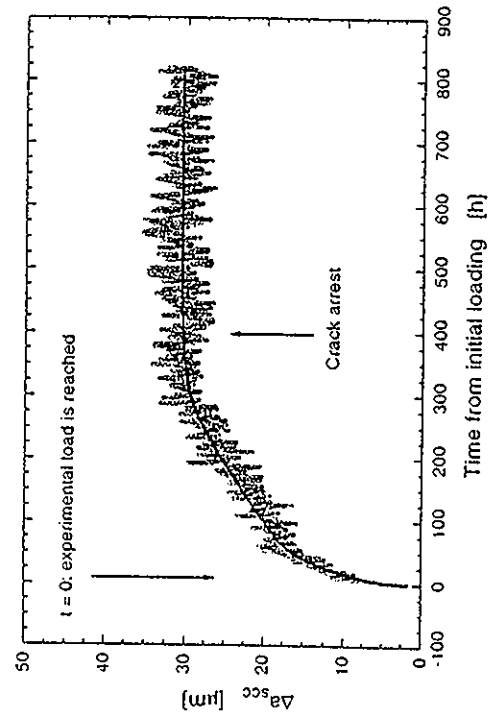
- No SCC was observed for $ECP \leq +150 \text{ mV}_{SHE}$ and for conductivity $\leq 0.25 \text{ } \mu\text{S/cm}$ (corresponding to $\leq 65 \text{ ppb SO}_4^{2-}$) as long as **small scale yielding conditions** were prevailing in the specimen ligament.
- Sustained, fast SCC growth ($> 1 \text{ cm/a}$) with respect to operational time scale of a BWR **cannot be excluded** for $ECP \geq 100 \text{ mV}_{SHE}$ and conductivity $\geq 1.0 \text{ } \mu\text{S/cm}$ (corresponding to $\geq 350 \text{ ppb SO}_4^{2-}$ or to chemistry conditions exceeding EPRI action level III) and/or in specimens with a **high degree of plasticity** in the remaining ligament.
- The given margins can be shifted to much **lower values** of both **ECP** and **concentration of specific anions** if there is a **positive strain rate** acting at the crack tip.

11.05.99/C:\eigene dateien\wortrag\cvg\cvg99\en\margins

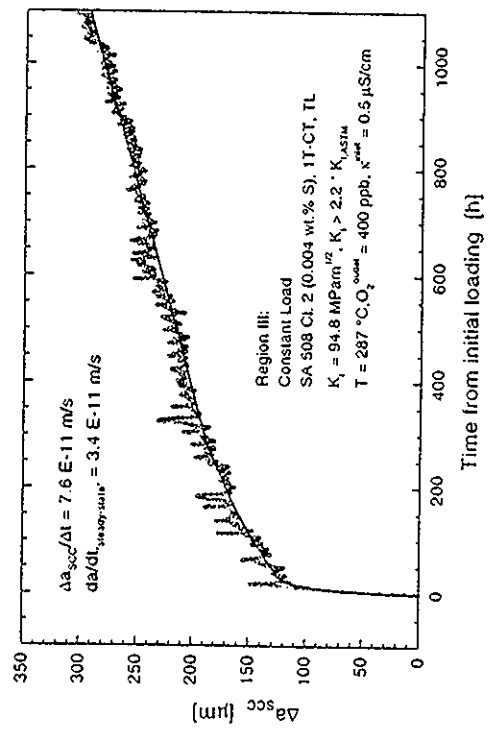


11.05.99/C:\eigene dateien\wortrag\hsk97\ecp02\en.doc

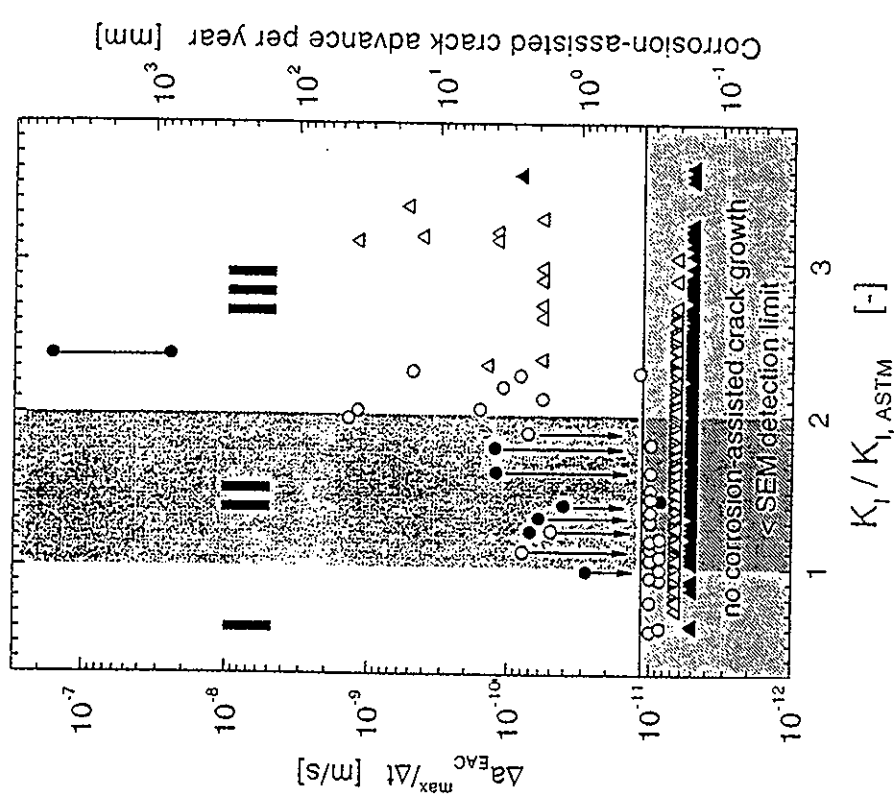
Region II: SCC limited in time, < test period



Region III: Sustained SCC, > test period



Results of Standard Tests under Static Loading



Experimental parameters:

- $T = 288^\circ \text{C}$ $\leq 0.5 \mu\text{S/cm}$ (Na_2SO_4)
- Open (red): $O_2 = 200 - 600 \text{ ppb}$
- Solid (blue): $O_2 = 8000 \text{ ppb}$, $ECP = +150 \text{ mV}_{SHE}$
- Circle: constant active external load (1T-CT)
- Triangle: constant deformation (WOL DCB)

Materials:

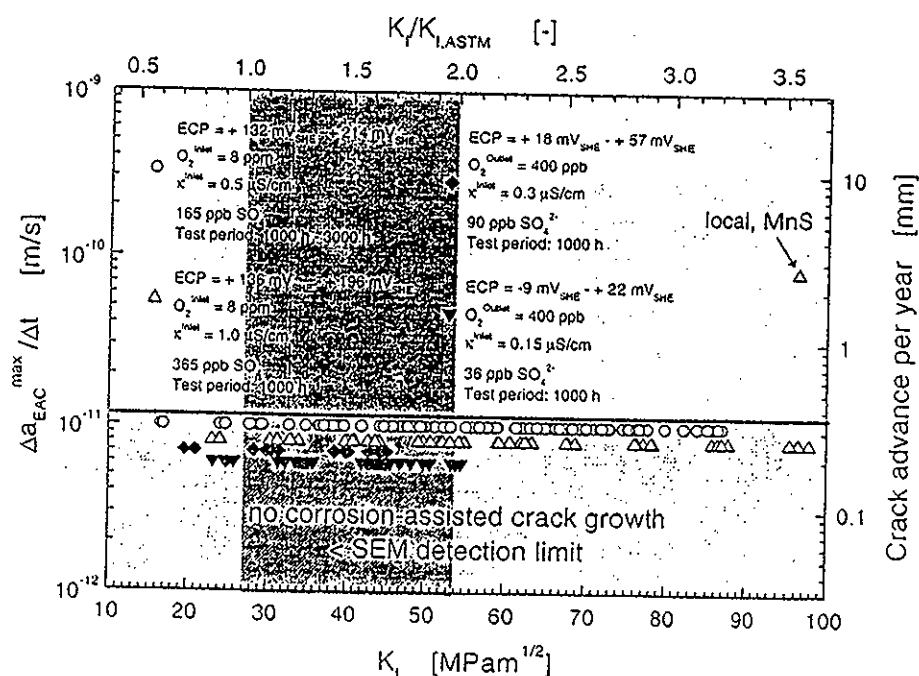
- 20 MnMoNi 5.5 (0.004, 0.009, 0.010 wt.% S), SA 508 Cl.2 (0.004 wt.% S)
- SA 533 B Cl.1 (0.018 wt.% S) Orientation: TL, LT, TS, ST, LS, SL

Summary of Standard SCC Tests under Static Load

I	II	III
$K_I < K_{I,ASTM}$	$K_{I,ASTM} \leq K_I < 2 \cdot K_{I,ASTM}$	$K_I \geq 2 \cdot K_{I,ASTM}$
plane strain linear elastic	transition region	(gross) ligament yielding
transferable to RPV	?	not transferable to RPV
$\Delta a_{EAC}^{max} (1000 \text{ h}) < 30 \mu\text{m}$ < SEM detection limit	$\Delta a_{EAC}^{max} (1000 \text{ h}) < 1 \text{ mm}$ $\leq$ periodicity of microstructure	$\Delta a_{EAC}^{max} (1000 \text{ h}) \geq 1 \text{ mm}$ > periodicity of microstructure
< 300 $\mu\text{m}/\text{year}$	< 1 cm/year	$\geq 1 \text{ cm}/\text{year}$
no SCC	SCC limited in time	sustained SCC > test period of 1000 h

14.05.99/C:\eigene dateien\vortrag\cgc\cgc99\wol\csum

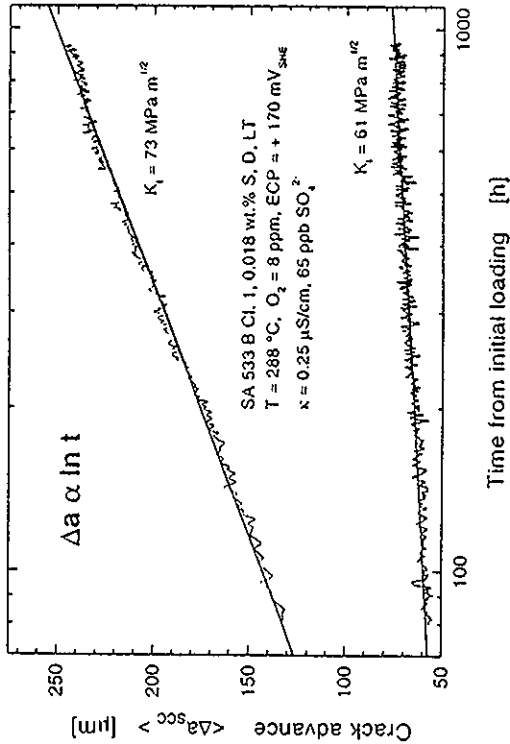
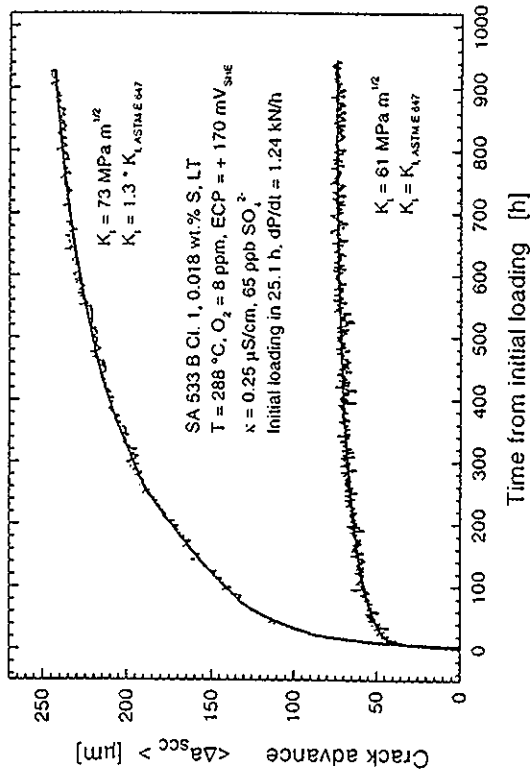
New Results of Tests under Constant Deformation (WOL DCB)



slow positive dynamic (plastic) straining is essential for SCC crack initiation

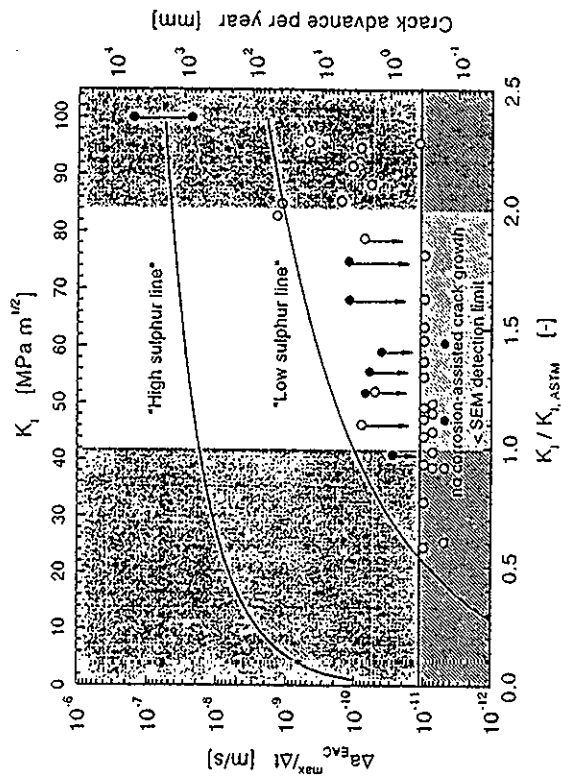
14.05.99/C:\eigene dateien\vortrag\cgc\cgc99\wol

Time-dependent SCC Crack Growth under Static Load



$\Delta a \propto \ln t$ → indication that SCC crack growth under static loading is controlled by the low temperature creep of the specimen

Results of Constant Load Tests



Standard tests under constant active external loading with 1T-CT specimens:

$T = 288\text{ }^{\circ}\text{C}$, $\kappa \leq 0.5\text{ }\mu\text{S/cm}$, $\leq 165\text{ ppb SO}_4^{2-}$

Open symbols: 200 - 400 ppb O_2

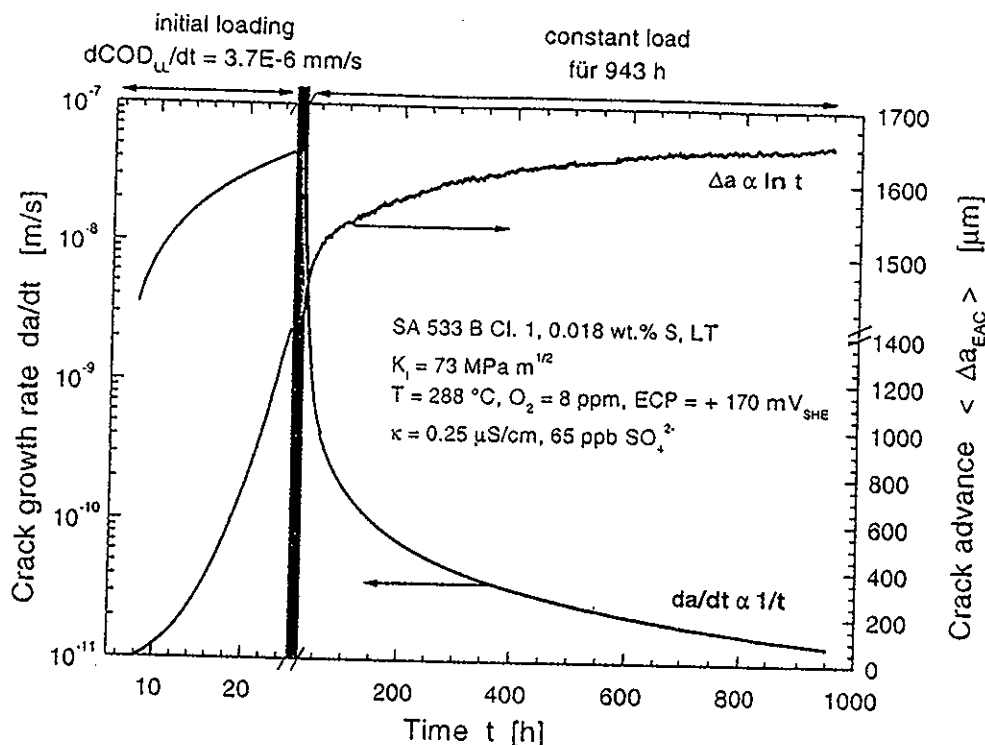
Solid symbols: 8 ppm O_2

Conditions:

	$K_{I,corr}$ [MPa m ^{1/2}]	$K_{I,LT}$ [MPa m ^{1/2}]	dCO_2/dt [mm/s]	dP/dt [kN/h]	dK/dt [MPa m ^{1/2} /h]	t_{max} [h]	t_c [h]	t_f [h]
Range	12 - 30	20 - 100	$3E-5 - 3E-4$	10 - 100	25 - 250	142 - 300	0.2 - 2	400 - 1100
Typical	12 - 18					168		1000

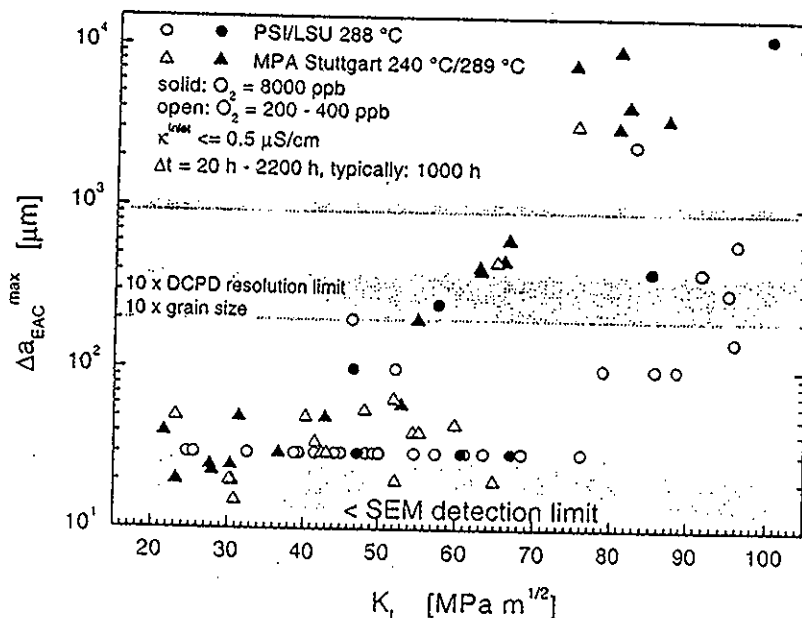
Alloy	Orientation	ECP [mV _{SHE}]	O_2 [ppb]	κ [μS/cm]	SO_4^{2-} [ppb]	T [°C]
B, D, E, F	TL, LT	-50 - +200	200 - 8000	0.06 - 0.5	1 - 165	288

EAC Crack Growth during Initial Dynamic and Subsequent Static Loading



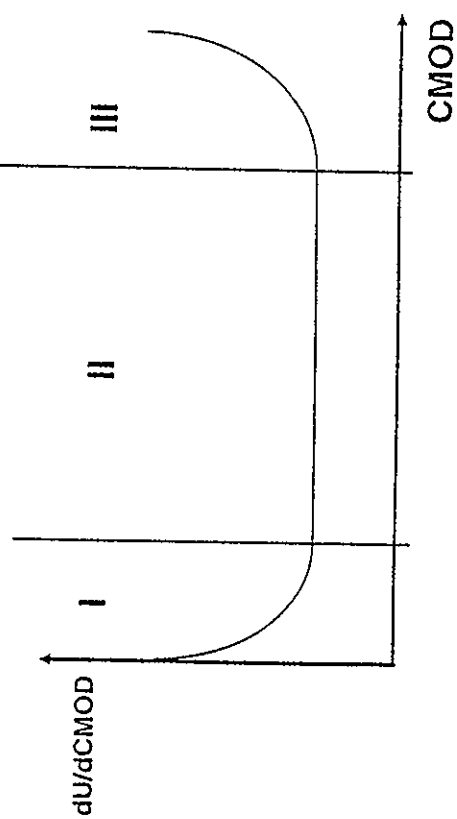
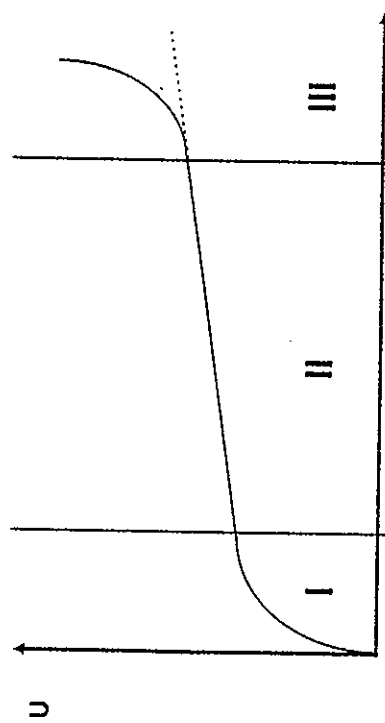
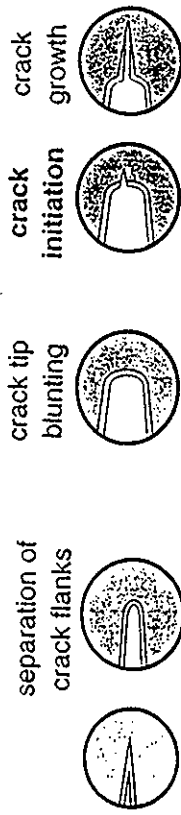
10.05.99/C:\eigene dateien\vortrag\log\log99\dadt\dynstat

Corrosion-Assisted Crack Advance in Constant Load Tests



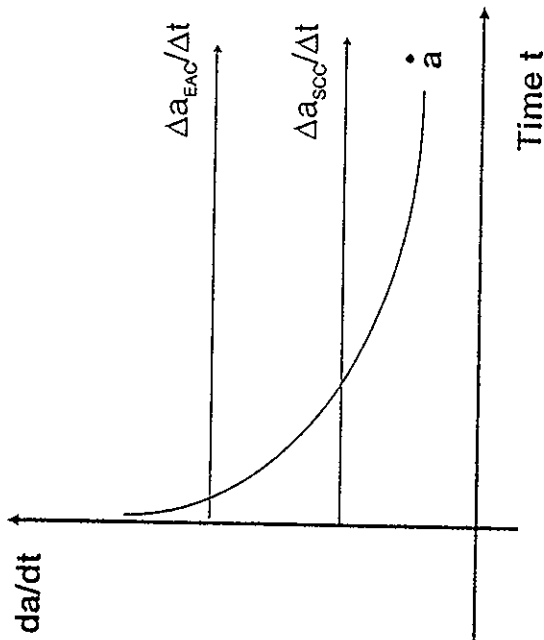
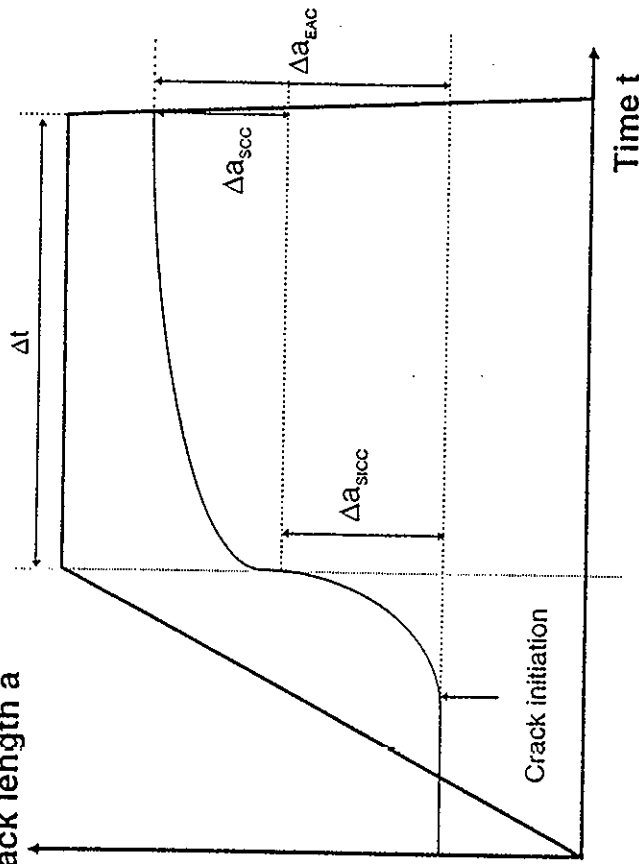
11.05.99/C:\eigene dateien\vortrag\log\log99\visfortschritt

Determination of the Crack Initiation Point by DCPD in Slow Rising Displacement/Load Tests

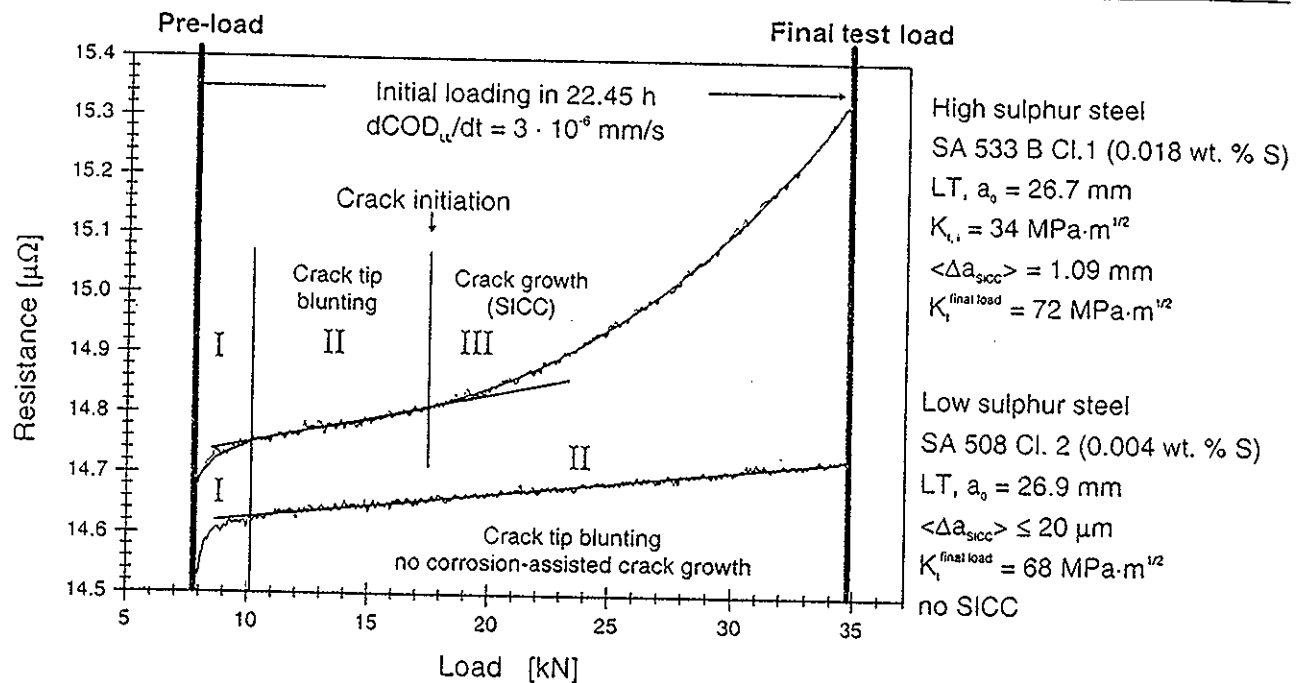


Load P

Crack length a



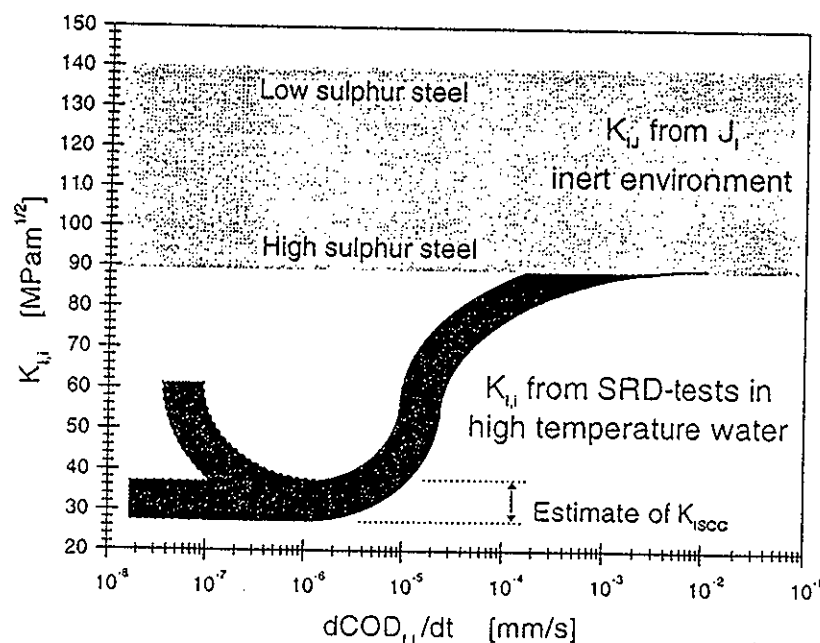
Effect of Sulphur Content on Crack Initiation and Growth



$T = 288$ °C, $O_2 = 8$ ppm, $ECP = +150$ mV_{SHE}, $\kappa = 0.25$ μS/cm, 65 ppb SO_4^{2-}
 quasi-stagnant conditions (3 autoclave exchange per hour)

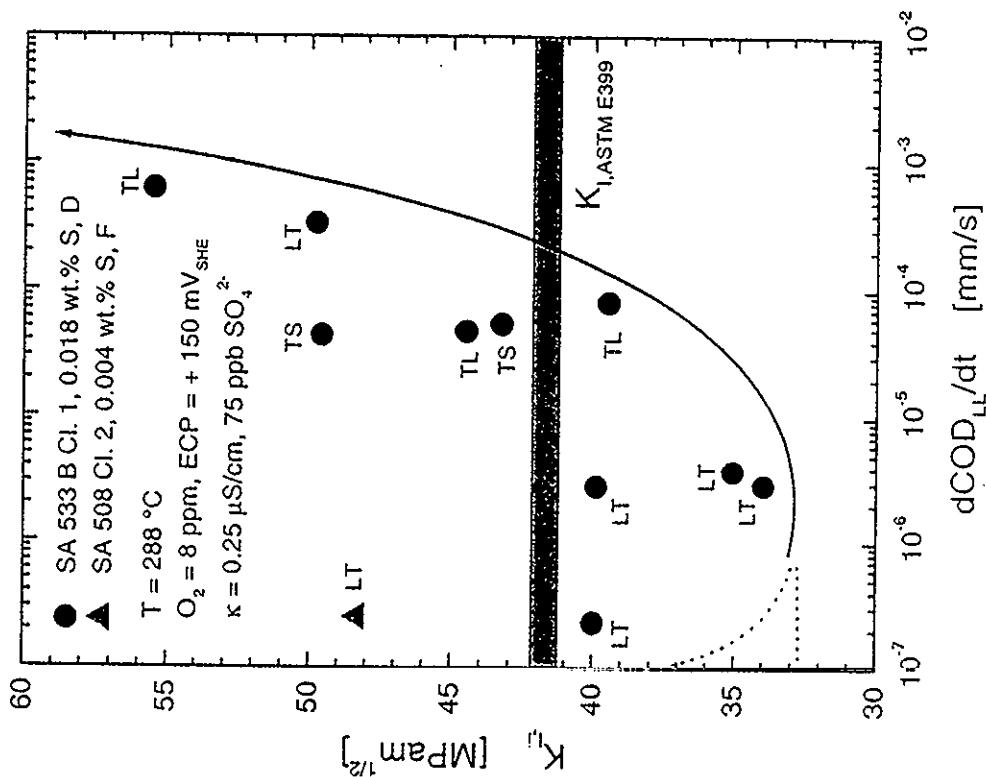
10.05.99/C:\eigene dateien\vortrag\hsk\hsk98\lowsthighs

Effect of Loading Rate on Crack Initiation

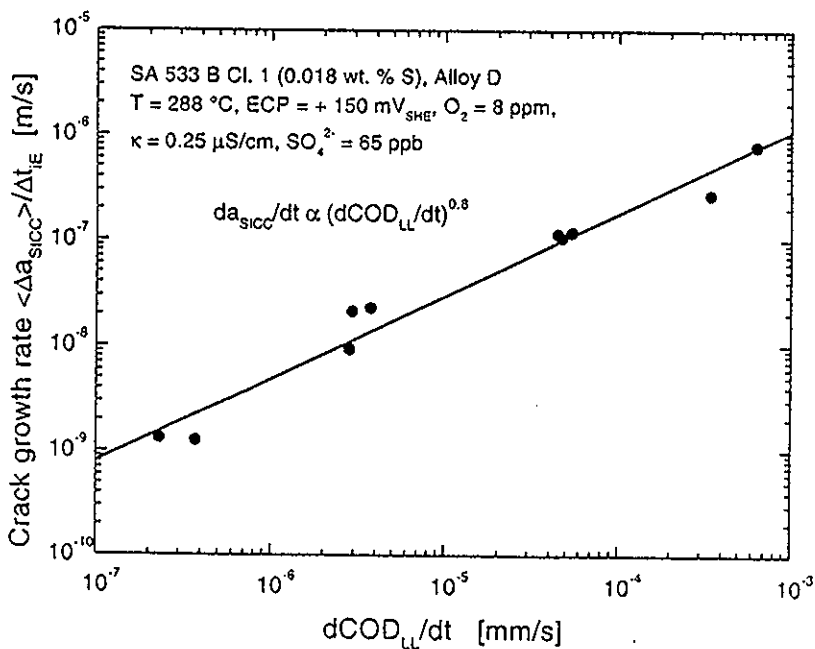


10.05.99/C:\eigene dateien\vortrag\hsk\hsk98\lowsthighs

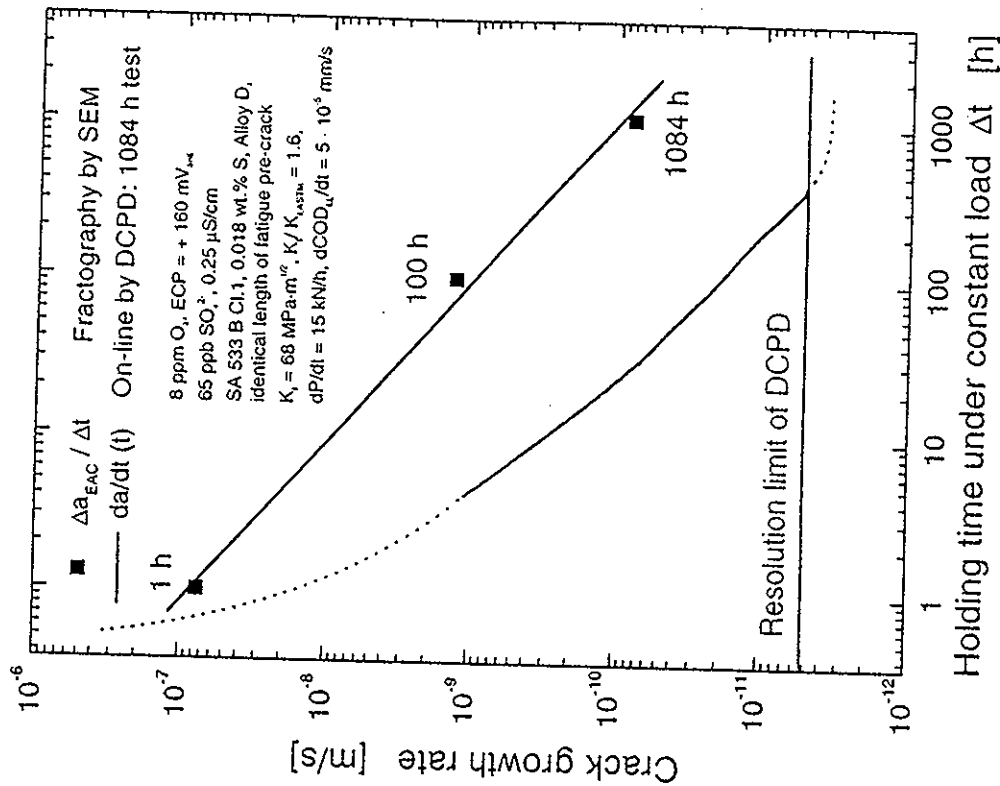
Effect of Loading Rate on SLCC Initiation



Effect of Loading Rate on SICC Crack Growth Rate



Effect of Test Duration and of Crack Length Evaluation Method



- 3 individual tests under identical loading/environment/material conditions with different holding periods Δt under constant load of 1 h, 100 h, 1084 h
- Crack arrest ($< 6 \text{ E-12 m/s}$) in the long term test (1084 h) after $\approx 400 \text{ h}$

K_I [MPa·m ^{1/2}]	Region	Corrosion-assisted crack growth				
		Initial loading	Subsequent static loading	$\Delta a_{EAC}^{tot} / \Delta t$ $\Delta t = 1000 \text{ h}$ [m/s]	$\Delta a_{SCC}^{SL} / \Delta t$ $\Delta t = 1000 \text{ h}$ [m/s]	$da/dt_{DCPD}(t)$ $t = 1000 \text{ h}$ [m/s]
$K_I < 30$	SSY	no	no	$< 10^{-11}$	$< 10^{-11}$	$< 10^{-11}$
$30 \leq K_I < 60$	$< \text{ASTM E647} \approx \text{SSY}$	yes	strictly limited in time $\approx 10^1 \text{ h}$ $\sim 10^2 \text{ h}$	$< 10^{-10}$	$< 2 \cdot 10^{-11}$	$< 10^{-11}$
$60 \leq K_I < 80$	transition region	yes	limited in time $\approx 10^2 \text{ h} \sim 10^3 \text{ h}$	$< 10^{-9}$	$< 10^{-10}$	$< 3 \cdot 10^{-11}$
$K_I \geq 80$	ligament yielding	yes	sustained $> 10^3 \text{ h}, > \text{test period}$	$> 3 \cdot 10^{-10}$ $< 10^{-7}$	$> 3 \cdot 10^{-10}$ $< 10^{-7}$	$> 3 \cdot 10^{-10}$ $< 10^{-7}$

Alloy	Δt_{SL} [h]	$dCOD_u/dt$ [mm/s]	dP/dt [kN/h]	T [°C]	κ [μS/cm]	SO_4^{2-} [ppb]	ECP [mV _{SWE}]	O ₂ [ppm]
A to F	0 to 1000	$2 \cdot 10^{-7}$ to $8 \cdot 10^{-4}$	0.1 to 160	288	0.06 to 0.25	1 to 75	-50 to +200	0.2 to 8

SCC Tests under Active External Loading

Initial loading:

- Crack initiation and growth by SICC during initial loading within the test environment (between 80 and 100 % of the total crack advance).
- If crack initiation did not occur during or directly after initial loading, no SCC was observed so far under subsequent static load. Incubation periods > 1000 h cannot be excluded.
- Both SICC initiation and growth during initial loading are dependent on the loading rate:

$$\Delta a_{EAC} = \Delta a_{SICC} \text{ (initial loading)} + \Delta a_{SCC} \text{ (static load)}$$

$$\Delta a_{EAC} > \Delta a_{SCC}$$

$$K_{II} = f(\dot{C}OD) \quad \text{Minimum at } 10^{-6} \text{ mm/s or saturation below } 10^{-6} \text{ mm/s?}$$

$$\dot{a}_{SICC} = f(\dot{C}OD) \quad \dot{a}_{SICC} = A \cdot \dot{C}OD^n$$

12.05.99/C:\eigene dateien\vortrag\rskk198\aktiv1 eng

SCC Tests under Active External Loading

Subsequent static load:

- no stable, stationary corrosion-assisted crack growth $\dot{a}_{SCC} = f(t)$
- If further crack growth (> detection limit) under constant load was detected, the rate of crack advance continuously decayed during the test and often fell below the DCPD detection limit during long-term tests („crack arrest“).

$$t \uparrow \rightarrow \dot{a}_{SCC} \downarrow \quad \Delta a_{EAC} / \Delta t > \Delta a_{SCC} / \Delta t > \dot{a}_{SCC}$$

$$\dot{a}_{SCC} = f(\text{initial loading rate, test period } \Delta t, \text{ crack length measurement method, ...})$$

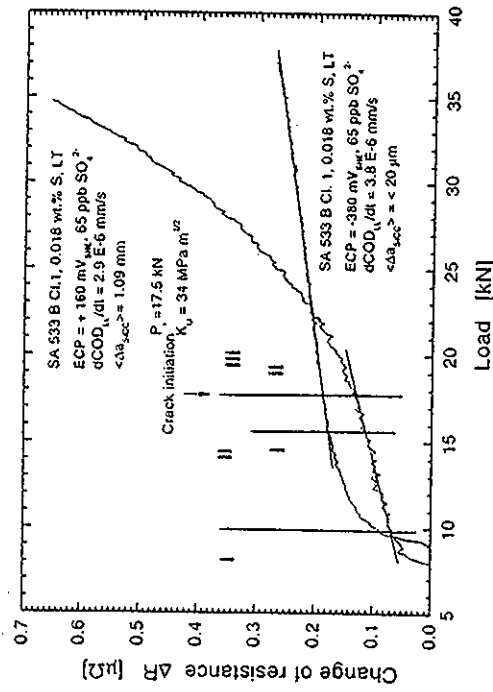
$$\Delta a_{SCC} \approx \infty \ln t \quad \dot{a}_{SCC} \approx \infty t^{-1} \quad \leftarrow \text{low temperature creep}$$

- If crack arrest had occurred, crack growth could be re-initiated by a small load increase or by a partial unloading/loading cycle.

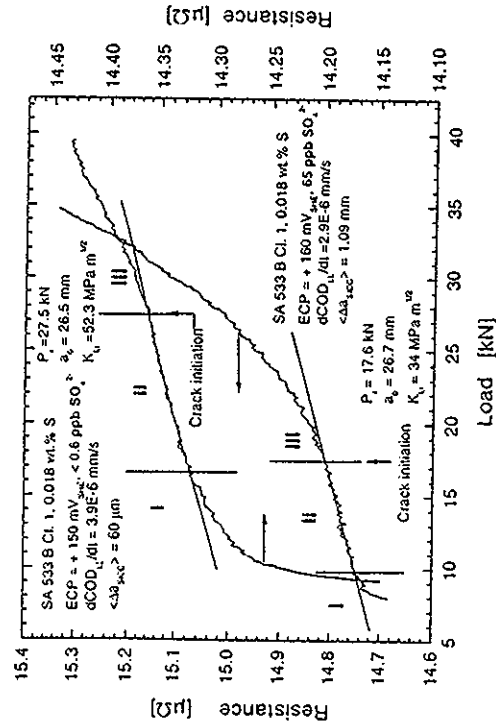
→ superimposed small dynamic or cyclic load changes
can have a distinct effect on crack growth

12.05.99/C:\eigene dateien\vortrag\rskk198\aktiv2

Effect of Environmental Parameters on SICC

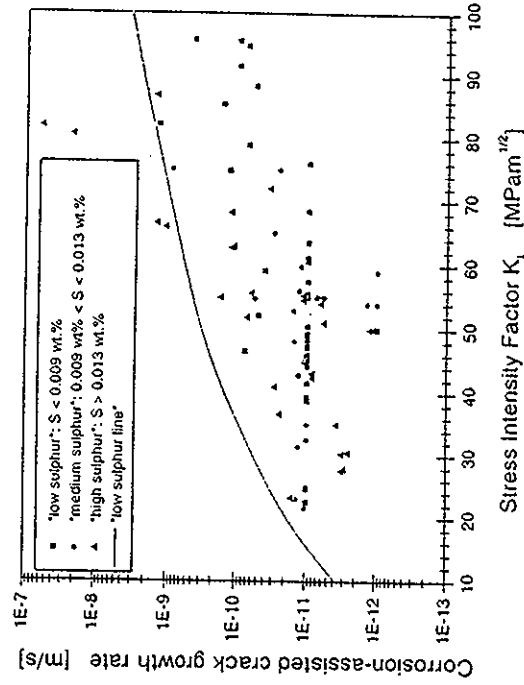
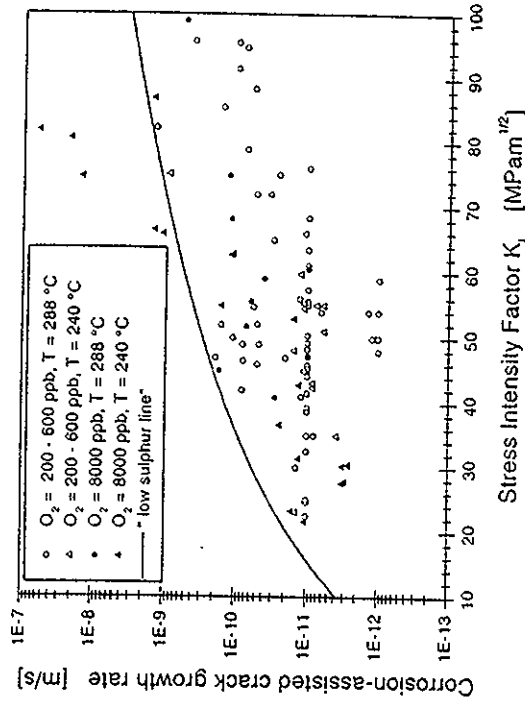


8 ppm O_2 , + 160 mV_{SHE} vs. < 5 ppb O_2 , -380 mV_{SHE}
65 ppb SO_4^{2-} , 0.25 $\mu S/cm$



< 0.6 ppb SO_4^{2-} , < 0.06 $\mu S/cm$ vs. 65 ppb SO_4^{2-} , 0.25 $\mu S/cm$
ECP = + 150 mV_{SHE}

Effect of Environmental and Material Parameters on SCC

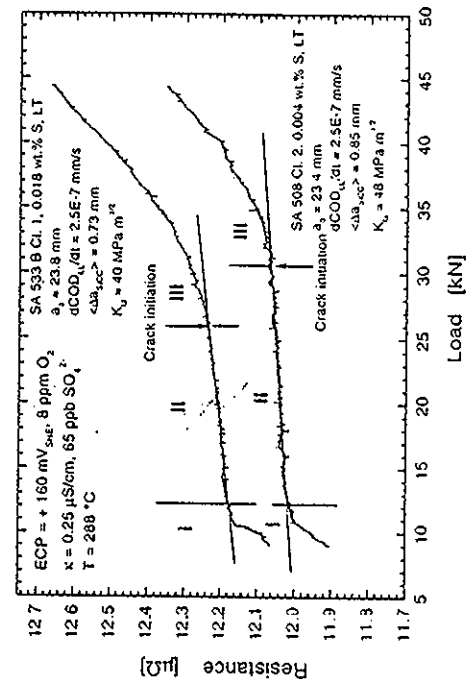
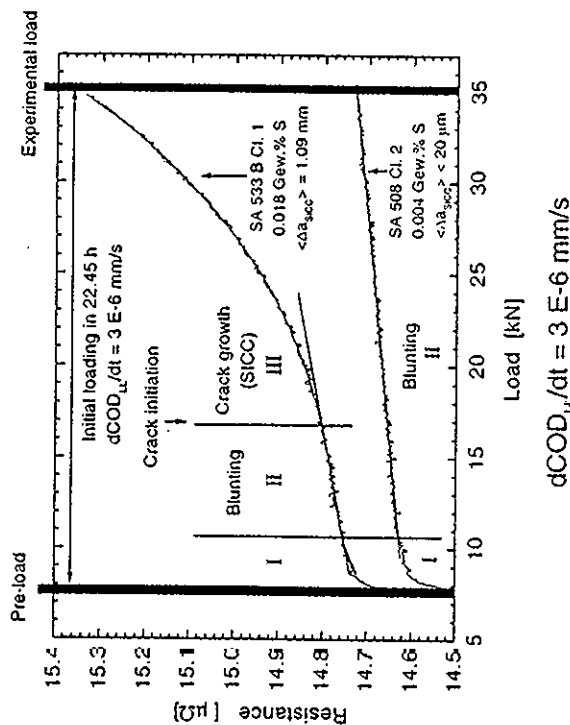


Source of literature data:

MPA Stuttgart, Siemens KWU: D. Blind: „Zur Korrosionsrissbildung in druckführenden Kraftwerkskomponenten infolge Einwirkung von Hochtemperaturwasser“, Habilitationsschrift, 18. 6. 91.

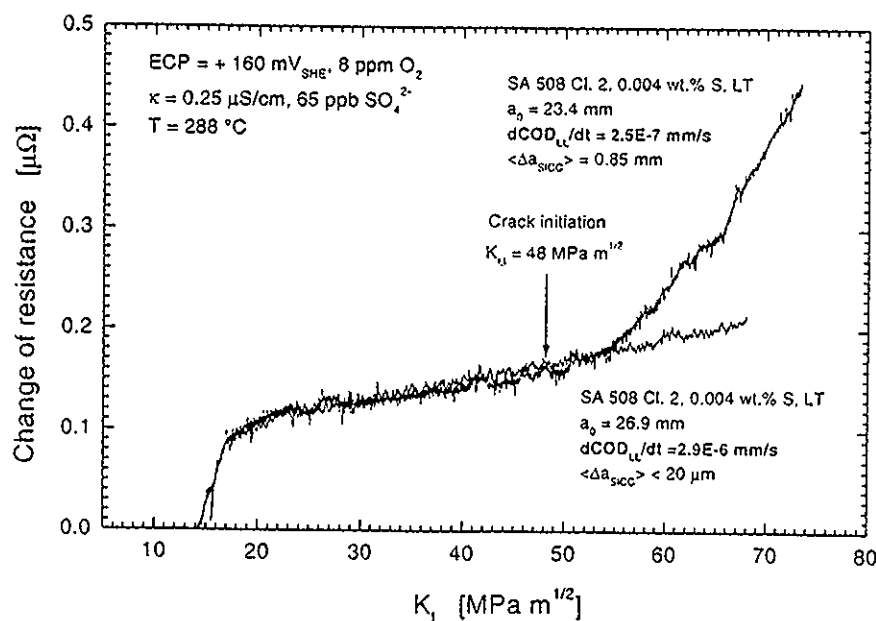
Effect of Sulphur Content on SICC

low sulphur steel 0.004 wt.% S vs. high sulphur steel 0.018 wt.% S



$dCOD_L/dt = 2.5 E-7$ mm/s

Effect of Loading Rate on SICC Initiation



$dCOD_L/dt = 2.9 E-6$ mm/s vs. $dCOD_L/dt = 2.5 E-7$ mm/s

Effect of Material Parameters

- No systematic investigations on the effect of microstructure
- Similar behaviour of low carbon and different low alloy steels

A106 $\approx$ A 333-6 $\approx$ SA 508 Cl.2 $\approx$ SA 533 B Cl.1 $\approx$ 20 MnMoNi 5 5 $\approx$ 22 Ni MoCr 3 7

ferritic-pearlitic $\approx$ bainitic

as long as S-content and yield strength is comparable

- Main material parameter affecting EAC susceptibility:

S-content, size, shape, orientation and spatial distribution of MnS-inclusions
anisotropy, segregation $\rightarrow$ specimen orientation/location in plate/forging

- Possible relevant effect of yield strength R_p if $R_p > 800$ MPa
 $\rightarrow$ Hydrogen-assisted SCC
Hardness > 350 HV
 $\rightarrow$ weld heat affected zones

- Possible effect of Dynamic Strain Ageing (DSA)

$\rightarrow$ interaction between free interstitials as C, N, (H) with dislocations $\rightarrow$ free C, N-content
variations of free N,C-content respectively DSA response
= f(heat treatment, welding technique, steel making process,)

11.05.99/C:\eigene dateien\vortrag\hsk\hsk98\material1

Effect of Sulphur Content

- Stress Corrosion Cracking:

static loading, small scale yielding, water chemistry $\approx$ BWR/NWC reactor water:

$\rightarrow$ almost no susceptibility to SCC under these conditions

therefore no distinct effect of S-content on crack initiation and growth

- Strain-induced Corrosion Cracking

slow dynamic loading (SRD, vLCF), initial loading and ligament yielding in CL tests:

- distinct effect of S-content on both crack initiation and on crack growth rate
(strongly dependent on loading rate)

- different appearance of fracture surface (strongly dependent on loading rate):

Shape of corrosion-assisted crack growth:

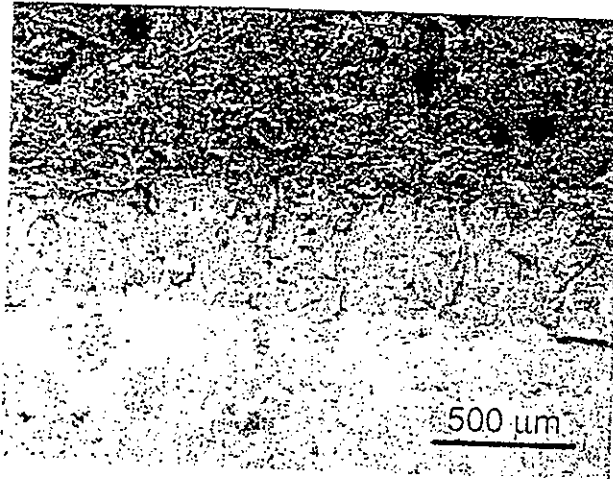
local, MnS (low sulphur steel) vs. uniform, even (high sulphur steel)

$\Delta a^{\max}$ (low sulphur steel) $\leq$ $\Delta a^{\max}$ (high sulphur steel)

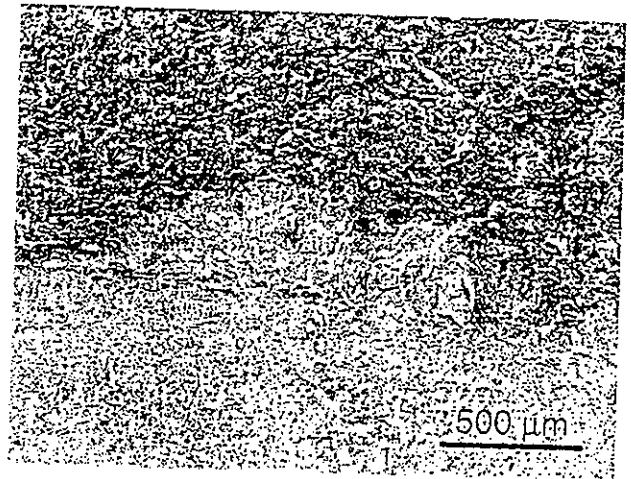
$\langle \Delta a \rangle$ (low sulphur steel) $\ll$ $\langle \Delta a \rangle$ (high sulphur steel)

14.05.99/C:\eigene dateien\vortrag\hsk\hsk98\material2

Shape of crack front



High sulphur (0.018 wt.%) steel
SA 533 B Cl.1 (alloy D)



Low sulphur steel (0.004 wt.%)
20 MnMoNi 5 5 (alloy B)

Summary I

- **Passive loading (WOL DCB):**

- No SCC was observed even under aggressive environmental conditions
→ slow positive dynamic (plastic) strain rate is essential for crack initiation

- **Active loading (SRD +/- or CL with 1T-CT) + ≈ BWR WC conditions:**

- $K_{ISCC} \approx 30 \text{ MPa} \cdot \text{m}^{1/2}$
- $30 \text{ MPa} \cdot \text{m}^{1/2} \leq K_I < 60 \text{ MPa} \cdot \text{m}^{1/2}$
 - crack arrest within 1000 h tests
 - $\Delta a_{SCC} / \Delta t \leq 2 \cdot 10^{-11} \text{ m/s}$ (600 μm/a)
 - $\Delta a_{EAC} / \Delta t < \text{"Low Sulphur Line"}$
- Fast SICC crack growth 10^{-8} m/s to 10^{-7} m/s ($\approx \dot{a}_p, \geq \dot{a}_{crit}; \Delta a_{SICC} \gg \text{grain size}$) during dynamic loading could not be maintained under subsequent static load and crack arrest occurred if SSY conditions were prevailing in the remaining ligament.
- $\Delta a_{SCC} / \Delta t = f$ (initial loading rate, test duration, crack length determination method,...)
→ up to 3 - 4 orders of magnitude in crack growth rate can be produced!

Summary II

- Within certain limits, neither environmental nor material parameter have a distinct effect on SCC crack growth under static load as long as SSY conditions are prevailing.
- Within certain limits, both SICC initiation and growth are dependent on
 - Bulk-Sulfate concentration SO_4^{2-}
 - ECP
 - Steel sulphur content
 - Crack tip strain rate respectively loading rate $\dot{K}_I$, $\dot{P}$, $\dot{\text{COD}}_{\text{LL}}$

1. a high sulphur anion activity in the crack tip electrolyte



2. a slow positive dynamic (plastic) crack tip strain rate

have to be maintained simultaneously
for a high degree of cracking!

- high ECP
- high Bulk- SO_4^{2-} concentration
- high S-content of steel
- long pre-existing crack
- quasi-stagnant conditions

- dynamic external loading
- high net section stress/
(gross) ligament yielding
- (- aggressive water chemistry)

14.05.99/C:\elgene dateien\vortrag\veg99\summary2

Corrosion-assisted crack growth

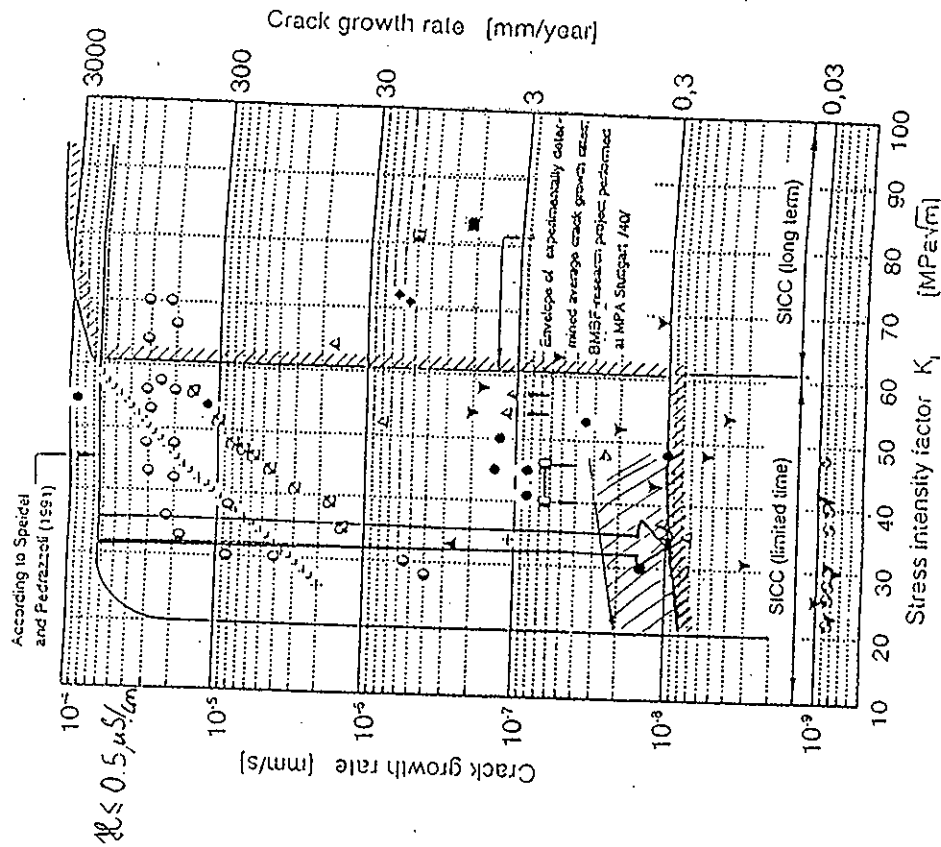
K_I [MPa·m ^{1/2}]	Region	Initial loading	Subsequent static loading	$\frac{\Delta a_{\text{EAC}}^{\text{tot}}}{\Delta t}$ $\Delta t = 1000 \text{ h}$ [m/s]	$\frac{\Delta a_{\text{SCC}}^{\text{SL}}}{\Delta t}$ $\Delta t = 1000 \text{ h}$ [m/s]	$\frac{da}{dt}_{\text{DCPD}}(t)$ $t = 1000 \text{ h}$ [m/s]
$K_I < 30$	SSY	no	no	$< 10^{-11}$	$< 10^{-11}$	$< 10^{-11}$
$30 \leq K_I < 60$	< ASTM E647 ≈ SSY	yes	strictly limited in time $\approx 10^1 \text{ h}$ - $\approx 10^2 \text{ h}$	$< 10^{-10}$	$< 2 \cdot 10^{-11}$	$< 10^{-11}$
$60 \leq K_I < 80$	transition region	yes	limited in time $\approx 10^2 \text{ h} - \approx 10^3 \text{ h}$	$< 10^{-9}$	$< 10^{-10}$	$< 3 \cdot 10^{-11}$
$K_I \geq 80$	ligament yielding	yes	sustained $> 10^3 \text{ h}, > \text{test period}$	$> 3 \cdot 10^{-10}$ $< 10^{-7}$	$> 3 \cdot 10^{-10}$ $< 10^{-7}$	$> 3 \cdot 10^{-10}$ $< 10^{-7}$

Alloy	Δt_{SL} [h]	$d\text{COD}_{\text{LL}}/dt$ [mm/s]	dP/dt [kN/h]	T [°C]	κ [μS/cm]	SO_4^{2-} [ppb]	ECP [mV _{SWE}]	O ₂ [ppm]
A to F	0 to 1000	$2 \cdot 10^{-7}$ to $8 \cdot 10^{-4}$	0.1 to 160	288	0.06 to 0.25	1 to 75	-50 to +200	0.2 to 8

14.05.99/C:\elgene dateien\vortrag\veg99\aktivzus

CGR Literature Data (up to 1995)

Low alloy steels in oxygenated high temperature water:



1. Loop experiments

2. Qualified experimental procedure and technique

3. Well characterised and documented experiments (→ assessable)

4. Large number of tested specimens

5. Consistent with MPA results

Conclusions

- The LAS investigated are **not susceptible to SCC crack growth** under **static loading** and **small scale yielding** conditions as long as **water chemistry** is maintained **within current BWR/NWC operation practice** to some extent.
- Sustained, fast SCC with respect to operational time scales cannot be excluded in specimens with a **high degree of plasticity** in the remaining ligament **and/or** at **elevated potentials** in hot water of **high conductivity** ($\geq 1.0 \mu\text{S/cm}$ as Na_2SO_4 at $\text{ECP} \geq 100 \text{ mV}_{\text{SHE}}$, $\geq$ EPRI action level 3).
- In comparison to the observed low susceptibility to SCC crack growth, crack advances and growth rates due to **SICC** under conditions of **slow, positive dynamic (plastic) straining** can be very high for critical combination of relevant system parameters (ECP , SO_4^{2-} , S-content of steel, ...).
- The results of this study correspond well with the operating experience of LAS pressure boundary components. Relevant dynamic straining (thermal stratification, start-up/shut-down, etc.) and oxidising agents (usually oxygen itself) were always involved in the few cases of service cracking. They could be attributed either to **SICC** or low cycle corrosion fatigue.