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Literature Survey on the Stress Corrosion Cracking of Low-Alloy Steels in High-Temperature Water

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Abstract

The present report is a summary of a literature survey on the stress corrosion cracking (SCC) behaviour/ mechanisms in low-alloy steels (LAS) in high-temperature water with special emphasis to primary-pressure-boundary components of boiling water reactors (BWR). A brief overview on the current state of knowledge concerning SCC of low-alloy reactor pressure vessel and piping steels under BWR conditions is given. After a short introduction on general aspects of SCC, the main influence parameter and available quantitative literature data concerning SCC of LAS in high-temperature water are discussed on a phenomenological basis followed by a summary of the most popular SCC models for this corrosion system. The BWR operating experience and service cracking incidents are discussed with respect to the existing laboratory data and background knowledge. Finally, the most important open questions and topics for further experimental investigations are outlined.

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0. Abbreviations

ASME	American Society of Mechanical Engineers
ASME BPV	ASME Boiler and Pressure Vessel Code
ASTM	American Society of Testing and Materials
ASTM E 399	Test Method for Plane-Strain Fracture Toughness of Metallic Materials
BWR	Boiling Water Reactor
BWR VIP	Boiling Water Reactor Vessel and Internals Project
C(T)	Compact Tension Specimen
CERT	Constant Extension Rate Test
CF	Corrosion Fatigue
CGR	Crack Growth Rate
COD_{LL}	Crack Opening Displacement at Load Line
DCPD	Direct Current Potential Drop Method
DO	Dissolved Oxygen
DSA	Dynamic Strain Ageing
EAC	Environmentally-Assisted Cracking
ECP	Electrochemical Corrosion Potential
EPFM	Elastic-Plastic Fracture Mechanics
EPRI	Electric Power Research Institute
FRAD	Film Rupture/Anodic Dissolution Mechanism
FW	Feed Water
GE	General Electric
HAEAC	Hydrogen-Assisted EAC Mechanism
HAZ	Heat-Affected Zone
HSK	Hauptabteilung für die Sicherheit der Kernanlagen
HWC	Hydrogen Water Chemistry
ICG-EAC	International Co-operative Group of Environmentally-Assisted Cracking of LWR Materials
IGSCC	Intergranular SCC
K_{ISCC}	K_I-Threshold for SCC
KTA	Kerntechnischer Ausschuss, Germany
LAS	Low-Alloy Steel
LCF	Low-Cycle Fatigue

LEFM	Linear-Elastic Fracture Mechanics
LFCF	Low-Frequency Corrosion Fatigue
LWR	Light Water Reactor
LWV	Labor für Werkstoffverhalten
MPA	Staatliche Materialprüfungsanstalt, University of Stuttgart, Germany
NDT	Non-Destructive Testing
NRC	National Regulatory Commission, USA
NWC	Normal Water Chemistry
PEER	Panel of Experts for Evaluation and Review
PWHT	Post-Weld Heat Treatment
PWR	Pressurized Water Reactor
QA	Quality Assurance
RPV	Reactor Pressure Vessel
SCC	Stress Corrosion Cracking
SEM	Scanning Electron Microscopy
SHE	Standard-Hydrogen-Electrode
SICC	Strain-Induced Corrosion Cracking
SRL	Slow Rising Load Test
SS	Stainless Steel
SSRT	Slow Strain Rate Test
SSY	Small Scale Yielding
TGSCC	Transgranular SCC
UTS	Ultimate Tensile Strength
VGB	Technische Vereinigung der Grosskraftwerksbetreiber, Deutschland
YS	Yield Strength

1. Introduction

The reactor pressure vessel (RPV) of both boiling water (BWR) and pressurized water reactors (PWR) is the most critical pressure-boundary component as far as safety and plant life are concerned [1.1, 1.2]. The high standards of safety and reliability on this pressure-boundary component in light water rectors (LWR) require that all potential relevant ageing and degradation mechanism affecting structural integrity are sufficiently understood so that even low probability failures can be ruled out by adequate (counter)measures. RPV structural integrity continues therefore to be a key concern within the context of both reactor safety and evaluation/extension of plant service life.

In the past, RPV ageing and degradation have been mainly discussed with respect to irradiation embrittlement and to thermal/mechanical fatigue. Both ageing mechanism have already been anticipated during the design phase and have been implemented to the nuclear codes and regulations (ASME BPV, KTA). They are controlled by suitable surveillance programmes and fatigue evaluation procedures. On the other hand, the possible effect of corrosion phenomena on RPV structural integrity has been ignored for many years. Environmental effects have therefore not been directly addressed in the guidelines for assessing both the initiation of fatigue cracks and the fatigue crack growth behaviour in the relevant nuclear codes (ASME III, XI). Early laboratory investigations clearly demonstrated that environmentally-assisted cracking (EAC) might occur in RPV steels in high-temperature water under certain critical system conditions. Based on these investigations the question on conservatism and adequacy of the relevant nuclear codes was arising and has resulted in intensive experimental and theoretical investigations on EAC during the last two decades.

Notwithstanding the absence of stress corrosion cracking (SCC) in the field, SCC has been observed in laboratory tests under simulated BWR conditions with crack growth rates ranging from 30 μm/year to 3 m/year even under nominally similar testing conditions. The SCC behaviour of low-alloy RPV steels in oxygenated high-temperature water and its possible relevance to BWR power operation has therefore been a subject of controversial discussions. There seemed to be a crucial discrepancy between the existing laboratory SCC crack growth data base and the excellent operating experience. With regard to the current BWR operating practice, it was not evident if an unacceptably high risk or potential for sustained growth of cracks in reactor pressure vessel steels by SCC actually existed or not. A large experimental and theoretical research programme on SCC of low-alloy RPV steels under BWR conditions was therefore initiated at PSI (SpRK II, 1996 – 1999). The working programme of this research project included:

- a literature survey on SCC of low-alloy RPV steels (this report).
- an experimental parameter study to characterise the SCC susceptibility of low-alloy RPV steels under BWR conditions [1.1, 1.2].
- the participation in an European Round Robin test programme [1.3, 1.4].
- a survey and assessment of SCC mechanism and models for low-alloy steels in high-temperature water and the development of a quantitative SCC model [1.5, 1.6].

1.1 Report outline

The present report is a summary of the literature survey on the SCC of low-alloy steels in high-temperature water performed at the beginning of this research programme. The survey roughly reflects the state-of-the art until the end of 1998 but also includes the results of some selected, newer papers on that topic. The report is divided into six individual sections:

After a short introduction on general aspects of SCC in metals (**Section 2**), the main influence parameters and available quantitative literature data concerning SCC of LAS in high-temperature water are discussed on a phenomenological basis (**Section 3**). In **Section 4**, a summary on the most popular SCC models for this corrosion system is given. The important role of crack-tip strain-rate and crack-tip sulphur-anion activity for SCC in LAS is outlined. The BWR operating experience and service cracking incidents are discussed with respect to the existing laboratory data and the mechanistical background knowledge (**Section 5**). The most important open questions and possible topics for future work are outlined in **Section 6** followed by an extended summary of the literature survey (**Section 7**).

1.2 References

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[1.2] **H.P. Seifert, J. Heldt, U. Ineichen, U. Tschanz,** „Spannungsrisskorrosion von Stählen für Reaktorkomponenten in Heisswasser", BFE-Final Report, February 2000, 41 p.

[1.3] **A. Wünsche, D. Blind, F. Hüttner (MPA Stuttgart), K. Küster (HEW), P. Karjalainen-Roikonen, U. Ehrnstén (VTT), A. Roth (Siemens KWU), H.P. Seifert, J. Heldt (PSI),** „European round robin test on EAC of LAS under BWR conditions", Final Report, MPA Stuttgart, March 2000.

[1.4] **A. Wünsche, D. Blind, F. Hüttner (MPA Stuttgart), K. Küster (HEW), P. Karjalainen-Roikonen, U. Ehrnstén (VTT), A. Roth (Siemens KWU), H.P. Seifert, J. Heldt (PSI),** „European round robin test on EAC of LAS under BWR conditions", Proc. 9th Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, ANS/NACE/TMS, 1. - 5. August 1999, Newport Beach, CA, USA, Eds: S. Bruemmer, P. Ford, G. Was, pp. 911 - 919.

[1.5] **B. Tirbonod,** „Modelling of the stress corrosion cracking behaviour for low-alloy steels in high-temperature water ", PSI-Report Nr. 00-08, November 2000, ISSN 1019-0643.

[1.6] **B. Tirbonod,** „Stress corrosion cracking behaviour of low-alloy steels in high-temperature water: description and results from modelling", PSI Annual Scientific Report 2000, Volume IV, Nuclear Energy and Safety, ISSN 1423-7334, March 2001, pp. 105 – 114.

2. General Aspects of Stress Corrosion Cracking

2.1 Environmentally-Assisted Cracking

EAC is an important environmental degradation mechanism, which covers both the **initiation** and **sub-critical growth** of cracks under the simultaneous and synergistic interaction of mechanical stress and a „chemically active" environment.

2.1.1 Types of EAC

On the basis of the applied, external, mechanical load, three different types of EAC can be differentiated (Table 1).

	EAC		
Mechanism	**SCC** Stress Corrosion Cracking	**SICC** Strain-Induced Corrosion Cracking	**CF** Corrosion Fatigue
Type of loading	**static**	slow monotonically rising or very low-cycle (vLCF)	**cyclic** low-cycle high-cycle
LWR operation condition	steady-state power operation	start-up/shut-down thermal stratification	thermal fatigue thermal stratification
Quantitative characterisation	BWR VIP 60 disposition lines	-	ASME III and XI

Table 1: Basic types of EAC. For the RPV, the basic EAC types can be assigned to different LWR operating conditions.

Almost every alloy/environment system is susceptible to CF, in contrast to SCC, which is very specific to certain combinations of alloy/environment/ material state ("critical conditions"). In SCC, the crack path can be either trans- or intergranular, whereas in CF, it is generally transgranular in nature. In contrast to CF, distinct limiting or threshold conditions concerning solution concentration, temperature and potential exist for SCC [1, 2].

2.1.2 Classical and Non-Classical SCC

SCC can be further classified by the crack propagation mechanism, crack path, etc. Because of its relevance for practical applications, the differentiation of SCC systems by their strain-rate dependence is further worked out here. In classical corrosion systems (type I SCC) SCC crack initiation (and subsequent growth) can occur if the strain-rate is virtually zero (or sometimes even negative). In non-classical systems (Type II SCC, strain-rate-sensitive SCC) SCC initiation only occurs, if a positive strain-rate $\dot{\varepsilon} > 0$ occurs (see Table 2 and Figure 1) [1, 2]. For both types, corrosion-assisted cracking only occurs, if the applied strain-rates are within a "critical range", limited by the upper ($\dot{\varepsilon}_1$) and lower ($\dot{\varepsilon}_2$) bound critical strain-rates (see Figure 1 and 2). At high strain-rates, mechanical processes leading to fracture occur faster than e.g. electrochemical reactions or corrosion-deformation interactions. Therefore mechanical fracture takes place without any relevant influence of the corrosive environment. At very low strain-rates, mechanical processes are not sufficiently effective to cause EAC in Type II SCC [1, 2].

The concept of Type I and Type II was originally applied for SCC tests with smooth tensile specimens, but it can be also transferred to notched or pre-cracked specimens or even to

components, if local stress/strain conditions at e.g. crack or notch-tip are considered. In particular, even under global static loading conditions sufficiently high positive crack-tip strain-rates can occur by low temperature creep processes. If $\dot{\varepsilon}_2$ at crack-tip is exceeded, a non-classical system may appear to be classical because there is SCC under global static loading. Otherwise, no SCC will occur if specimens were immersed to the test solution after cessation of low temperature creep process.

SCC types	Classical or Type I	Non-Classical or Type II
Straining	static straining	dynamic straining
Specimen	smooth	notched
$\sigma > \sigma_{crit}$	$\sigma_{crit} \approx$ constant	$\sigma_{crit} = f(\dot{\varepsilon})$
$\dot{\varepsilon} < \dot{\varepsilon}_1$	$\dot{\varepsilon}_2 \leq 0$	$\dot{\varepsilon}_2 > 0$
$\dot{\varepsilon} = 0$	SCC	no SCC

Table 2: Classical and non-classical SCC [1].

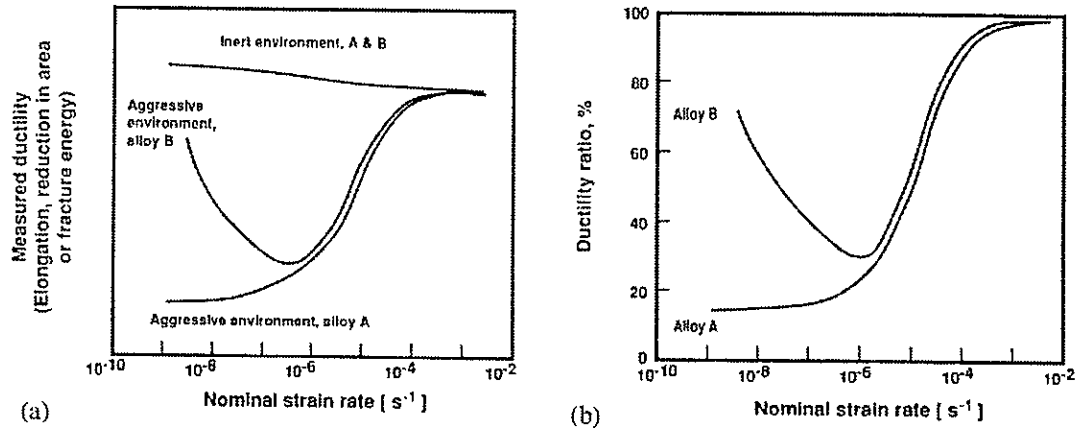


Figure 1: Classification of SCC systems by their strain-rate dependence [1]

The importance of strain-rate has implications not only for the evaluation of in-service parameters, but also for establishing the guidelines for laboratory testing (see Section 2.3). It is essential to know when critical strain-rates might occur during service, and how these conditions should be taken into account when performing laboratory SCC tests. Generally, both static and dynamic tests are necessary to characterize the SCC behaviour of a corrosion system.

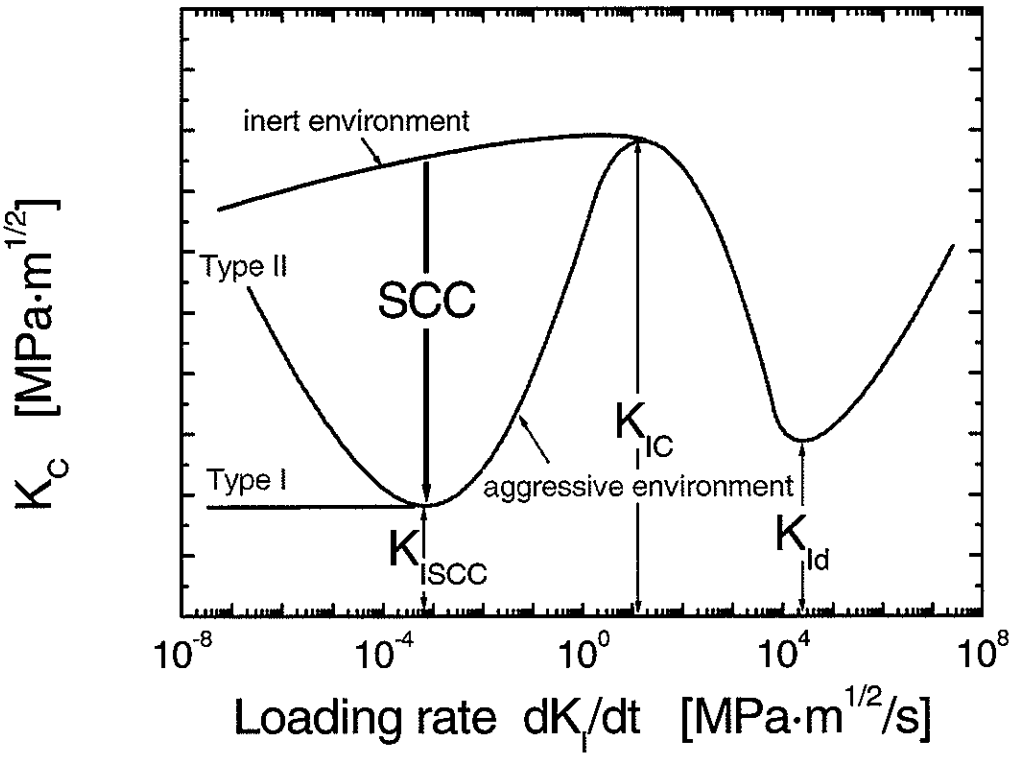


Figure 2: Classification of SCC systems by their dK_I/dt-dependence [3, 4].

2.2 Basic Aspects and Characteristic Features of SCC

SCC can be defined as the initiation and subcritical growth of cracks under the simultaneous synergistic interaction of approximately constant mechanical tensile stresses and a chemically active environment [3, 4]. In addition to this, the material often has to be in a susceptible microstructural state. There are always specific couples of alloy and environment establishing SCC under adequate mechanical loading conditions (Figure 3), while the stresses required to cause SCC may be rather small, usually below the macroscopic yield stress, and are tensile in nature [5].

Generally distinct environmental (temperature, solution concentration and potential) and loading (stress, strain-rate) limits and thresholds for the occurrence of SCC do exist. Such thresholds and limits are system parameters, in the sense that their values depend on each other and are generally only valuable in a limited range of the parameter space of the corrosion system.

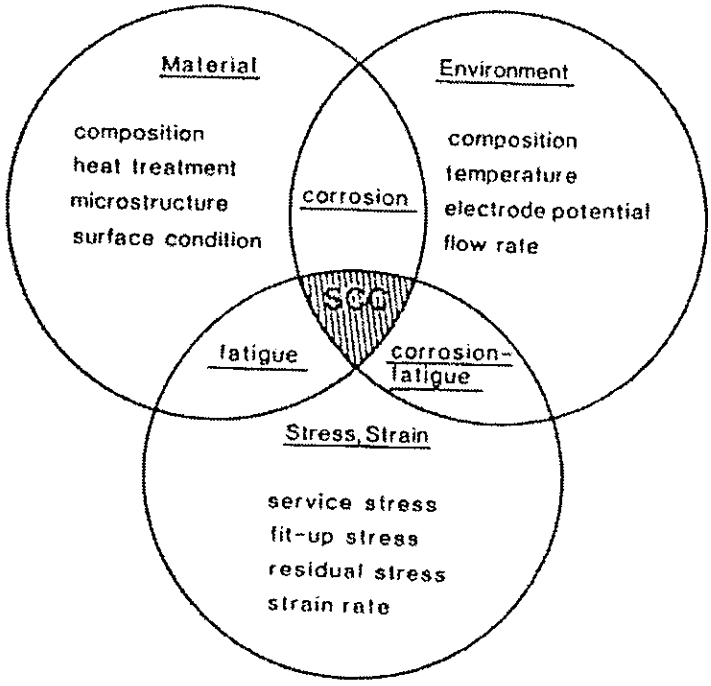


Figure 3: Major influential factors for SCC. Specific critical conditions must be simultaneously reached in each group for SCC to occur. Corrosion and corrosion-fatigue require specific values in only two groups [3, 4].

2.2.1 SCC Fracture Features

SCC cracks can initiate and propagate with little outside evidence of both, corrosion and mechanical deformation. The cracks frequently initiate at surface flaws that are either pre-existing or formed during service by corrosion, wear or other processes. Crack openings and deformation associated with crack propagation may be so small that cracks are virtually invisible except with special non-destructive examinations. Crack propagation can be either intergranular or transgranular. Often micro- or macrobranching of the crack path is observed [5].

2.2.2 Crack Initiation vs. Crack Growth

Classically, the stress corrosion life is divided into the period of "initiation" (sometimes furthermore divided into incubation and nucleation) and "propagation" of cracks. Consequently, remedies actions and test methods have also been categorised in terms of "avoiding initiation" or "slowing-down crack propagation" and "measuring initiation" or "measuring propagation" respectively. A differentiation between initiation and propagation is arbitrary, however, since the demarcation between the two periods will depend on both the sensitivity of crack propagation detection and the definition of the crack depth, which constitutes "initiation". Often crack initiation is defined from an engineering point of view by the NDT-detection limit or a characteristic length sufficiently long to enable description by continuum fracture mechanics approaches [6].

In practice, any stressed surface does contain geometrical discontinuities ranging in the depth from slip steps, pits and machining marks to gross weld defects. These may act both as stress concentrators leading to localised plastification and as occluded regions where a localised SCC promoting environment can be formed. Initiation respectively incubation may be

defined as the very time required to form a localised environment (by stress-independent corrosion processes) that is conducive to subsequent crack propagation. This initiation process can relatively rapidly occur if compared to LWR-design lives of 30 to 40 years. However, the subsequent SCC propagation rates under LWR conditions can be very slow and in this case, SCC crack propagation may determine the component life time. On the contrary, in aggressive environments e.g. found in chemical industry fast SCC crack growth can occur but the crack initiation period often exceeds the design lifetime of the component. Such components would not be used in practice, if an analysis would solely be based on fracture mechanics SCC tests taking the growth of pre-existing cracks into account only [6].

Otherwise, by a fracture mechanics approach the crack initiation period is often regarded as an additional safety margin. The high stress concentration at sharp fatigue pre-cracks is leading to significant local crack-tip plasticity and the restricted crack geometry favours the formation of an aggressive occluded water chemistry. Here, conditions for crack initiation appear to be more favourable than that at smooth „defect-free" surfaces. Thus, tests with pre-cracked specimens are sometimes regarded as extremely conservative with respect to practice, even if in these tests long incubation periods are sometimes observed (especially in the case of intergranular SCC where long periods can be necessary for the transition from the transgranular fatigue pre-crack to the intergranular SCC crack).

The most common SCC/SICC mitigation strategy is to exclude large pre-existing defects by adequate NDT and QA measures during and after fabrication of components before they were put in operation and to avoid during operation those conditions, which could lead to crack initiation. Nevertheless, cracking in operating components may be induced by transient or faulted operation conditions during service or may be detected by ND-inspection. Therefore additional investigations on the SCC crack propagation behaviour are necessary and essential for both safety and structural integrity assessments and to set-up ND inspection intervals, especially for safety-relevant components of LWR.

The factors controlling crack initiation and growth may significantly differ. Therefore both processes may show relevantly different responses to changes in the corrosion system.

Crack initiation is a complex sequence of different stochastic and deterministic microscopic processes and events which often include pit initiation, pit growth, multiple micro-crack initiation at pit ground, micro-crack coalescence and growth of a main-crack. Only the last step can be described by LEFM if the main-crack is long enough. Furthermore crack initiation is strongly affected by the surface state, a factor which is strongly dependent on fabrication process of the component. Parameters describing SCC/SICC crack initiation are therefore often subjected to a statistical distribution and to a large scatter. Therefore crack initiation is difficult to handle [5].

Crack growth is also based on a complex sequence of several individual steps (Figure 4). Each of these steps can depend in a different manner on the other system parameters and may be rate-limiting. A change of the system conditions can cause a change in the rate-limiting step, which can produce a significantly different behaviour [5].

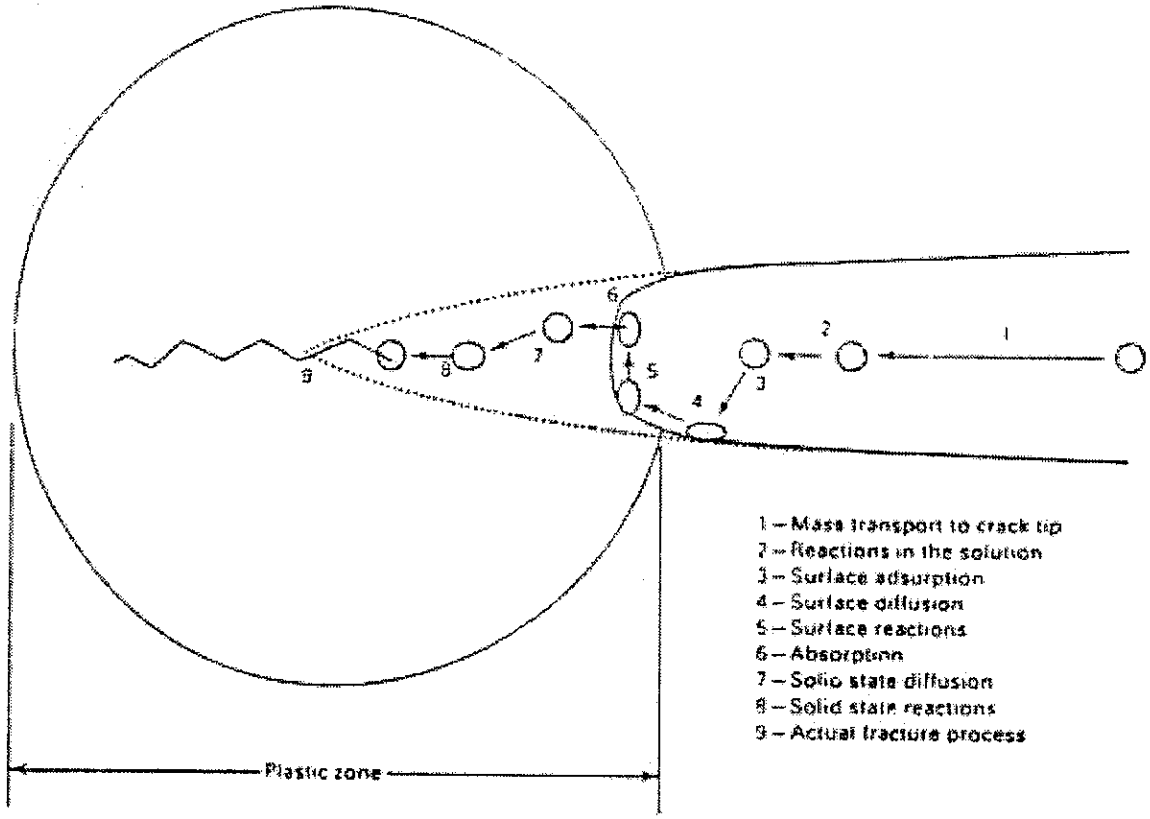


Figure 4: Schematic of crack-tip processes that may be the rate-determining step for SCC propagation. Factors that affect the rate-determining step have the strongest effect on crack propagation. If corrosion system parameters are modified, the rate-determining step and response to the corrosion system parameter can change [5].

2.2.3 SCC Crack Growth Rate vs. Stress Intensity Factor Curves

Most frequently, the SCC propagation behaviour is quantitatively characterised by tests with pre-cracked fracture mechanic specimens. Mode I loading is generally used, because it is most severe for SCC and results in lowest thresholds [5]. Tests under slow monotonically rising load with different loading rates are necessary to derive minimum K_{ISCC} values for type II SCC (see Figure 2). Under constant load the stress intensity factor is increasing with increasing crack length, whereas it decreases under constant deformation. Crack growth rate vs. stress intensity factor diagrams are derived from several individual tests (see Figure 5). Such tests have to be performed either under conditions where LEFM is valid (SSY-conditions) or EPFM parameters as J have to be used to characterise mechanical crack-tip conditions.

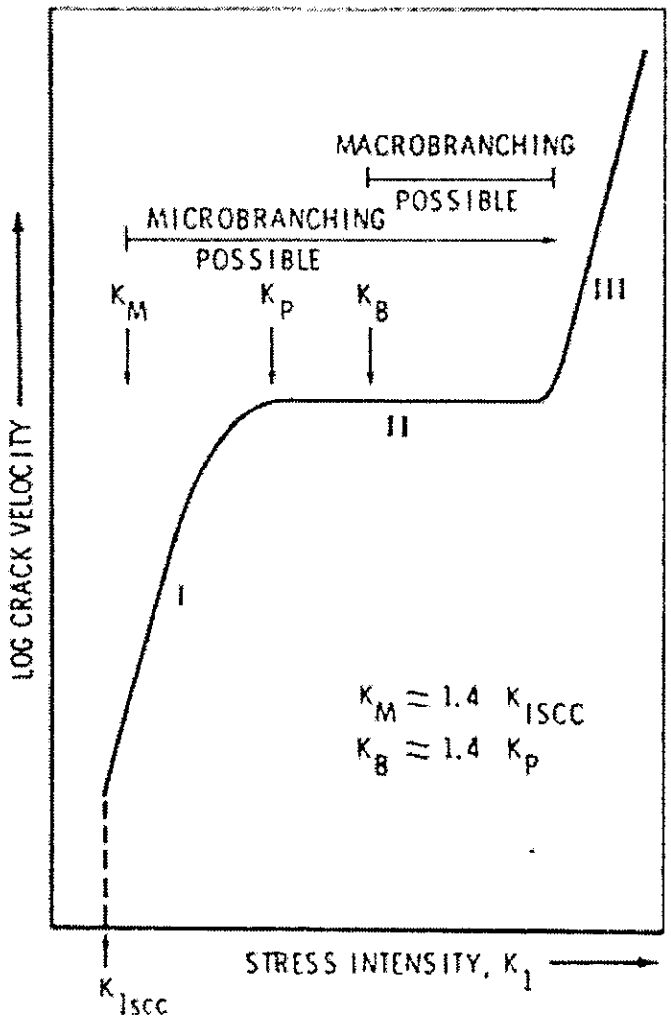


Figure 5: Schematic of the dependence of the SCC crack propagation rate, micro- and macro-branching on the applied stress intensity factor [3, 4].

Important parameters characterising the crack growth behaviour are K_{ISCC}, K_{IP}, $\dot{a}_P$, which are all system parameters and may therefore depend on environmental material and loading conditions [3, 4].

Four different regions can be differentiated in Figure 5 [3, 4]:

Region I: $K_I < K_{ISCC}$

Below the threshold stress intensity factor K_{ISCC}, no detectable corrosion-assisted crack growth is observed. K_{ISCC} has to be derived under plane strain conditions, otherwise its value may depend on specimen thickness. In type II SCC K_{ISCC} is strongly dependent on $\dot{\varepsilon}$ and $\dot{K}_I$. Generally, the minimum value observed is taken as K_{ISCC}. Moreover, different values have been observed for plane strain and stress conditions in many systems [7]. In LAS/high-temperature water a lower K_{ISCC} is expected under plane stress than under plain strain conditions. In some other corrosion systems (in particular with hydrogen embrittlement mechnaims) the contrary is observed. In addition to this, the test procedure and especially the initial loading procedure may have a strong effect on the observed thresholds.

Region II: $K_{ISCC} \leq K_I < K_{IP}$

In this region crack growth rate increases with increasing stress intensity factor, often with a power law function ($\dot{a} = A \cdot K_I^n$). In some corrosion systems a direct transition from region I to III is observed within a very small stress intensity range. Above $\approx \sqrt{2} \cdot K_{ISCC}$ micro-branching may be observed.

Region III: $K_{IP} \leq K_I < K_{IC}$:

In this region crack growth rate is not or just slightly dependent on the stress intensity factor. It is often considered that mass transport controls crack growth in this region. Above $\approx \sqrt{2} \cdot K_{IP}$ macro-branching may be observed.

Region IV: $K_I \geq K_{IC}$ or K_{IJ}

If K_I reaches K_{IC} or K_{IJ} sudden catastrophic failure or onset of pure ductile mechanical crack growth without any relevant environmental effect occurs.

2.3 Laboratory EAC Test Methods and Their Relevance to LWR Components

The thermo-mechanical loading conditions of operating LWR pressure-boundary components are very complex; the corresponding load spectrum is a complex superposition and/or sequence of different loading modes (static, cyclic). Therefore, in laboratory tests a wide range of loading (static, dynamic, cyclic) and environmental conditions reflecting the different operating conditions (start-up/shut-down, steady-state power operation, stand-by, transients, ...) are necessary to reliably evaluate and assess the possible effect of EAC on the long-term structural integrity of low-alloy pressure-boundary components in LWR. Different types of specimen (smooth, notched, pre-cracked) are necessary to characterize the EAC initiation and growth behaviour.
Dynamic SCC tests cannot clearly differentiate between Type I and Type II SCC. On the other hand pure static tests can feign a high stability against SCC/SICC if the system is susceptible to Type II SCC or if exposure time is too short with respect to typical incubation periods for Type I SCC. In Figure 6 an hierarchy of SCC test methods is given [8], which allows an efficient and rational screening for SCC/SICC susceptibility in a given alloy/environment system.
In Figure 7 an overview on typical EAC test methods and their relevance to LWR components is given [9]. Consequently, the component behaviour under operating conditions can only be assessed if several of the presented test methods were deliberately combined.

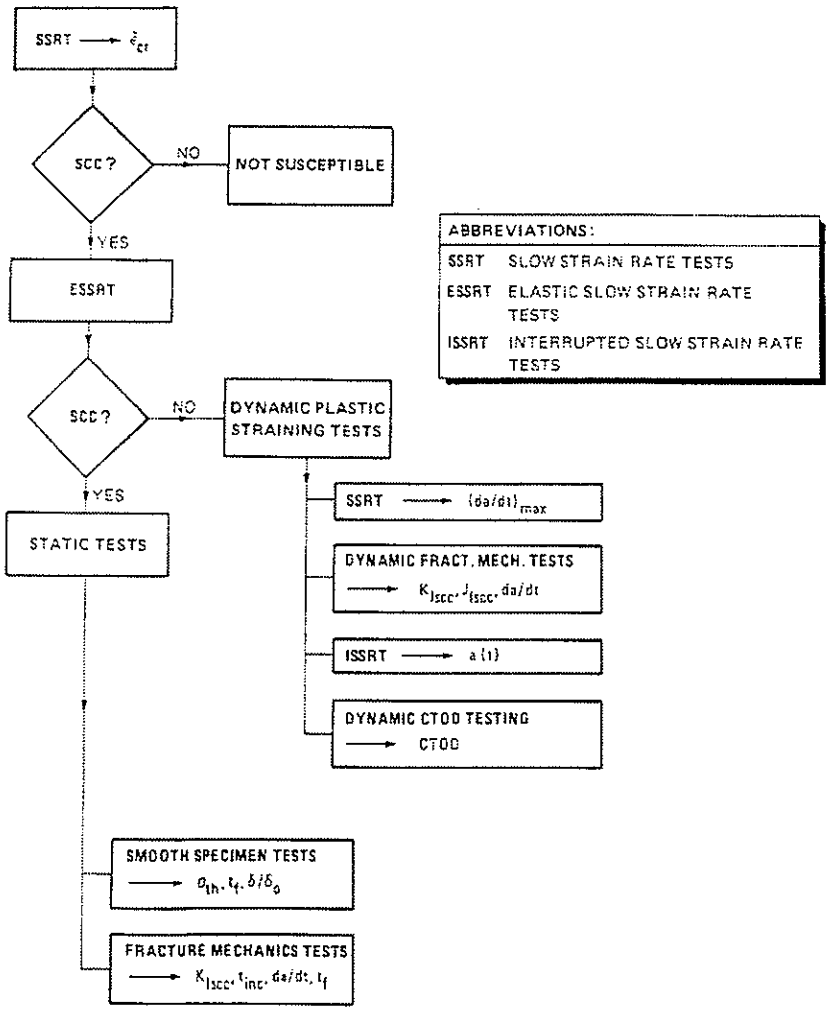


Figure 6: Hierarchy of SCC test methods [8].

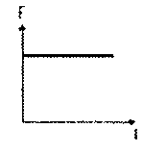
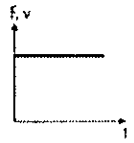
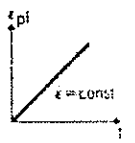
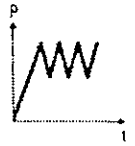
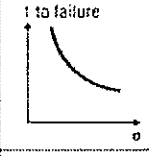
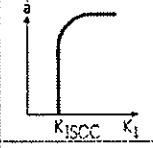
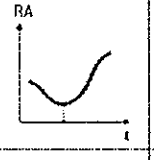
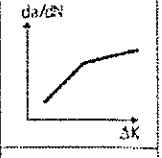
	SCC		CERT	SICC*)	Corrosion fatigue	
Type of specimen	Unnotched	Precracked	Unnotched	Unnotched	Unnotched	Precracked
Loading				LCF		
Result						
Objective, application	Susceptibility, material selection	Safety - margins	Susceptibility, material select., environmental parameters	Optimization of start-up procedure	Design	Evaluation of Δa and safety margins
Height of loading	Variable (up to full plastic load)	Linear elastic	Increasing to fracture	Variable (up to full plastic load)	Variable (up to full plastic load)	Linear elastic
Applicable to the compon. behaviour	Yes	Yes, if cond. of LEFM are fulfilled	Qualitative indications	Yes	Yes	Yes

Figure 7: EAC test methods and their relevance to LWR components [9].

3. SCC/SICC of Low-Alloy Steels in High-Temperature Water

The SCC/SICC susceptibility and propagation of low-alloy pressure-boundary component steels in oxygenated high-temperature water is governed by a complex system of interrelated and synergistic factors, such as material, environmental and loading parameters, by design, manufacturing, process and operating related features. The sum of these features are characterising the corrosion system. SCC/SICC initiation and growth are only observed under specific combinations of environmental, loading and material conditions. Crack initiation and growth may be controlled by different microscopic processes and may therefore show a different response to the various system parameters. The term SCC/SICC susceptibility is related to crack initiation in this report, if not further specified.

3.1 Main Influencing Factors for SCC/SICC

The following main influencing factors for SCC/SICC have been identified during the last decades [11 - 27]:

• Environmental parameters:

- corrosion potential ECP

$$ECP = f(O_2, H_2O_2, H_2, pH, T, \text{flow rate, impurities, chemical composition of alloy (Cr, Ni, ...), history, exposure time, ...})$$

- temperature T

- concentration of specific (anionic) impurities: SO_4^{2-}, Cl^-, HS^-, S^{2-}, H_2S, ...

- flow rate

• Material parameters:

- sulphur content

- morphology, size, spatial distribution and chemical composition of MnS-inclusions

- free nitrogen and carbon content (DSA response of alloy)
→ nitrogen/aluminium-ratio, PWHT- or annealing-temperature

• Loading parameters:

- loading or strain-rate: dK_I/dt, $d\varepsilon/dt$

- load, stress or strain level: K_I, σ, ε

3.2 SCC/SICC Susceptibility Conditions

It is known from both experimental and field experience that EAC may occur in low-alloy pressure-boundary component steels in oxygenated, high-temperature water if the following conditions are simultaneously attained:

- Corrosion potential: $ECP > ECP_{crit} = -200\ mV_{SHE}$ (if $\kappa \leq 0.3\ \mu S/cm$)

- Strain-rate: $0 < \dot{\varepsilon}_{crit,min} \leq \dot{\varepsilon} \leq \dot{\varepsilon}_{crit,max} = 10^{-1}\ \%/s$

- Strain: $\varepsilon \geq \varepsilon_{crit} = 0.1 - 0.3\ \% >$ elastic limit ($\sigma_{crit} > R_p$)

In particular, slow, positive, dynamic tensile straining with associated plastic yielding appears to be essential for EAC initiation and growth. The extent of EAC cracking is crucially

dependent both on maintaining a positive crack-tip strain-rate and a high sulphur-anion activity in the crack-tip environment. Hence, high EAC crack growth rates (CGR) are observed in steels with a high MnS-inclusion content in highly oxidising environments with high impurity level in the water and, in particular, under dynamic loading conditions.

The SCC/SICC promoting susceptibility conditions specified in Table 3 were primarily derived from laboratory experiments (Constant Load-, SSRT- and LCF-tests with smooth and pre-cracked specimens) [11, 16, 18, 22, 24, 25, 28 - 41]. The experimental evidence for some of the given parameter ranges is still weak. The given thresholds are system parameters and therefore dependent on the other system parameters. Outside the specified susceptibility conditions, SCC/SICC may still occur, whereas both, the probability and extent of environmental effects are significantly reduced. The given SCC/SICC susceptibility conditions can be compared with those of different components under different LWR operating conditions (steady-state power operation, start-up/shut-down, stand-by, transients, faulted conditions, ...).

The susceptibility conditions given in Table 3 are valuable in oxygenated high-temperature water with high or moderate purity (≈ < EPRI action level 2) for low-alloy pressure-boundary component steels in the quenched and tempered state with a characteristic yield strength level of 300 to 600 MPa and a sulphur-content of ≤ 0.020 wt.% S. Because of the limited number of tests with welds and weld HAZ, the conditions are not well established and should therefore be regarded with caution for these material states.

SCC/SICC crack initiation or crack growth can only occur if the conjoint conditions in Table 3 are simultaneously attained during a sufficient long period. If one of the threshold conditions is not satisfied, no or only minor environmental effects on crack initiation and growth are observed.

Crack initiation („susceptibility“)	Crack growth of long (pre-existing) cracks	Remarks
$T > 120$ °C to 180 °C Maximum at 200 - 250 °C	$T > 25$ °C to 180 °C $T\uparrow \rightarrow \dot{a}\uparrow$, $E_A \approx 42$ kJ/mol	
$ECP > ECP_{crit}$ = -300 mV_{SHE} to -100 mV_{SHE}	$ECP > ECP_{crit}$ = -300 mV_{SHE} to -100 mV_{SHE}	> 20 - 100 ppb O_2 = f (flow rate, T, MnS, ...) ECP_{crit}= f(MnS, SO_4^{2-}, T,...)
$10^{-8}\ s^{-1} < \dot{\varepsilon} < 10^{-2}\ s^{-1}$	$K_I \geq K_{ISCC} = f(\dot{\varepsilon}_{CT})$ $\dot{\varepsilon}_{CT} > 0$	$\dot{\varepsilon}$: External loading (start-up/shut-down, transients), low-temperature creep crack growth
$\varepsilon_{crit} \geq 0.1$ to 5 % $\sigma \geq \sigma_{crit}$ $\sigma_{crit} \geq R_p$ to $0.95 \cdot R_m$	$\varepsilon_{CT} \geq \varepsilon_{crit}$? certain amount of plastic deformation at crack-tip ?	$\sigma_{design} < R_p/S \rightarrow$ regions of increased (local) stress: notches, weld defects, ... high secondary stresses
$t > t_{Incubation}$	$t > t_{Incubation}$	eventually incubation period

Table 3: Susceptibility conditions for SCC/SICC derived from laboratory experiments.

Table 4 provides an assessment scheme for SCC susceptibility of low-alloy steels according to Hickling [40, 41]. Table 3 and 4 fit well to each other. Conditions in Table 3 are more conservative, since results of SSRT and LCF tests have also been included to establish the susceptibility conditions. Table 4 is primarily based on static loading conditions and the weighting of operating experience and of the effect of flow rate has been higher than in Table 3.

As shown in Table 4, flow rate is a further fundamental parameter. Quasi-stagnant or low-flow conditions favour the formation of an aggressive occluded water chemistry in small surface defects or corrosion pits and therefore also the initiation of SCC/SICC. Otherwise, under high-flow conditions, which are characteristic for most RPV locations, the crack initiation may be relevantly retarded or even completely suppressed, because hydrodynamics mitigates the build-up of a locally high sulphur-anion activity in e.g. corrosion pits [42, 43]. In pure water, crack growth rates may also substantially slowed down by high flow rates, if complete flushing of the crack-tip environment occurs in short surface cracks or in fracture mechanics specimens with through-the- thickness cracks [19, 38, 42, 44-47]. The beneficial effect of high flow rate is expected to be significantly reduced for realistic, sufficiently deep semi-elliptical surface cracks, especially if the interdentritic/intergranular structure of an SCC/SICC crack in the cladding of the RPV is considered.

Operating medium: high-temperature water or steam condensate with T > 170 °C						
O_2 content in ppm	Flow conditions	Conductivity* in µS/cm	Crack initiation through SCC?	Derivation	Crack growth through SCC?	Derivation
< 0.2	typical for reactor	typical for reactor (i.e. < 0.1)	no susceptibility	1	no susceptibility	1
< 0.2	quasi-stagnant	(approx. 0.2)	no susceptibility	1	no susceptibility	2
< 0.2	quasi-stagnant	raised (e.g. through lubricants)	x (for stress levels at the water-wetted surface in the region of the HT yield point)	2	o	3
0.2—0.4	typical for reactor	typical for reactor (i.e. approx 0.2)	no susceptibility	1	no susceptibility	1
0.2—0.4	quasi-stagnant	(approx. 0.2)	x (for stress levels at the water-wetted surface > the HT yield point)	2	o	2
0.2—0.4	quasi-stagnant	raised (e.g. through lubricants)	x (for stress levels at the water-wetted surface in the region of the HT yield point)	2	o	2
>> 0.4	typical for reactor	typical for reactor (i.e. < 0.2)	in general, no susceptibility (? at stress levels >> HT yield point)	1 3	susceptibility is suppressed through flow	2
>> 0.4	quasi-stagnant	< 1 (approx. 0.2)	x (for stress levels at the water-wetted surface > = the HT yield point)	2	o	2
>> 0.4	quasi-stagnant	raised (e.g. through lubricants)	x (for stress levels at the water-wetted surface in the region of the HT yield point)	2	o	2

x possibility cannot be excluded, perhaps after long incubation time
o possibility cannot be excluded, perhaps after incubation time even with pre-existing crack
* measured at 25 °C

Derivation:
1 from experiments in more aggressive environments
2 from appropriate autoclave experiments
3 no experimental results of direct relevance

Table 4: Assessment scheme for SCC susceptibility for low-alloy pressure-boundary components (at normal strength levels) in BWR [40, 41].

SCC/SICC cracks at smooth defect free surfaces most often initiate at corrosion pits or at MnS-inclusion, which intersect the steel surface. Pitting in low-alloy steels is favoured by high oxygen concentrations and low temperatures as well as by dynamic straining (see Figure 8). Low-flow conditions which promotes the build-up of an aggressive occluded water

chemistry in these small surfaces defects strongly favours SCC/SICC initiation at the pit ground.

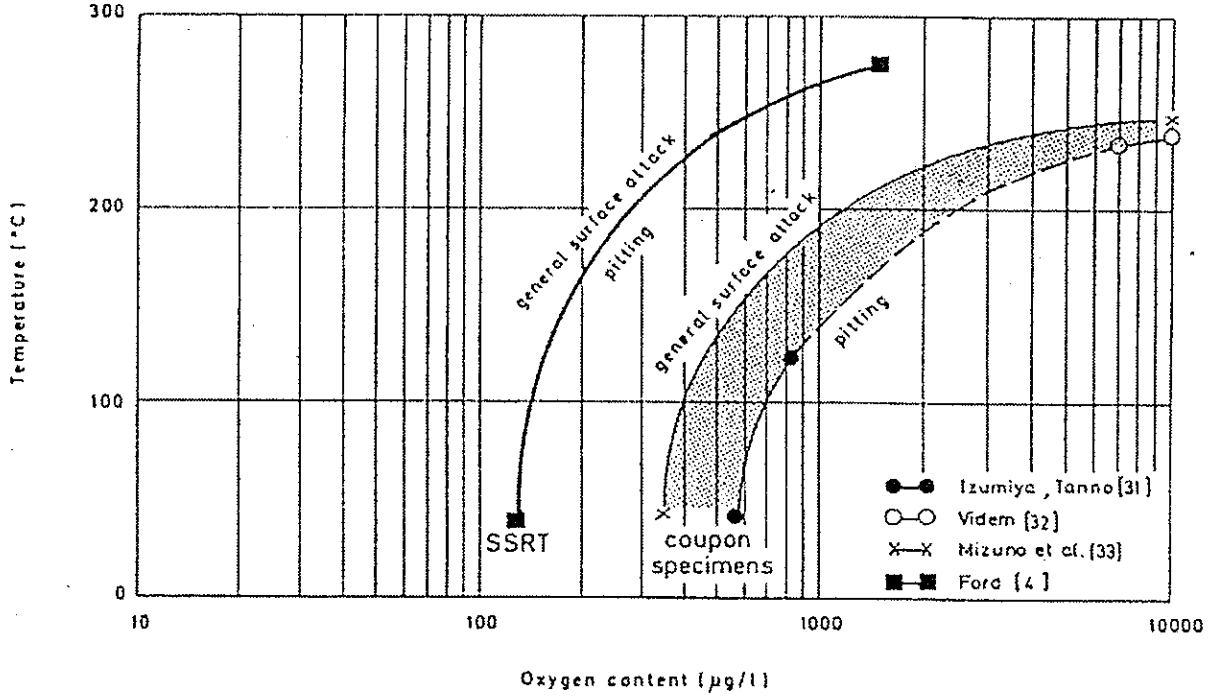


Figure 8: Effect of DO, temperature and strain-rate on pitting in LAS [32].

In the following sections some important phenomenological aspects are further worked out. Most influencing parameters are interrelated and synergistic, and therefore cannot be discussed independently. In many cases, the effect of system parameters on the crack initiation and crack growth process cannot be clearly separated. Therefore, both aspects are generally discussed together. Most system parameters have not yet been systematically studied. The analysis of the effect of different system parameters based on experimental studies of different authors with significant variability in system conditions from study to study and test to test, is therefore associated with uncertainty.

3.3. Environmental Parameters

3.3.1 Temperature

The effect of temperature on SCC/SICC initiation and growth has not yet been systematically studied. There are only a few crack growth investigations in high-purity water and most of them have been performed in the temperature range of 270 to 300 °C. Temperature effects should be studied under constant process conditions. Because of significant variations in ECP, steel sulphur content and mechanical loading conditions, comparison of literature data is difficult and no satisfactory conclusion on temperature effects can be derived from these tests. Furthermore, in most cases it is often difficult to clearly separate the effect of temperature on crack growth from its effect on the thresholds for the onset of EAC. Therefore, the effect of temperature on crack initiation and crack growth is not yet fully understood.

The SCC/SICC susceptibility of low-alloy pressure-boundary component steels seems to be low below 100 °C, but the few tests at low temperatures indicate that EAC may still occur [15, 67, 99]. From SSRT tests with smooth tensile specimens, a maximum susceptibility can

be derived between (150 °C) 200 °C and 250 °C (see Figure 9) [11, 19, 33, 49, 98, 99], depending on dissolved oxygen content and sulphur content of the steel. A minimum oxygen concentration is needed in this temperature range to exceed the ECP_{crit} [44, 49]. Dynamic strain ageing (DSA) (and free nitrogen and carbon content of the steel) may be a further contributing factor for this maximum of susceptibility and for variations in temperature trends between different alloys [27]. In LCF-tests, fatigue life (which is defined as the number of cycles required to form an engineering-size crack form a "defect-free surface", e.g. 3 mm-deep crack) decreases linearly with temperature above 150 °C and up to 320 °C [36, 71], when the other threshold conditions for environmental effects are satisfied. Fatigue life is insensitive to temperatures below 150 °C or when any other threshold condition is not satisfied [36, 71]. The temperature effects may depend on factors such as DO, ECP, strain-rate, strain, and steel sulphur content [36]. It is generally believed that the decrease in fatigue life is caused primarily by the effects of environment on the growth of short cracks that are < 100 µm [101]. Nevertheless, the temperature effect in both test types (LCF, SSRT) on initiation and propagation cannot be clearly separated.

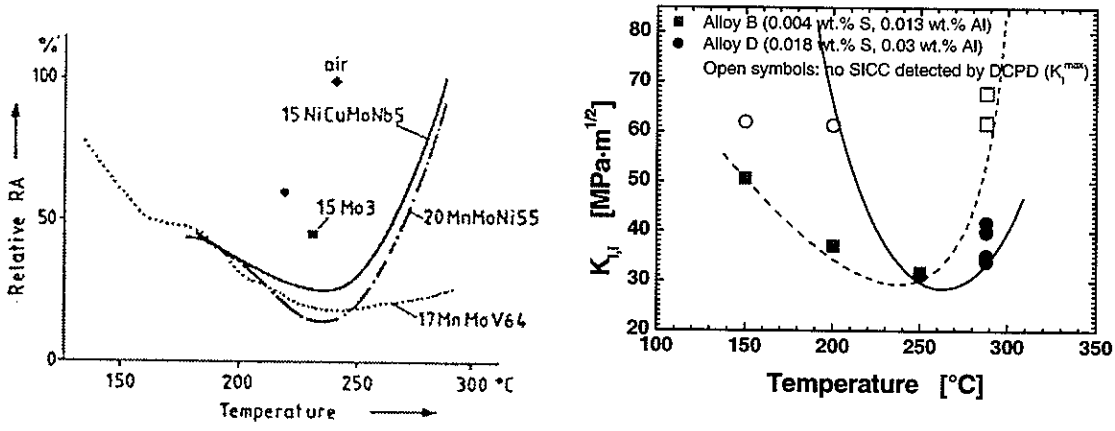


Figure 9: Maximum SICC susceptibility at intermediate temperatures in SSRT tests [11] with smooth specimens and slow rising load tests with pre-cracked specimens [29].

The SCC crack growth rate seems to decrease with decreasing temperature [15, 21] (see Figure 10). An activation energy of 42 KJ/mol has been determined with plateau-crack growth rates under aggressive environmental (high impurity content, highly oxidising) and extremely loading conditions (outside LEFM) with pre-cracked specimens under static loading in static autoclaves [15, 21]. This activation energy can be taken as a rough estimate of corresponding crack growth rates at different temperatures. In high-purity water, there is almost no susceptibility to sustained SCC growth [28, 29], making it impossible to determine activation energies and temperature trends under these conditions. In SSRT tests in oxygenated high-temperature water, increasing SICC CGR were observed with increasing temperatures between 150 °C and 288 °C [11, 33, 97, 98].

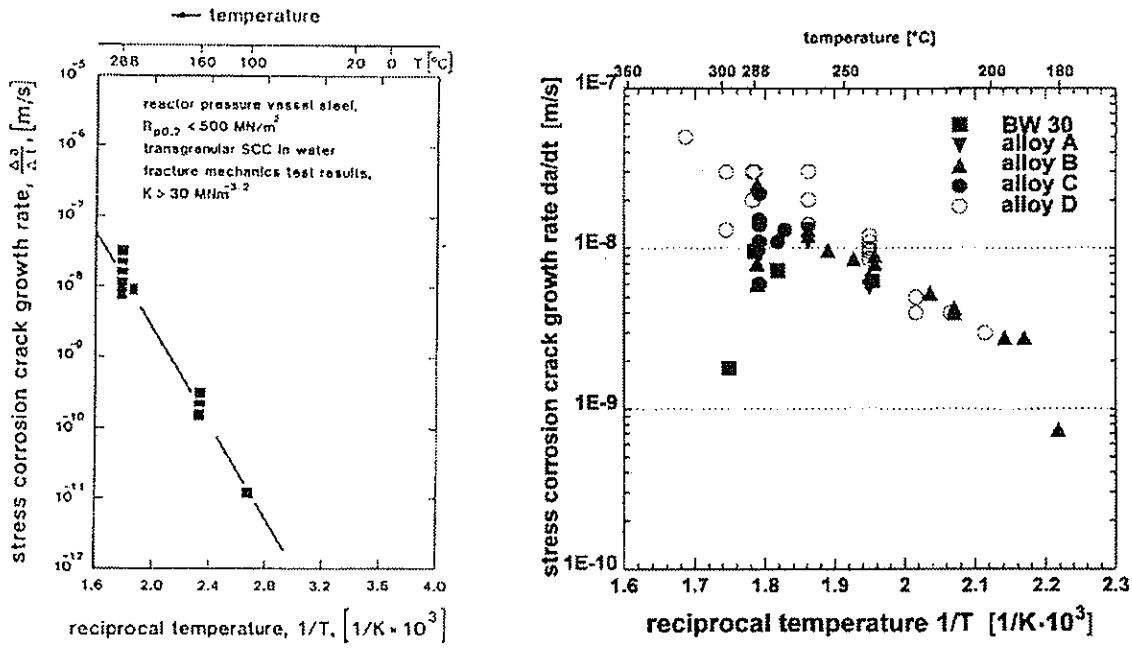


Figure 10: Temperature dependence of SCC crack growth rates [15, 41].

The situation is even more complex under cyclic loading conditions (corrosion fatigue), where depending on loading conditions (frequency/strain-rate, load amplitude and R-value), crack growth rates between 150 °C and 300 °C were either monotonically increasing with temperature or showing a maximum at intermediate temperatures between 180 ° to 240 °C [14, 38, 72 - 84] (see Figure 11). In some cases even a minimum at intermediate temperature was reported [75, 78]. Thresholds and crack growth rates may show different temperature trends. It has been proposed, that both plateau thresholds and plateau CGR in corrosion fatigue increase with increasing temperature [72]. The region of EAC might therefore be significantly extended at lower temperatures compared to 290 °C.

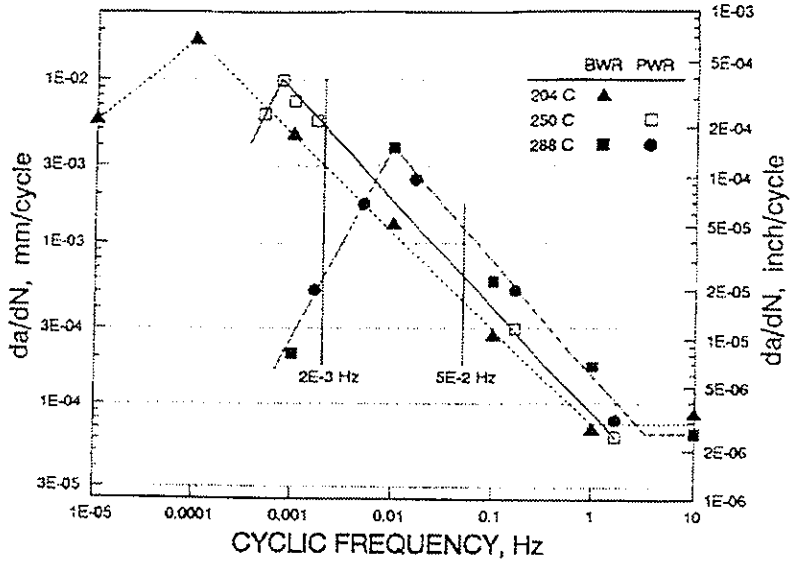


Figure 11: Effect of loading frequency and temperature on CF CGR [84]. 2E-4 Hz: Maximum at 250 °C. 5E-2 Hz: CF CGR monotonically increases with temperature.

Within certain limits, there is a trend, that EAC CGR increase with increasing temperatures for given fixed testing conditions. DSA and the temperature dependence of different EAC thresholds (ΔK_{Pl}, strain-rate,...) are probably the two major reasons for deviations form this trend and for a more complex behaviour. A change in crack growth mechanism (FRAD to HAEAC, true CF to stress corrosion fatigue) may be further contributing factors. DSA may explain a CGR maximum at intermediate temperature for certain strain-rates by both its effect on CGR and on thresholds. Differences in the free nitrogen and carbon content of the steel may explain the quite different temperature response sometimes observed of otherwise similar alloys. A lower plateau thershold ΔK_{Pl} in corrosion fatigue at lower temperatures may explain a negative temperature dependence of EAC in the case where the ΔK of the tests does exceed the threshold ΔK_{Pl} at lower temperatures, but not at higher temperatures. There are several experimental indications that the range of environmental, material and loading conditions leading to EAC may significantly extended at intermediate and low temperatures compared to tests at 290 °C.

3.3.2 ECP and Oxygen Content

The ECP is more fundamental for SCC/SICC than the content of oxygen respectively content of all oxidising agents [16, 59]. Depending on flow rate, temperature and material, 5 ppb to 100 ppb dissolved oxygen is sufficient to exceed the critical cracking potential of ca. - 200 mV_{SHE} [16, 33 – 35, 97, 98] in high-purity water. The critical potential ECP_{crit} is dependent on temperature, steel sulphur content, bulk sulphur-anion concentration and strain-rate (see Figure 12 – 15, 17). ECP_{crit} decreases with increasing sulphur content of the steel [34, 35, 60], and with increasing sulphate content of the environment [34, 35] (see Figure 13). The critical potential has sometimes been related to the passivation potential E_p or the stability boundary of Fe_2O_3/Fe_3O_4 [85], but the role of ECP is probably better understood by its effect on mass transport in the crack enclave and on the enrichment of sulphur-anion species in the crack-tip environment and by the dominant effect of sulphur-anion species on crack growth and repassivation (low/high sulphur behaviour (see Section 4)). The ECP, steel sulphur content and bulk sulphur-anion content are interrelated by crack-tip sulphur-anion activity. The critical potential can then be related to a critical sulphur-anion concentration in the crack-tip environment and to the transition between the low/high sulphur crack growth behaviour. Above ECP_{crit}, the EAC susceptibility range (temperature/strain-rate/strain) is significantly extended [11] with increasing ECP. In relative pure high-temperature water, the crack growth rates may increase with increasing ECP and then probably saturates, when the high sulphur behaviour is achieved [86 - 88]. In LCF tests, when all threshold conditions are satisfied, fatigue life decreases logarithmically above a DO of 50 ppb and the effect seems to saturate at 500 ppb DO [102, 103]. Fatigue life is insensitive to DO levels below 50 ppb or when any other threshold conditions is not satisfied.

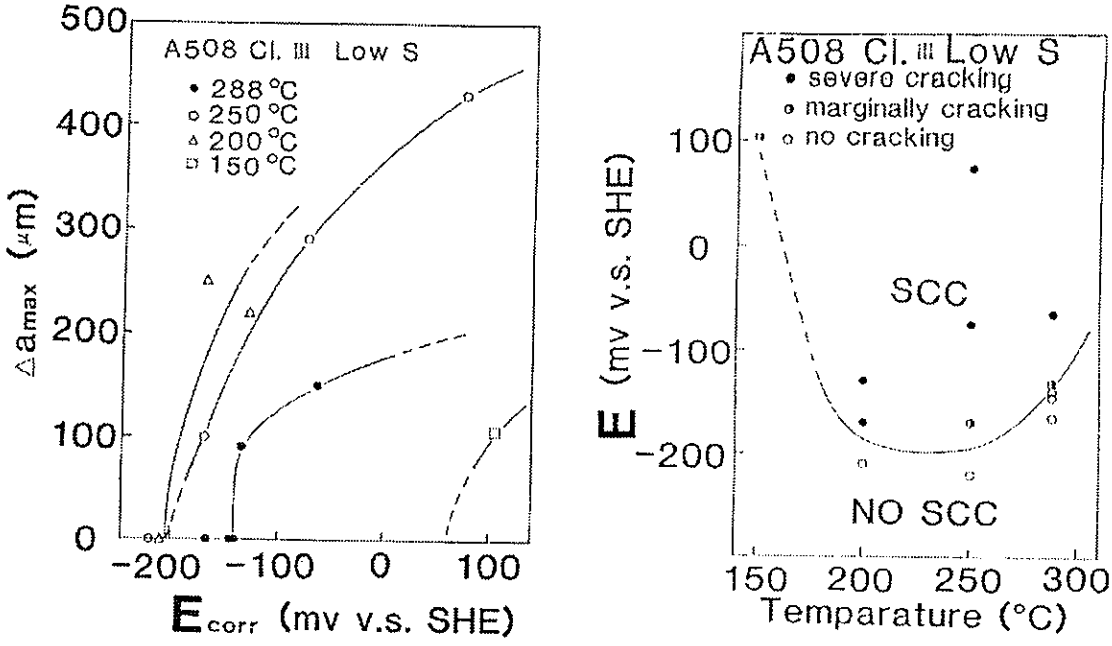


Figure 12: Effect of temperature on critical cracking potential. Maximum susceptibility around 200 - 250 °C [34, 35].

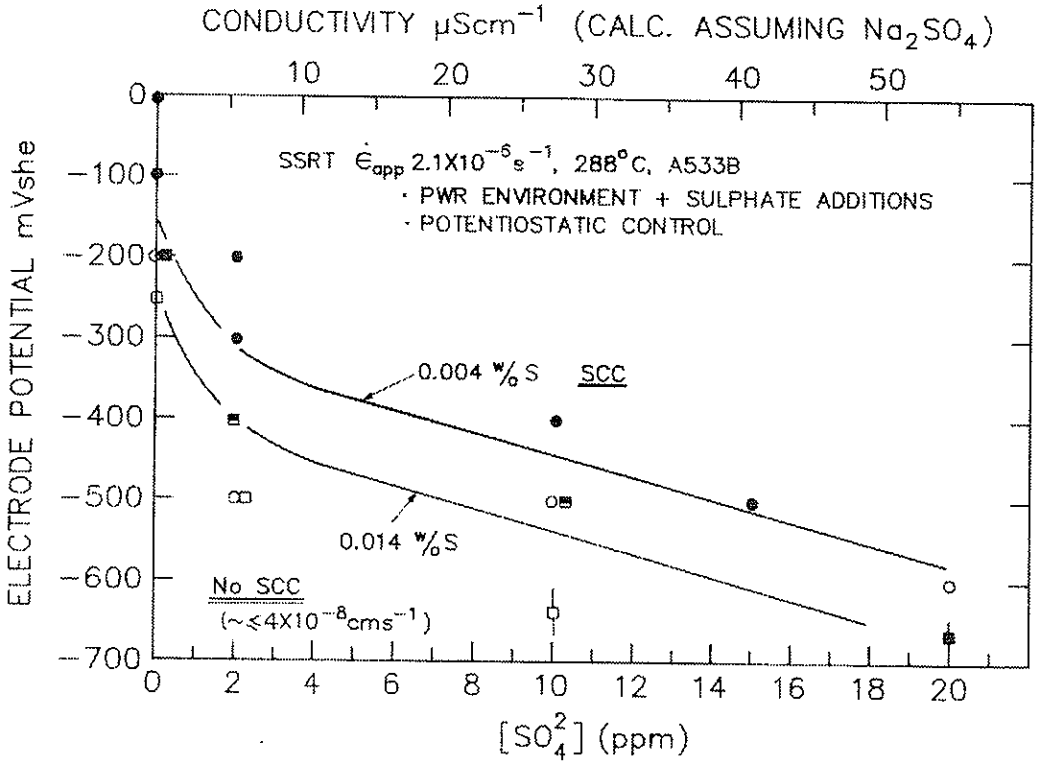


Figure 13: Effect of steel sulphur content and bulk sulphate concentration on ECP_{crit} in oxygenated high-temperature water [34, 35].

The ECP of low-alloy pressure-boundary components under water chemistry conditions representative for PWR primary circuit coolants under steady-state power operation is typically around - 800 mV_{SHE} to - 600 mV_{SHE}, which is significantly below the critical cracking potential of around - 200 mV_{SHE}. This is the main reason for the excellent stability of these steels under PWR conditions.

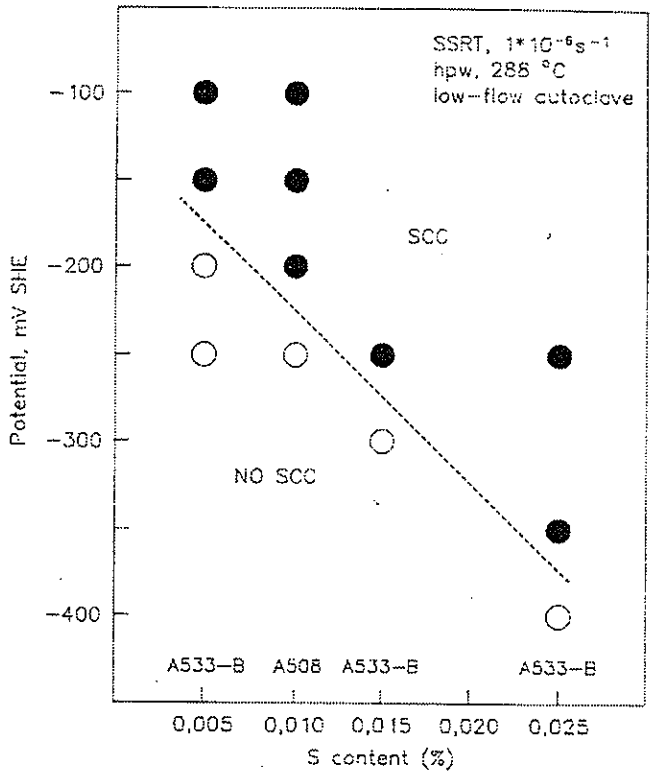


Figure 14: Effect of steel sulphur content on critical potential [62].

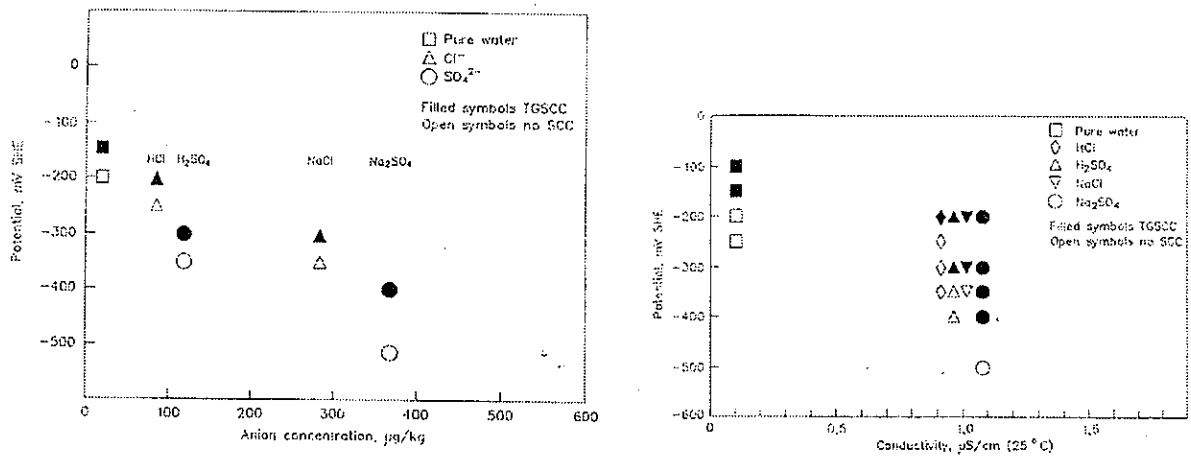


Figure 15: Effect of sulphate and chloride on critical potential [62].

3.3.3 Sulphate Concentration of Environment

The sulphate concentration may have a relevant effect on SCC initiation [34,35, 61, 62] (see Figure 15) and crack growth [17, 21, 29]. The amplitude of the effect strongly depends on the ECP [46]. Under oxidising conditions both Na_2SO_4 and H_2SO_4 may accelerate crack growth. H_2SO_4 (and probably also Na_2SO_4) may also accelerate crack growth under reducing PWR conditions at sufficiently high concentration levels [46]. Under oxidising conditions the transition from a very low SCC crack growth rate susceptibility to a high one occurs at sulphate concentrations of the bulk environment of ca. 100 ppb to 1 ppm [17, 21, 29], which is above EPRI action level 3. Under dynamic loading conditions less sulphate is necessary to accelerate SICC crack growth. Similar effects are expected for H_2S and chlorides.

3.3.4 Possible Irradiation Effects on EAC

Irradiation could affect the EAC behaviour of low-alloy RPV steels in two major ways, by a change of the oxidising power of the environment by radiolysis of the reactor coolant by n- and γ-irradiation and by the change of the microstructure and mechanical properties by n-irradiation (n-embrittlement).

• Change of the oxidising power of the environment by irradiation:

This aspect is mainly of relevance for BWR, whereas in PWR (or BWR running under HWC), the large hydrogen overpressure suppresses the build-up of oxygen and hydrogen peroxide arising from the water radiolysis. Under reducing PWR conditions very low ECP significantly below the critical cracking potential ECP_{crit} can be expected near to the RPV wall.

Radiolytic decomposition of the reactor coolant mainly occurs in the high n- and γ-flux region of the reactor core. The "stable" radiolytic products are H_2, O_2, H_2O_2. The concentration of dissolved radiolysis gases in the reactor water of a BWR is determined by dynamic equilibrium of, on the one hand the radiolytic decomposition of the water in the reactor core zone and, on the other hand, of the physical distribution behaviour between reactor water and the live steam being produced. Up to 300 ppb dissolved oxygen were measured in German BWR between the RPV wall and the core shroud [40]. Hydrogen peroxide is relatively stable at reactor operating temperature in high-purity water, but it decomposes through homogenous catalysis in connection with certain water impurities and, even more pronounced through heterogeneous catalysis at material surfaces. The highest concentration is postulated to exist in the coolant within the reactor core zone. A decrease in concentration proportional to the distance travelled by the coolant after exciting the reactor core, is expected for the remaining water containing regions with the RPV.

Furthermore, recent measurements of ECP (mainly on stainless steels) in BWR suggests that the normal free corrosion potential is elevated by about 100mV due to irradiation. This is mainly caused by the presence of oxidizing species other than oxygen, particularly hydrogen peroxide. An ECP of at maximum ≈ + 200 mV could be expected on the inner RPV wall. The slightly increased ECP can be simulated in tests by higher DO. In tests under proton irradiation with stainless steels only small shifts (some few 10 mV) in corrosion potentials on external surface and at crack-tip have been observed over a wide range of water chemistry conditions [104, 105] compared to tests without irradiation, confirming the above mentioned aspect.

• Change of material properties by irradiation:

Neutron-irradiation embrittlement of low-alloy RPV steels reduces their toughness and ductility and increases their hardness and yield strength which can almost reach the ultimate tensile strength under worst case situations.

Due to the large core-to-RPV wall annulus in BWR, the irradiation effects are minimal, especially for modern optimized low-alloy RPV steels with improved n-embrittlement resistance. For example, typical end of life fluences for 40-year operating period are 2 to $5 \cdot 10^{23}$ n/m^2 (E > 1MeV) for PWR and approximately 10^{22} n/m^2 (E > 1MeV) for BWR. Relevant changes of mechanical properties can be observed above fluences of > 10^{18} n/m^2. This concerns the late state of design life. Neutron-embrittlement is more relevant for PWR, but this aspect is somehow compensated by the very low ECP, which are significantly below the critical cracking potentials, even if ECP shifts would occur under irradiation.

There are only few EAC investigations with spot check character on irradiated RPV materials and/or under irradiation in high-temperature water [106 - 114] (see e.g. Figure 16). So far no systematic investigations were available. These tests carried out on pre-irradiated and non-irradiated pressure vessel steels under or without irradiation have so far not indicated any cause for concern on these two aspects. The corrosion behaviour of irradiated materials did not significantly differ from that of un-irradiated ones. The general lack of observations of significant effects of low strength low-alloy steel composition, microstructure (except sulphur content and inclusion morphology and excessive hardness) and yield strength (as long as $\leq$ 800 MPa) does not give rise to any theoretical reason to suspect a strong influence of irradiation. The small ECP-shift due to irradiation is unlikely to have more than a slight accelerating effect relative to oxygenated high-temperature water on crack propagation rates. This ECP-shift can readily be simulated, at least for pre-cracked specimens (see Section 4.2), in loop experiments by an increased oxygen content. Furthermore, the few cracking incidents in BWR RPV can be readily rationalized by the EAC laboratory data base without irradiation and there is no direct indication that these cracking incidents could have been accelerated or promoted by irradiation.

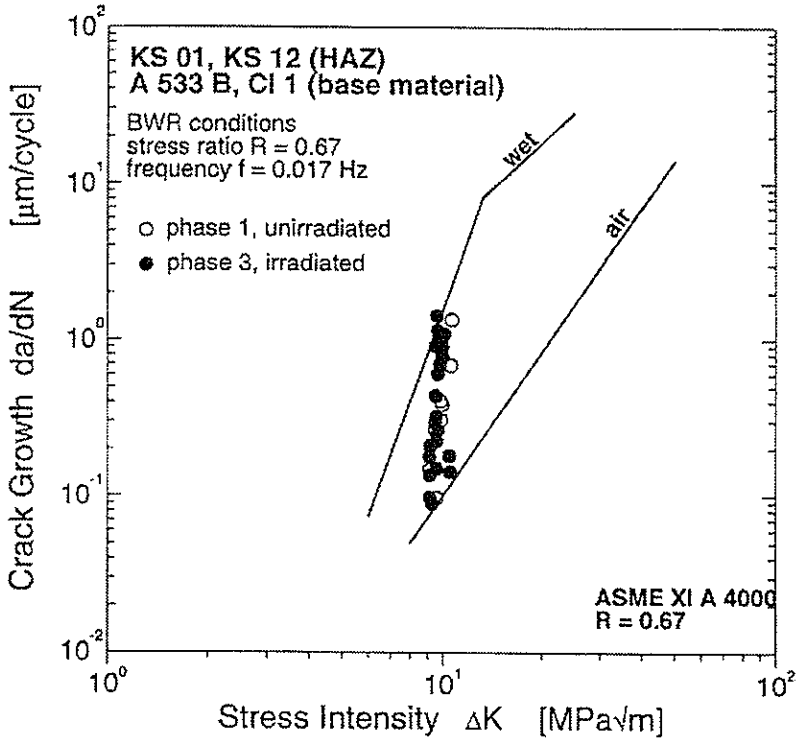


Figure 16: Absence of irradiation effects on CF CGR in high-temperature water in EAC experiments in a tests reactor [115].

A major effect of irradiation on EAC propagation rates in low strength low-alloy steels is therefore not expected, but a slight accelerating effect cannot be completely excluded. A currently running project at REZ sponsored by the VGB [113, 114], where pre-irradiated and non-irradiated pre-cracked low-alloy RPV (base metal and HAZ) specimens are tested under constant active load under BWR conditions in in-pile and out-of pile loops in a test reactor did **not** reveal a higher SCC susceptibility of irradiated RPV steels.

3.4 Mechanical/Loading Parameters

3.4.1 Critical Strain-rates and Strains

Both SCC/SICC crack initiation and crack growth show a high sensitivity to strain-rate (see Figure 17 and 18). Slow dynamic straining with a positive strain-rate (tensile loading) in the range of 10^{-7} s^{-1} to 10^{-3} s^{-1} with associated plastic yielding is generally necessary for crack initiation [11, 18, 22, 24, 36 - 38]. The range of maximum susceptibility (crack initiation) is often observed between 10^{-7} s^{-1} to 10^{-4} s^{-1} depending on other relevant system parameters, as ECP (oxygen content), temperature, steel sulphur content and bulk sulphate concentration of environment [11, 18, 33 - 35]. Above a strain-rate of 10^{-3} s^{-1} to 10^{-2} s^{-1}, no environmental effect is observed. At the moment, it is not clear if a lower strain-rate threshold > 0 exists or if susceptibility saturates below 10^{-7} s^{-1}. No reliable experiments have been performed so far at these extremely low strain-rates.

Dynamic straining in the purely elastic region does not lead to cracking. Microplasticity at microstructural inhomogenities below the yield strength is not sufficient to induce crack initiation. The critical strains for crack initiation derived from SSRT tests with smooth tensile test specimens were generally lying in the range between of 1% to 5 % depending on applied strain-rate, ECP (oxygen content), temperature, sulphur-content of steel and sulphate concentration of environment and surface state [16, 22, 24]. In LCF tests no relevant environmental effect has been observed so far at strains below 0.1- 0.3 % [36 -38], showing that a certain extent of „macroscopic" yielding is a necessary pre-requisite for crack initiation. Critical strains have often been related to the oxide film rupture strain [89]. When all other threshold conditions are satisfied, fatigue life decreases in LCF tests logarithmically below 10^{-2} s^{-1} and the effect of environment on life saturates at 10^{-5} s^{-1} [36,]. Above 10^{-2} s^{-1} no environmental effects are observed and strain-rate effects are consistent with those in air.

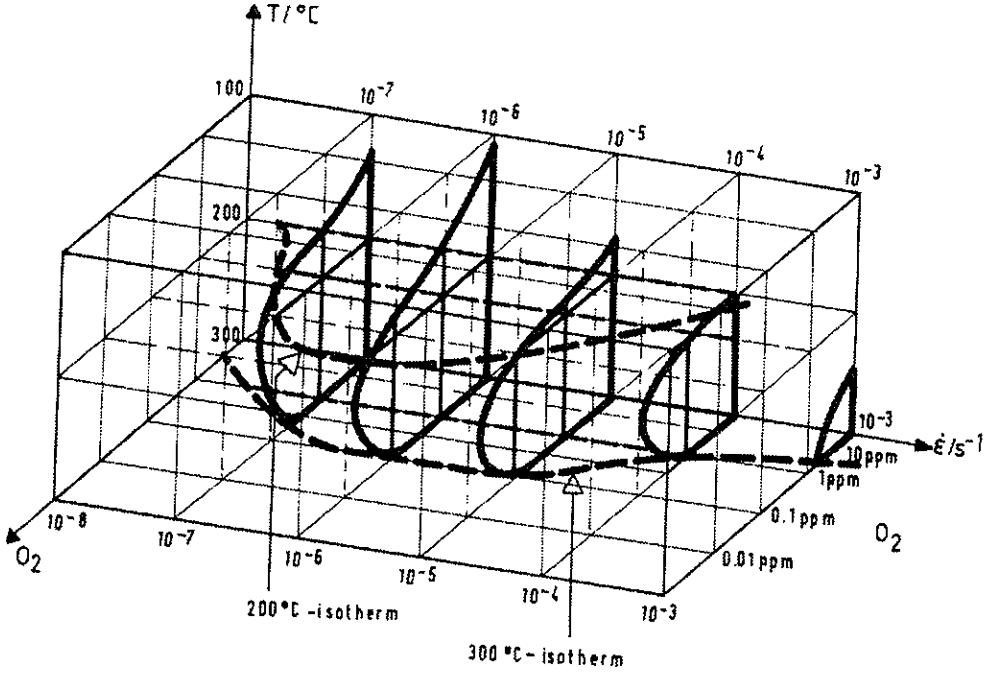


Figure 17: Effect of strain-rate, temperature and oxygen content on SCC/SICC susceptibility of LAS in high-temperature water [11].

In static test with smooth tensile test specimens, crack initiation was only observed at stress levels above the high-temperature yield strength [31, 38], if specimens where exposed to the environment before cessation of the low-temperature creep [38]. No SCC was observed with pre-cracked specimens, which have been loaded in an inert environment and where complete exhaustion of low temperature creep has been allowed to occur prior to the exposure of the specimens to the test environment [29]. These observations are demonstrating again the importance of slow dynamic straining for crack initiation.

The primary design stresses are limited to values below the yield strength R_p (R_p/S, S: safety factor). Therefore, in general plastic yielding in service is only observed at pre-existing defects, in regions of increased (local) stress, and/or for high secondary (thermal) stresses or residual stresses. Dynamic straining primarily arises from dynamic/cyclic external loading (transient LWR operation conditions: thermal and pressurisation cycles during start-up/shut-down, stand-by, thermal fluctuation, stripping or thermal stratification), low temperature creep in highly stressed regions (notches, welding defects, ...) or by the crack growth (pure mechanical (fatigue) or corrosion-assisted) itself.

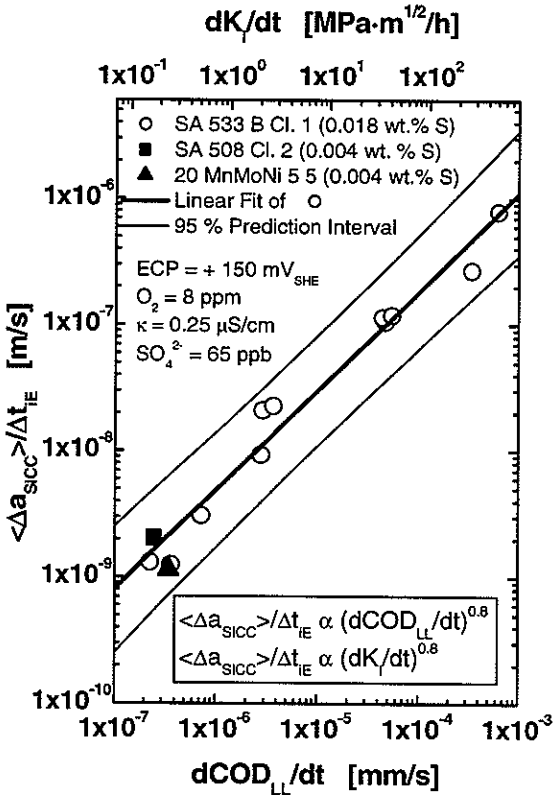


Figure 18: Effect of loading rate ("strain-rate") on SICC crack growth rates [29].

Corrosion-assisted crack growth rate is strongly related to strain-rate. For given environmental and material conditions, the crack growth rate is increasing with increasing strain-rate following roughly a power law (see also Figure 18 and Section 4.1.1). At very high strain-rates no corrosion-assisted crack growth is observed up to the onset of pure mechanical ductile crack growth. Again it is not fully clear at present time, if a lower strain-rate threshold limit for corrosion-assisted crack growth > 0 exists or not. The strain-rate effect may be rationalised by rupture/reformation cycles of the protective oxide film by both anodic dissolution or hydrogen-assisted SCC mechanisms. Dynamic strain ageing may be an alternative explanation or additional contributing factor for the strain-rate dependence of SCC/SICC crack growth.

3.4.2 Stress Intensity Factor Threshold for SCC K_{ISCC}

The stress intensity factor threshold K_{ISCC} for SCC depends on **strain-rate** (initial loading procedure) and on other system parameters such as ECP, temperature, sulphur-content of steel, sulphate concentration of environment, etc. For nominal static loading conditions apparent K_{ISCC}-values from 20 MPa·m$^{1/2}$ to 60 MPa·m$^{1/2}$ [15, 21, 28, 29, 45] have been reported in oxygenated high-temperature water (simulated BWR conditions). Lower thresholds were observed in surface-cracked specimens with significant plastic yielding making K_I-calculations invalid [63]. In slow rising displacement/load respectively J-R-tests at different displacement rates, the lowest K_{ISCC}-values where cracking has been observed under slow rising loading were ranging from 23 MPa·m$^{1/2}$ to 40 MPa·m$^{1/2}$ [29, 45, 64 - 67] depending on the steel sulphur content and the environmental conditions. The K_{ISCC}-value decreases with decreasing load/strain-rate [29]. It is not yet clear if K_{ISCC} saturates or increases again at very low strain-rates [29]. At very high loading rates crack initiation occurs at K_{IJ} without any remarkable environmental effect [64 -67].

In oxygenated high-temperature water of high and moderate purity SCC crack initiation with minor cracking and subsequent crack arrest has been observed above 20 to 30 MPa·m$^{1/2}$, whereas sustained (with respect to operational time scales) SCC crack growth has only be observed above 40 MPa·m$^{1/2}$ to 60 MPa·m$^{1/2}$ [17, 28, 29, 90]. In oxygenated high-temperature water with high impurity levels (SO_4^{2-} + Cl^- ≥ 500 ppb) under low-flow or quasi-stagnant conditions, sustained cracking has been observed down to stress intensity factors of 20 – 30 MPa·m$^{1/2}$ [15, 21, 45]. Under reducing PWR conditions no SCC crack growth was observed up to very high K_I-values near to 100 MPa·m$^{1/2}$ or to K_{IJ} [16, 68].

3.5 Material Parameters

3.5.1 Steel Sulphur-Content, MnS-Inclusions

The sulphur content of the steel, the size, type (chemical composition), morphology and spatial distribution of MnS-inclusions are the material parameters having the strongest effect on SCC/SICC susceptibility [14, 16, 22-24, 34-35, 84, 86, 91-96]. It has been shown that EAC initiation [36 –38, 97, 98], EAC growth [12 –14, 16, 34, 35, 97, 98] and the pitting behaviour [116 - 118] of LAS are affected by the presence of MnS-inclusions.

Although the majority of the embedded inclusions appear to be mainly MnS, few of them are stoichometric MnS, and some inclusions are FeS or mixed (Mn,Fe)S. The variations in sulphide compositions may be related to the steel-making process [119], and different sulphide compositions may produce different levels of electrochemical attack [120 - 122]. MnS is readily soluble in acidic water, FeS and NiS are somewhat less soluble, and CrS is „sparingly" soluble [123]. The dissolution of embedded sulphides intersected by the growing crack results in sulphide-anions (S^{2-}, HS^-) in the crack-tip environment.

The local sulphur content and morphology of MnS-inclusions depend on the steel making (→ segregation) and fabrication process of the plate (forming: hot rolling, forging,...). and they can significantly differ in large plates [124]. Sulphur strongly accumulates in the liquid phase during the solidification process. MnS is a relatively low melting compound, and hence migrates in the molten state toward the centre of a solidifying ingot. The concentration of sulphides is generally higher in the centre of the plate. In segregation zones local sulphur content can be several times larger than the mean bulk sulphur content [125]. Sulphides tend to be rod-like in unidirectionally-rolled plates, and disk-like in cross-rolled plates, while in forgings the sulphides tend to be more spherical. Modern RPV steels have both a smaller

sulphur content and a more homogeneous sulphur distribution than older ones. The orientation (TL, LT, TS, ...) and location of the specimens may therefore be further important factors and may be an important source of scatter of experimental SCC/SICC data.

It has been reported, that the T-L orientation produces higher CF CGR than the LT orientation which, in turn, produces higher CF CGR than the LS orientation [126], while in an other reference, the rates for the LS, LT and TL orientation were found to be essentially similar [127]. The size and morphology of the MnS-inclusions seem to be as important as the sulphur content itself [16]. Plate-like or rod-shaped sulphides are often reported to be more detrimental than spherical inclusions. This all suggests that steel making process and product form (plate vs. forging vs. weld) may play a role in EAC susceptibility. The low apparent EAC susceptibility of welds is attributed to the very small, uniformly-distributed sulphides, as well as to the compositional differences between wrought steels and welds [16].

As mentioned above, the bulk sulphur content as generally provided on material certifications, is not an optimum indicator of the EAC susceptibility of a given steel. Other attributes (shape, size, ...) may be as least as important as the sulphur content. A promising parameter is the area fraction of MnS-inclusions, which correlated well with the EAC susceptibility of the materials in some investigations [128].

The effects of steel sulphur content are synergistic with environmental variables, such as (sulphur-) anionic impurities in the bulk environment, ECP (dissolved oxygen content) and flow rate. This is believed to be due to the creation of a sulphur-rich crack-tip environment responsible for EAC, which arises from the dissolution of MnS intersected by the crack and by the transport of sulphur-anions by migration/diffusion/convection in the crack enclave. The sulphur-anions can either be present from the dissolution sulphides intersected by the growing crack or they can be present in the water as an impurity. A high steel sulphur content is therefore not a pre-requisite for the occurrence of EAC. The controlling factor is the sulphur-anion concentration at the crack-tip. Further important factors controlling the crack-tip sulphur-anion concentration are the crack growth rate itself (which governs the intersection rate of new, fresh, dissolvable MnS-inclusions) and the dissolution rate of the MnS-inclsuions, which is not well known. The dissolution rate is dependent on temperature, potential and pH, type of sulphide-inclusions and eventually also on their size and shape [84].The effect of MnS-inclusions on EAC and the interrelation between ECP/MnS/bulk sulphur-anion content are discussed in detail in Section 4.1 and 4.2. It has been proposed that a critical sulphur-anion concentration in the crack-tip environment has to be achieved for EAC [84]. A high ECP and/or high sulphur-anion concentration in the bulk environment and low flow rate favour the formation of a sulphur rich crack-tip environment and susceptibility of low sulphur steels can be as high as in high sulphur steels under these conditions.

In smooth specimens SCC/SICC initiation and pitting often occurs at MnS-inclusions which intersect the steel surface [33, 44, 60, 96]. In high sulphur steels generally more MnS-inclusions intersect the steel surface, which increases the probability for crack initiation. Kunyia [31] showed that whilst SICC rates where the same for low and medium sulphur steels, the number of initiation sites was greater in the latter case. Hurst et al. [129] showed that if specimen orientation was such as to maximise access of the environment to the crevice created by decohesion of an outcropping sulphide inclusion, localized SICC could be observed in a stagnant autoclave in nominally deoxygenated conditions. If the MnS-inclusions intersecting the steel surface were removed before starting an SSRT test, no SICC in high-purity water is observed [93]. Under highly oxidizing conditions at low or intermediate temperatures and low flow rate conditions, where pitting and the formation of an aggressive occluded water chemistry is strongly favoured [93, 94], initiation occurs often at

pits and the effect of MnS is less dominant. In pre-cracked specimens, large area of dissolvable MnS-inclusions intersected by the crack plane are available and the restricted mass transport in the crack enclave favours the formation of a high sulphur-anion crack-tip environment. The effect of MnS is less distinct for crack growth than for crack initiation. MnS-inclusions which intersect the pre-crack front are found to be less dominant for the location of crack initiation in pre-cracked specimen than in smooth specimens [29].

SICC/SCC susceptibility is generally decreasing with decreasing steel sulphur content and, higher SICC/SCC CGR are sometimes observed in steels with higher sulphur content. The effect of steel sulphur content is less pronounced for crack growth than for crack initiation, in particular under oxidizing BWR conditions. The critical cracking potential is decreasing with increasing steel sulphur content [34, 35, 60, 62]. In many cases, a high steel sulphur content is significantly extending the range of EAC conditions (ECP, DO, bulk sulphur-anion content, strain-rates, ...) and shifting the thresholds to less severe conditions [16]. For example, lower ECP, smaller bulk sulphur-anion contents and lower strain-rates are necessary to induce EAC in high sulphur materials than in low sulphur ones [16]. If there is a relevant effect of steel sulphur content on SCC/SICC or not, depends on the values and combination of the following interrelated and synergistic system parameters as the ECP, bulk sulphur-anion concentration, flow rate, temperature, strain-rate and crack growth rate. The synergism with other system parameters is one further reason for some apparent disparity concerning the effect of MnS on EAC.

In LCF tests, the effect of sulphur content on fatigue life depends on the DO content of the water. When the threshold conditions are satisfied and for DO content of 1.0 ppm, the fatigue life decreases with increasing sulphur content [100]. Limited data suggest that environmental effects on fatigue life saturate at a sulphur content of 0.015 wt.%. At high DO levels, e.g. > 1.0 ppm, the fatigue life seems to be insensitive to sulphur content in the range of 0.002 – 0.015 wt.% [100]. When any one of the threshold conditions are not satisfied, environmental effects are minimal and relatively insensitive to changes in sulphur content.

Steels with a sulphur-content of less than 0.003 wt.% show a very low susceptibility to EAC crack growth over a wide range of environmental and loading conditions and are often regarded as „immune", but SICC has even been observed in SSRT tests in extremely low sulphur (0.001 wt. % S) forging material in oxygenated high-temperature water at DO > 100 ppb in the temperature range form 150 °C to 250 °C [97, 98]. Furthermore, the low sulphur content results in a higher toughness, larger critical crack sizes and higher safety margins. But the beneficial effect of a low steel sulphur content concerning EAC disappears under strongly oxidising (high ECP) and/or at high bulk impurity levels (high bulk sulphur-anion concentration) or under suitable strain-rate/temperature conditions [29, 216]. Sustained SCC under static loading may be even observed in deoxygenated high-temperature water at very low ECP, if H_2SO_4 is added to the bulk water in high concentrations [46, 86].

3.5.2 Yield Strength R_p, Microstructure

Although, the effect of microstructure on SCC/SICC susceptibility has not yet been systematically studied in low-alloy steels in high-temperature water, the following trends appear:

In contrast to high strength low-alloy steels, where K_{ISCC} is decreasing and crack growth rates are increasing with yield strength [3,4, 48], in low and moderate strength low-alloy steels no distinct effect of the yield strength on both SCC crack initiation and crack growth is observed [3,4] (see Figure 19). As long as sulphur-content, MnS-inclusion morphology and yield strength are similar, the behaviour of carbon and moderate strength low-alloy steels is often

very similar independently if they have ferritic-pearlitc (equilibrium state) or a bainitic microstructure (quenched and tempered). Variations in the EAC behaviour may here primarily arise from a different DSA-response of the materials [131].

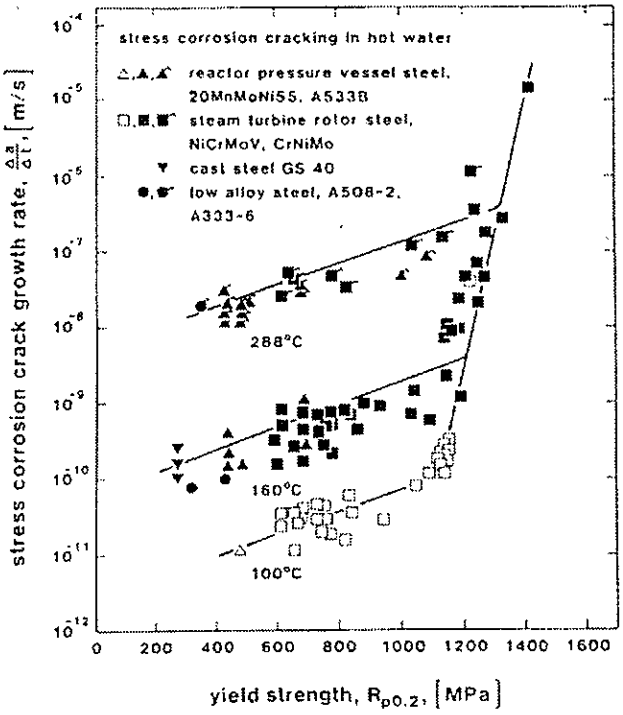


Figure 19: Effect of yield strength on SCC crack growth rates in different LAS [4].

H-assisted (intergranular/transgranular) SCC in high-purity high-temperature water has been observed in high strength LAS with a high yield strength > 800 MPa and high hardness (> 350 VH) at least up to a temperature of 200 °C [18, 48]. The susceptibility is high below 100 °C and increasing with increasing strength level, increasing grain size and decreasing temperature [18, 48]. The low-alloy steels used in LWR for pressure-boundary components have a significantly lower yield strength if they were in the proper material conditions. The peak hardness of the HAZ of welds in LAS components can be limited to values below 350 VH by PWHT and stress relieving. Intergranular/transgranular SCC has been observed in quenched low-alloy RPV steels (with martensitic/bainitic microstructure) which have been austentitized at high temperatures with significant austenite grain growth [130, 131]. A higher SCC susceptibility may therefore be postulated for the peak hardness coarse-grain region of weld heat affected zones, especially if welding and post weld heat treatment have not been properly carried out or in the case of repair welding [17].

3.5.3 Dynamic Strain Ageing, Free Nitrogen and Carbon Content in Steel

DSA effects on EAC are discussed in detail in Section 4.1.3. Atkinson et al [132 - 134] have suggested recently that dynamic strain ageing (DSA) in steel, which manifests itself as discontinuous, inhomogeneous yielding, but reduced overall ductility [135], may be very influential in determining both EAC cracking strain-rate sensivity and its temperature dependence. It provides an alternate possible explanation for strain-rate thresholds and more significantly, it may offer an explanation for the cracking peak at intermediate temperatures and rationalize the scattered data in this temperature range (see also Section 3.3.1). Furthermore it may provide a possible explanation for the observed quasi-cleavage fracture surface observed in EAC.

DSA response of LAS is governed by the concentration of free interstitials such as nitrogen and carbon. Nitrogen seems to cause more severe DSA than carbon, since its residual solubility at room temperature is greater than that of carbon and its tendency for complete precipitation during slow cooling is smaller. The free carbon and nitrogen content are not specified in the relevant nuclear guidelines and regulations (KTA, ASME BVP) for the low-alloy LWR primary pressure-boundary component steels. The free nitrogen and carbon content may relevantly depend on the steel making (killing) and welding process respectively on the heat treatments applied. Silicon killed, air poured carbon or low-alloy steels show a much more pronounced DSA effect than aluminium killed vacuum ladle degassed steels, since in aluminium killed steels, aluminium nitrides are formed and the remaining free nitrogen content is very low. The Al/N-ratio is therefore an important parameter governing the free N content respectively the resulting DSA effect. Weld metal often have a very little Al content and eventually can uptake small amounts of nitrogen during the welding process which are not properly performed. Therefore welds might be more susceptible to EAC than generally thought so far. The free carbon and nitrogen content in low-alloy steels can be varied by the heat treatment. Therefore also weld HAZ might show more pronounced DSA effects than the base metal. Since the free Nitrogen content is not specified, it can vary between 0 ppm and the solubility limit (or even higher in the supersaturated state). Differences in free nitrogen and carbon content of otherwise identical or similar low-alloy steels may be one important further reason for the relevant scatter of EAC crack growth rate data, and especially for the sometimes observed different trends in temperature dependence of EAC.

3.6 Incubation Period

Long incubation periods could feign a low SCC susceptibility in short-term tests if the test duration is shorter than the smallest incubation periods. In particular, this aspect is of relevance for BWR conditions, where only few long-term experiments >> 1000 h exist [26, 69]. Some extremely high incubation periods (> 1 year) for pre-cracked specimens have been reported under PWR conditions for pre-cracked specimens [70]. Thus, extremely long incubation periods cannot be completely ruled out based on relatively short-term experiments. Otherwise, it has to be considered, that many tests with pre-cracked specimen started with a growing crack by SICC or CF by dynamic or cyclic loading and SCC cracking susceptibility under subsequent static loading was extremely low. At this point, the world-wide accumulated operating experience of uncladded low-alloy pressure-boundary components over many decades and the cracking incidents in BWR feedwater nozzles does not support the view of long incubation periods/high SCC growth rates (see Section 5).

3.7. Quantitative SCC/SICC Crack Growth Rate Data

3.7.1 SICC Crack Growth Rates

Under suitable dynamic/cyclic loading conditions maximum SICC crack growth rates can reach up to 10^{-6} m/s in oxygenated high-purity high-temperature water. The SICC crack growth rates decrease with decreasing strain-rate (see Figure 18) following approximately a power law relationship [136]. High SICC CGR of 10^{-9} to $8 \cdot 10^{-7}$ m/s were observed in the loading rate range dK_I/dt of 0.1 to 500 $MPa \cdot m^{1/2}/h$ for ECP ≥ 150 mV_{SHE} and K_I-values > 30 $MPa \cdot m^{1/2}$ [136]. Under low-flow and highly oxidizing conditions SICC CGR in the range of $5 \cdot 10^{-10}$ to $5 \cdot 10^{-8}$ m/s were observed under (very) low-cyclic loading conditions at frequencies < 10^{-3} Hz [136].

3.7.2 SCC Crack Growth Rates and K_{ISCC}

In oxygenated high-temperature water, SCC plateau crack growth rates of 10^{-8} m/s up to 10^{-7} m/s have been observed under pure static loading under highly faulted water chemistry conditions (high concentrations of specific anionic impurities > EPRI action level 3) and/or for highly stressed specimens either loaded near to K_{II} or with a high degree of plasticity in the remaining ligament [15, 21, 29, 45]. For nominal static loading conditions K_{ISCC}-values from 20 MPa·m$^{1/2}$ to 60 MPa·m$^{1/2}$ [15, 21, 28, 29, 45] have been reported for simulated BWR conditions. In oxygenated high-temperature water of high and moderate purity SCC crack initiation with minor cracking and subsequent crack arrest has been observed above 20 to 30 MPa·m$^{1/2}$, whereas sustained (with respect to operational time scales) SCC crack growth has only be observed above 40 to 60 MPa·m$^{1/2}$ [17, 28, 29, 90]. In oxygenated high-temperature water with high impurity levels (SO_4^{2-} + $Cl^- \geq 500$ ppb) under low-flow or quasi-stagnant conditions, sustained cracking has been observed down to stress intensity factors of 20 - 30 MPa·m$^{1/2}$ [15, 21, 45]. Under reducing PWR conditions no SCC crack growth was observed up to very high K_I-values near to 100 MPa·m$^{1/2}$ or to K_{II} [16, 68].

Figure 20 shows a compilation of experimental results on corrosion-assisted crack growth rates under static loading conditions in low-alloy pressure-boundary component steels in oxygenated high-temperature water at 288 °C/240 °C [4, 12, 15, 18 -26]. Additionally, an upper bounding line according to Speidel [15] and an envelope of newer results of MPA Stuttgart [23] are shown. Also included in Figure 20 are the „low sulphur" and „high sulphur line" due to the work of Ford et al. [4] taking both into account mechanistical considerations based on the film rupture/anodic dissolution mechanism and the SCC data base, as shown in the diagram. The tremendous scatter of 3 to 5 orders of magnitude under nominally identical, or at least similar testing conditions makes rational life prediction impossible and has therefore led to divergent assessments on the possible effect of SCC on the RPV structural integrity.

Many tests revealing the high crack growth rates plotted in Figure 20 have been performed under a combination of both gross yielding of the remaining specimen ligament, which is not relevant to the thick-walled RPV structure, and aggressive water-chemistry conditions, which are not representative of current BWR operation practice [17]. Attempts have been made to reduce this tremendous scatter by data reduction methods, taking into account the different quality and performance of the experiments [41]. It was shown that, in older investigations, system parameters having a strong influence on crack growth were neither sufficiently controlled and monitored, nor documented. Thus, the transferability and relevance of these data to pressure-boundary components and to BWR power operation conditions cannot be satisfactorily evaluated. Consequentially, assessment of the different data quality [41] clearly revealed a need for further experimental parameter studies, since only a few, well-characterised and reproducible experiments, which fulfil current quality requirements on testing [137, 210], have been reported in the literature.

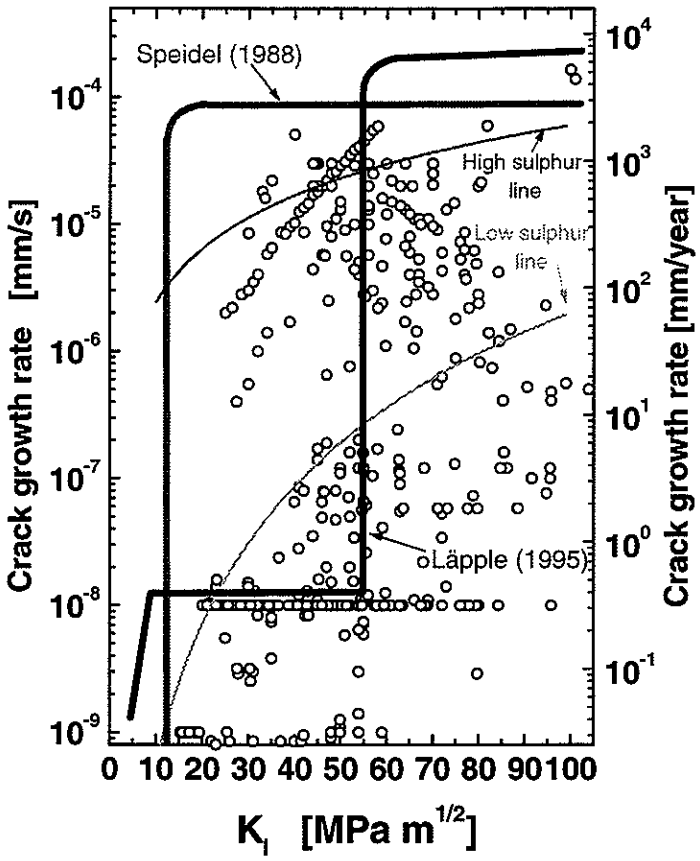


Figure 20: Compilation of literature data on apparent SCC crack growth rates of low-alloy, pressure-boundary-component steels in oxygenated, high-temperature water at 288 °C/240 °C ("simulated BWR conditions"). Additionally an upper bounding line according to Speidel [15] and an envelope of results from MPA Stuttgart [23] are plotted.

In contrast to faulted BWR conditions, a very low SCC susceptibility and very slow SCC growth rates (< 600 µm/a) up to high K_I-values of 50 – 60 MPa·m$^{1/2}$ have been observed under more realistic conditions in reactor site testing in autoclave systems attached to the primary coolant system of BWR (ABB, GE [25, 26]) and in recent experiments in modern high-temperature loops with water refreshment, on-line crack growth monitoring and documentation of all relevant test parameter (MPA [28], PSI [29, 138], European Round Robin [30]). From these investigations and the reassessment of all available literature data by an international group of experts [25, 26], it is now more and more apparent that the „low sulphur line" of the General Electric model (see Section 4.1 and Figure 22)

$$\text{„Low- sulphur line":} \quad da/dt\ [m/s] = 3.29 \cdot 10^{-17} \cdot K_I^{\,4}\ [MPa \cdot m^{1/2}]$$

can be regarded as a conservative upper bound for possible SCC crack growth rates under current stationary BWR operating practice at temperatures around 288 °C and static loading conditions. In those cases were sufficient background information on testing characteristics was available ("assessable data"), the "low-sulphur line" in fact either bounded all of these data points or plausible reasons for the deviations form this behaviour based on the accumulated well accepted experimental and theoretical EAC background knowledge for the system LAS/high-temperature water could be given (see section below). Relevant additional dynamic loading is necessary to maintain "low-sulphur" crack growth rates if water

chemistry conditions were maintained within current BWR operation practice to some extent. Otherwise crack arrest was observed under purely static loading. Very recent preliminary test results [131] arise the question concerning the conservatism of the "low-sulphur line" at lower intermediate temperatures (200 – 250°C) in susceptible materials (DSA?) and for small load fluctuations at very high load-ratios (R > 0.95) near to fatigue thresholds ΔK_{th}.

3.7.3 Possible Reasons for Data Scatter and High SCC Crack Growth Rates

The typical inherent scatter of SCC CGR under constant, reproducible test conditions is typically within one order of magnitude. Slight differences in the test design and operating practice are some of the most important reasons for the large scattering of literature SCC data in Figure 20 [14, 137]. Much of the observed scatter is due to primarily an inadequate definition of system and due to a high sensivity of the propagation rate to small uncontrolled or unmonitored changes in some of the system parameters [137]. Other possible reasons for inherent data scatter have been discussed in the preceding parts of this section.

Much of the observed scatter in Figure 20 can be attributed to one or several of the following interrelated factors:

1. Strain-rate effects:

External loading, crack growth (corrosion-assisted or fatigue) and low temperature creep may contribute to maintain a positive, tensile (crack-tip) strain-rate and therefore strongly affect the SCC growth behaviour (see Section 4.1.1). The strain-rate at the beginning of the experiment may be > 0 or virtually zero depending on test procedure:

- different initial loading procedure: initial loading rate, initial loading: in test environment vs. in air [14, 29, 138].
- significantly different test durations: especially in short-term tests crack growth is significantly overestimated under static loading [28, 29, 138]
- start of test with actively growing EAC crack (pre-cracking in autoclave, change from high too low SCC CGR conditions)
- SSY vs. gross ligament yielding: Many tests were performed with significantly overloaded specimens (gross ligament yielding), where small scale yielding conditions evidently do not prevail [29]. Under these conditions a sustained crack-tip strain-rate may be maintained by low temperature creep. Many tests were performed under conditions where the onset of pure mechanical ductile crack growth cannot be excluded in air (loaded near to the plastic limit load of the material or to K_{II}). In many of these tests, crack growth mechanism (TGSCC vs. ductile) has not been verified by post-test fractography in the SEM.
- pure static loading vs. periodical partial unloading, ripple loading, slow monotonically rising load: This aspect can be attributed at least in part to the term SCC which can be understood either in a narrow sense (EAC under purely static mechanical loading) or as part of the broader spectrum of EAC (including the transition to SICC and low-cycle corrosion fatigue) [20, 25].
- constant load vs. constant displacement [138].
- different pre-cracking procedure (in air vs. in autoclave).
- too short test period after transition from high too low SCC CGR conditions.

2. ECP, flow rate, specific impurities

- relevant difference in ECP in spite of similar DO at inlet, because of different flow rates, designs of autoclaves and inadequate electrical isolation of specimens. In older tests ECP is often not specified.
- specified DO and conductivity at inlet do not represent the real electrochemical and water chemistry conditions near the specimen surface (large differences between DO and conductivity in inlet and outlet in some older investigations), especially under quasi-stagnant or very low-flow conditions in large autoclave systems.
- flushing of crack-tip electrolyte under high flow rate conditions (see Section 4.4.5)
- inadequate controlling of environmental parameters (static autoclaves) respectively water chemistry conditions which were not representative for current BWR operating practice (quasi-stagnant, > 1.0 µS/cm, ≥ 1 ppm Cl^- + SO_4^{2-}).
- different type and concentration of impurities in spite of similar inlet conductivities.

3. Material parameters:

- material state which is not representative for LWR primary pressure-boundary components (as specified in the nuclear regulations) (significantly different strength level, hardness, microstructure or heat treatment).
- steel sulphur content, spatial distribution and morphology of MnS, DSA (N/Al).

4. Crack length measurement aspects:

- inadequate determination of crack advance: generally the combination of suitable on-line crack growth measurement methods (DCPD, ..) with fractographical analysis by SEM (inclusive removement of the oxide film) is necessary for reliably assessing the SCC crack growth behaviour, otherwise relevant error can be produced [29, 138].
- $\Delta a_{EAC} \leq$ grain diameter, resolution limit of crack length measurement, cyclic plastic zone size.
- no clear indications for EAC often in connection with too small test duration.

5. Transition CGR, which are not representative for specified testing conditions:

- (unsteady) transition crack growth behaviour after changes of system parameters, too short test duration in multiple parameter tests after change of system parameters.
- memory/hysteresis effects because of water chemistry and DO transients (Section 4.4.4).
- crack retardation/acceleration because of crack closure effects after mechanical transients.

4. Mechanistical Aspects of EAC of LAS

The following discussion is focused to the crack growth from incipient, mechanically and microstructurally long cracks. The dominant effect of crack-tip strain-rate and crack-tip chemistry and the influence of MnS-inclusions and the content of free nitrogen and carbon in the steel will be explained in Section 4.1 by the most popular crack growth models. In Section 4.2 it will be briefly shown how local crack-tip chemistry is related to the bulk chemistry outside the crack enclave by the different mass transport mechanism (diffusion, migration, convection) and to the local metallurgy and microchemistry in the steel by the dissolution of the MnS-inclusions.

4.1 Crack Growth Mechanisms

EAC mechanisms have been the topic of many reviews [6, 20, 139 - 144] and have been recently discussed with their relevance to LAS in high-temperature water [140, 142 - 144]. It is in the view of many authors (e.g.[20]), that there is a common mechanism for transgranular EAC of LAS under LWR conditions, in the sense that corrosion fatigue and stress corrosion cracking are fundamentally related phenomena and governed by the same processes. In the following, it will not be differentiated between corrosion fatigue and stress corrosion cracking, if not necessary.

For the case of low-alloy steels in high-temperature water, the following potential cracking mechanism have been mainly discussed in literature:

- Film rupture/anodic dissolution (FRAD) (Section 4.1.1)
- Hydrogen-assisted EAC (HAEAC) (Section 4.1.2)
- Dynamic strain ageing (DSA) (Section 4.1.3)

The controlling factors in EAC of LAS are phenomenologically well known but the direct experimental evidence for a specific microscopic crack extension process is still very weak. The exact crack growth mechanism is therefore still under discussion. None of the proposed mechanism can satisfactorily explain all experimentally observed cracking aspects. Currently, the observed cracking behaviour can be best rationalized by a combination of these three fundamental cracking mechanism. At lower temperatures (< 100 °C) and/or high strength levels (R_p > 800 MPa) hydrogen effects are more pronounced. At high temperatures (≥ 150 °C) and/or lower yield strength levels (R_p < 800 MPa) anodic dissolution seems to dominate. Under certain combinations of temperature and strain-rate dynamic strain ageing may give an additional contribution to the crack growth in susceptible materials with a high concentration of interstitial nitrogen and carbon.

4.1.1 Film Rupture / Anodic Dissolution Mechanism (FRAD)

The quantitative EAC crack growth models (GE-model [20], CEFM [145-146]) in the system LAS/high-temperature water are all based on the film rupture/anodic dissolution mechanism:

In high-temperature water, a protective oxide film is formed on low-alloy steels which delays or suppress further corrosion attack and acts as a diffusion barrier for retarded hydrogen uptake. The brittle oxide film can rupture by plastic straining at the crack-tip. Bare metal is then exposed to the crack-tip electrolyte. Consequently, accelerated local anodic metal dissolution can take place, which finally leads to corrosion-assisted crack growth. The anodic dissolution is stopped by the reformation of the protective oxide film (repassivation). These two processes are strongly dependent on the aggressivity of crack-tip water chemistry. The

crack-tip chemistry itself is related to the bulk water chemistry outside the crack enclave by mass transport processes and to the dissolution of MnS-inclusions respectively the exposure of fresh MnS-inclusions by crack growth. For a sustained corrosion-assisted crack growth repeated rupture of the protective oxide and therefore sustained crack-tip straining is necessary.

The relevant parameters in this model are therefore the crack-tip strain-rate, the oxide film rupture strain and the dissolution/repassivation behaviour, which strongly depends on the crack-tip chemistry. The following discussion is primarily based on the GE-model [20]:

Film rupture occurs, if the crack-tip strain reaches the rupture strain of the oxide. Currently, no information on the films formed during active crack growth in these steels in high-temperature water are available. There is limited information on the crack-tip chemistry from micro-sampling [46, 86, 147] and crack-tip ECP measurements [148, 149]. Based on the crack-tip chemistry (ECP, pH) conditions extrapolated from these investigations, it is expected, that the oxide formed at the crack-tip is basically magnetite Fe_3O_4. Informations on the film rupture strain are basically arising from different experimental measurements under simulated crack-tip chemistry conditions. The pre-oxidation, test conditions and measurement method may affect the measured oxide film rupture strains, which were ranging from to 0.01 to 0.5 % [150 - 155].

With increasing crack-tip strain-rate, the oxide film ruptures more frequent and crack growth rate increases. The crack growth rate is therefore strongly dependent on crack-tip strain-rate:

$$\dot{a} = f(\dot{\varepsilon}_{CT}) \quad (1)$$

Sources of dynamic crack-tip straining arise from dynamic/cyclic external loading, low temperature creep and the crack growth into less strain-hardened regions itself. Corrosion-deformation interactions and strain localisation by DSA may be further sources of crack-tip strain-rate. Under static loading conditions the crack growth itself and the low temperature creep are the major source of crack-tip strain-rate.

In general, crack-tip strain-rate depends on stress intensity factor level and rate as well as on the crack growth rate. The stress intensity factor rate and crack growth rate, in turn, depend on crack-tip strain-rate again:

$$\dot{\varepsilon}_{CT} = f[\dot{K}_I(\dot{P}, \dot{a}(\dot{\varepsilon}_{CT})), K_I(P,a), \dot{a}(\dot{\varepsilon}_{CT})] \quad (2)$$

The following simplified relationships for cyclic, slow rising and static load reflect the different basic sources of crack-tip strain-rate:

Cyclic load/rising load: $\dot{\varepsilon}_{CT} = A \cdot \dot{K}_I + B \cdot \dot{a}$ (3)

Static load: $\dot{\varepsilon}_{CT} = C \cdot \dot{\varepsilon}_{creep} + D \cdot \dot{a}$ (4), where $\dot{\varepsilon}_{creep} = f(K_I)$ (5)

In all cases, crack growth itself may significantly contribute to the crack-tip strain-rate. Both EAC crack growth rate and strain-rate depend on each other and are not independent. Depending on their exact values, the crack growth rate term or the left term in equation (3) and (4) may dominate under certain conditions.

After film rupture, the crack grows by directed anodic dissolution of the new fresh bare crack front. Dissolution current and crack advance are directly related by the Faraday law. The crack growth is stopped by the nucleation and reformation of the protective oxide film. Both the anodic dissolution and repassivation are strongly dependent on the composition of the crack-tip electrolyte. Repassivation measurements under simulated crack-tip conditions

indicate that dissolution and repassivation kinetics are strongly affected by both anionic sulphur species as sulphate or sulphides and by pH [20, 23, 154, 155]. High concentrations of sulphur-anions (SO_4^{2-}, HS^-, S^{2-}) relevantly retard repassivation and increase therefore the crack advance by anodic dissolution between two film rupture events. Based on the measured film nucleation and growth kinetics, two limiting conditions, the so-called low and high sulphur behaviour can be defined (equations 6 and 7). Below 20 ppb fast repassivation occurs and the repassivation is not dependent on sulphur activity. Above 2 ppm repassivation is significantly retarded and not dependent on sulphur activity. Between 20 ppb and 2 ppm retardation of repassivation increases with increasing sulphur-anion activity. The crack propagation rate/ crack-tip strain-rate relationships are therefore bounded by two limiting algorithms:

"Low sulphur activity (< 20 ppb S^{2-})": $\dot{a} = N \cdot \dot{\varepsilon}_{CT}^{\ 1}$ (6)

"High sulphur activity (>2 ppm S^{2-})": $\dot{a} = L \cdot \dot{\varepsilon}_{CT}^{\ 0.35}$ (7)

The dissolution of the MnS-inclusions which are intersected by the pre-existing crack and which will be exposed to the electrolyte by the crack growth itself and the concentration of sulphur-anions in the bulk environment outside the crack are the major sources of sulphur-anion species in the crack-tip environment. The crack-tip environment is related to the bulk environment by mass transport process (diffusion, migration convection) and it is also dependent on the crack growth rate itself. The local sulphur activity in the crack-tip environment is governed by a system of interrelated corrosion system parameters such as the applied load, strain or loading rate, the ECP or dissolved oxygen content, the bulk concentration of specific anionic impurities as SO_4^{2-} and the steel MnS-inclusion content and morphology (see Section 4.2). A high ECP, high bulk sulphur-anion concentration, quasi-stagnant or low flow rate, a high steel sulphur content and a long pre-existing crack with a large area of dissolvable MnS-inclusions favours the formation of sulphur-anion rich crack-tip environment.

The precise crack propagation rate/crack-tip strain-rate relationships can be more complicated than equations 6 and 7, since the propagation rate will depend on the specific dissolved sulphur-anion activity that is maintained at the crack-tip. This, in turn, depends on the crack growth rate (exposure rate of new fresh dissolvable MnS) itself and on the mass transport in the crack enclave, which will govern the transition between the "low" and "high sulphur line" (see Figure 21 and 22). Transition lines form the low to the high sulphur behaviour can be established for different ECP, flow rates and sulphur contents of the steel [20, 156- 158].

Figure 21 shows the relationship between EAC crack growth rate and crack-tip strain-rate in the GE-model [20]. The lower crack-tip strain-rate threshold is related to the blunting of the crack-tip by corrosion, since crack growth rates are in the same order as corrosion rate perpendicular to the crack plane. At high strain-rates > 10^{-3} to 10^{-2} s^{-1}, crack growth is either dominated by pure mechanical fatigue without any relevant environmental effect in the case of cyclic loading or gets independent of crack-tip strain-rate (continuous dissolution). If crack-tip strain-rate is high enough there is no environmental effect or acceleration of crack growth since there is not enough time for corrosion processes.

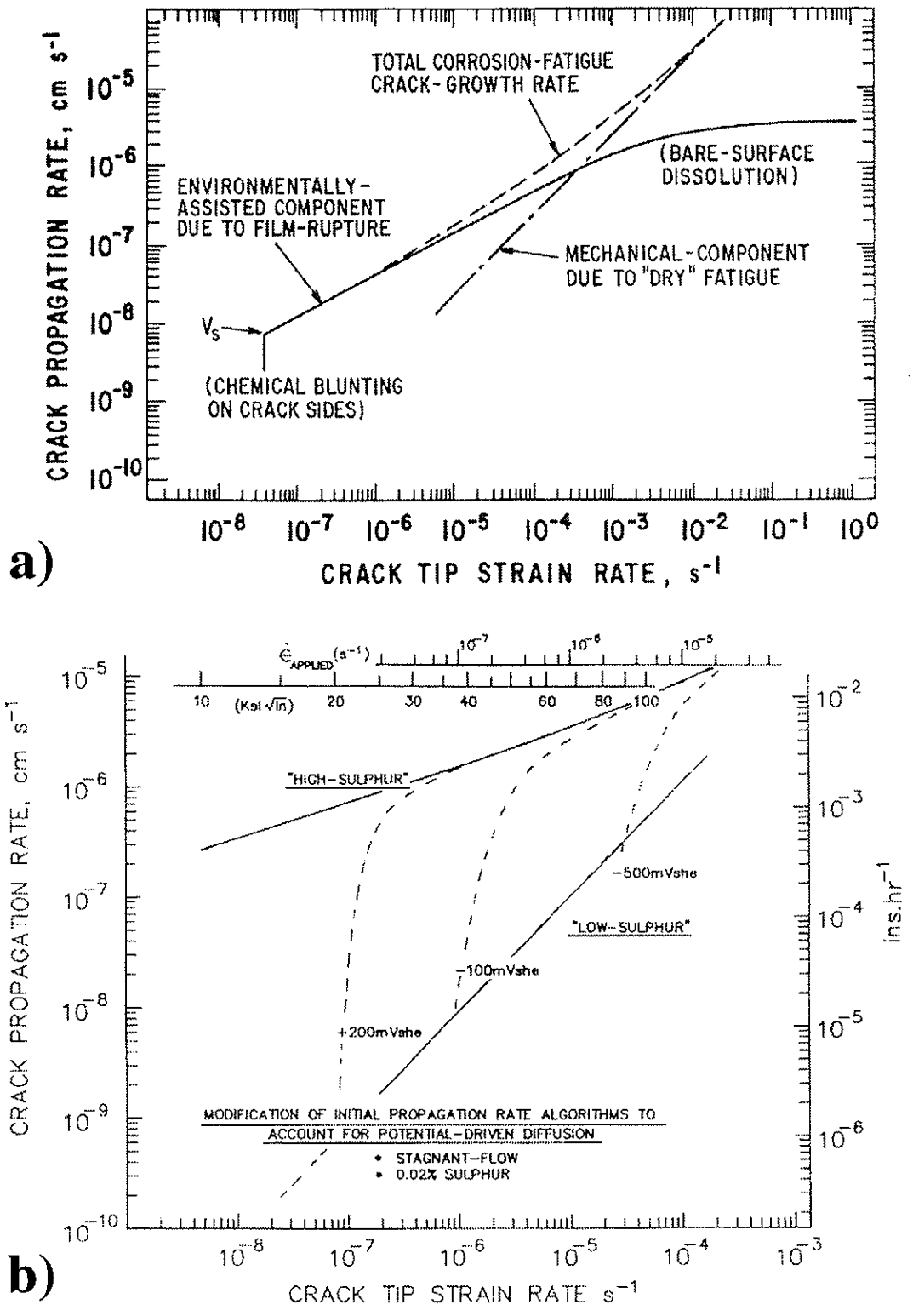


Figure 21: Schematic of relationship between EAC crack growth rate and crack-tip strain-rate in the GE-model (a). In (b) the low sulphur and high sulphur line and transition curves for different ECP are shown for a steel sulphur content of 0.020wt.%.

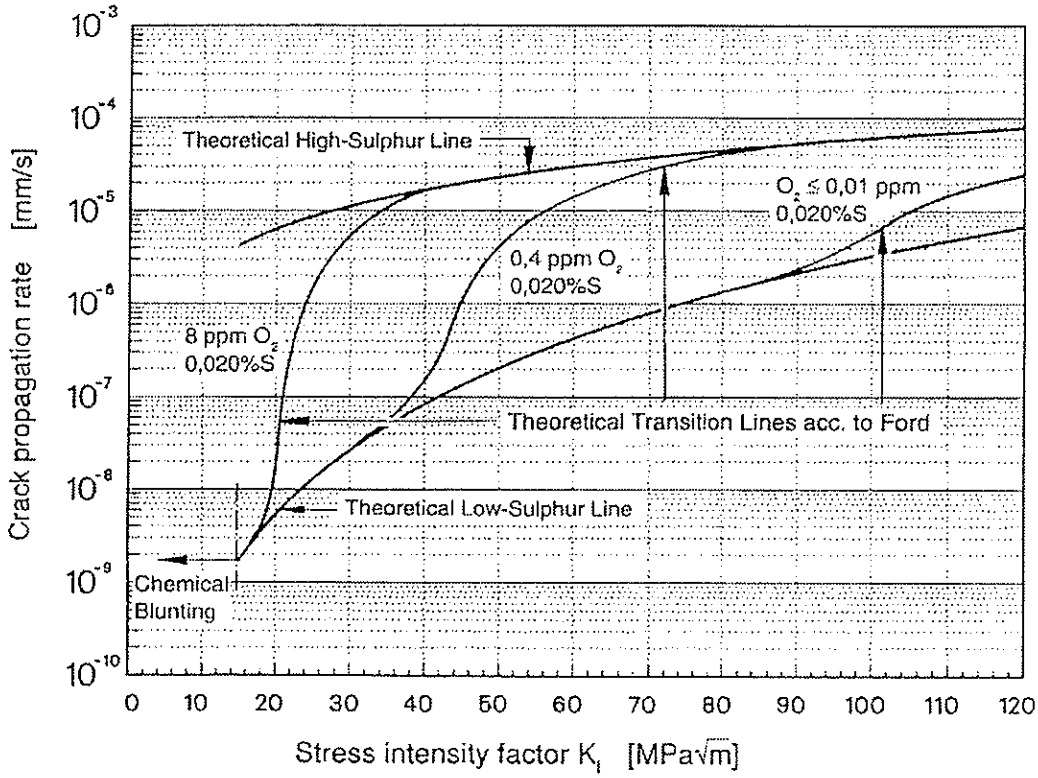


Figure 22: Relationship between SCC CGR and applied stress intensity factor according to the GE-model. Transition curves for different DO are shown for a steel sulphur content of 0.020 wt.%.

The extent of EAC cracking is crucially dependent on maintaining a positive crack-tip strain-rate and a high sulphur-anion activity in the crack-tip environment [20]. Sustained fast EAC crack growth occurs, if a complex balance between interrelated factors as crack growth rate, crack-tip strain-rate, exposure and dissolution of fresh MnS-inclusions respectively crack-tip water chemistry is maintained. If this balance is disturbed, the corrosion-assisted cracking may be arrested or locally pinned. Cessation of EAC growth may be especially observed under static loading conditions, in particular in high purity high-temperature water and a steel with a low sulphur content and at low stress intensities. Here, the corrosion-assisted crack advance may be not large enough to significantly contribute neither to crack-tip strain-rate nor to build-up and to maintain an aggressive crack-tip electrolyte by exposure and by dissolution of new and fresh MnS-inclusions. Thus under static loading and high purity water conditions, the crack-tip strain-rate may be predominantly governed by the low temperature creep effects:

Static load and $\dot{a} \rightarrow 0$: $\dot{\varepsilon}_{CT} = C \cdot \dot{\varepsilon}_{creep}$ (8)

where

$\dot{\varepsilon}_{creep} = M \cdot K_I^{\,n} \cdot t^{-1}$ (9)

Therefore, SCC crack growth rate may decay with a reciprocal time law under static load a short time interval after initial loading.

$\dot{a}_{SCC}(t) \propto t^{-1}$ (10)

In fact, such a behaviour has been experimentally observed in constant load tests at PSI [138] and MPA Stuttgart [28].

4.1.2 Hydrogen-Assisted EAC (HAEAC)

The role of hydrogen in EAC of LAS under LWR conditions has been widely discussed for two decades since hydrogen is always present in LAS in high-temperature water. Because hydrogen-assisted EAC and film rupture/anodic dissolution mechanism (FRAD) are both thermodynamically and kinetically viable under crack-tip conditions relevant for LAS under LWR conditions, there has been a long debate which mechanism might be active under these conditions.

4.1.2.1 Sources of Hydrogen in LAS under LWR Conditions

Under LWR conditions the dissolved hydrogen in the coolant is the main source of hydrogen. A further relevant source may arise from corrosion reactions (e.g. hydrolysis of metal cations from anodic dissolution, dissolution of MnS-inclusions). Transmutation is not relevant. Hydrogen atoms are generated electrochemically on the metal surface as a partial reaction of the corrosion process (hydrogen reduction for pH smaller than neutral or water reduction for pH greater than neutral). Hydrogen entry and permeation through oxide films occurs relatively rapidly with respect to the observed cracking kinetics. Hydrogen is therefore always present in LAS in high-temperature water and concentrations of several ppm have been measured.

4.1.2.2 Effects of Hydrogen [see references in 20, 140 –144, 160 – 163]

The main characteristics of atomic hydrogen in metals are its small solubility and its large mobility, which favours its segregation, its large molar partial volume, which makes it sensitive to stress fields, and its large electronic interaction, modifying the electronic environment of the atoms of the metal and their cohesive energy which may affect the dislocation motion (Peierls potential) and the rupture behaviour (cleavage). These phenomena make hydrogen to segregate at trap centres such as impurities, vacancies, precipitates, dislocations, grain boundaries, inner surfaces (voids) and to regions of large hydrostatic stress, and to contribute to the embrittlement properties of hydrogen. Depending on their binding energy of hydrogen, weak (impurities, elastic interactions with dislocations) and strong traps (dislocation cores, phase and grain boundaries, internal surfaces) can be differentiated. Because of thermal activation, the trapping efficiency is decreasing with increasing temperature. Hydrogen embrittlement effects are therefore generally only observed at low temperatures ($\leq$ 100 °C). Above 300 °C hydrogen trapping is no more active.

Because of its segregation tendency, low concentrations of hydrogen are sufficient to cause embrittlement. If a critical hydrogen concentration over a critical volume is achieved, cracking may occur. Critical concentrations of hydrogen are mainly achieved in regions of high lattice defect/trap site density and/or of high triaxial stress (crack-tip, ...). Crack advance therefore often occurs along phase or grain boundaries or regions of high dislocation density. It is well accepted that HE may occur and there is a strong „macroscopic" experimental evidence for that whereas the picture on the underlying microscopic mechanism is still unclear and very confusing. A plenty of different mechanism have been proposed in literature, which can be roughly classified to hydrogen related phase change mechanism, hydrogen enhanced local plasticity mechanism and hydrogen effects on cohesive energy. The direct experimental evidence for most of them is still very weak. The hydrogen transport and embrittlement mechanism are very sensitive to the microstructure, micromechanics and plasticity and depend on several parameters such as, for example, the chemical composition, the microstructure and the thermal and mechanical history of the material.

Hydrogen may pin dislocations and increase the stress required for dislocation motion. The dislocation network may act as strong traps for hydrogen. On the other hand it has also been reported, that hydrogen can locally enhance the mobility of dislocations, which are thereby also a very efficient transport mechanism of hydrogen into the metal. Hydrogen transport and trapping by dislocations are competing to a certain extent. The transport of hydrogen by mobile dislocations during plastic deformation can be 10^3 -10^6 times larger than by normal diffusion and is dependent on the dislocation velocity respectively strain-rate. The hydrogen transported by dislocations may be trapped at internal surfaces or precipitates and result in high local concentrations. Under certain temperature/strain-rate combinations, the velocity of mobile dislocations can be similar to the diffusion rate of hydrogen and dynamic strain-rate effects (Portevin - Le Chatelier effect) might eventually be observed. Hydrogen trapping and transport by dislocation may give an interesting alternate explanation for the importance of (micro-)plasticity, for strain thresholds and for the strain-rate dependence of EAC.

4.1.2.3 General Aspects of HAEAC in Aqueous Environments

Hydrogen embrittlement and HAEAC mechanisms are usually associated with high strength alloys because of the ease of attainment of high triaxial respectively hydrostatic stress conditions in front of the crack-tip and, thereby, the thermodynamic possibility of hydrogen supersaturation in this region. Once this supersaturation is achieved then localized crack initiation and propagation can occur by a variety of rupture mechanisms, e.g. hydrogen gas rupture, hydrogen absorption (surface energy), decohesion, brittle hydride phase formation, martensite formation and hydrogen enhanced local plasticity.

Models of cracking associated with hydrogen atoms have to take into account the electrochemical kinetics of hydrogen atom generation, the absorption of hydrogen atoms, the transport and localisation of hydrogen atoms in the metal, the interaction of material with the absorbed hydrogen under conditions of localised stress and strain, i.e. the mechanism of hydrogen embrittlement. The subcritical crack propagation rate due to hydrogen embrittlement in aqueous environments depends on a sequence of events in the following order (see Figure 23 and 24):

1. Diffusion of a reducible hydrogen-containing species, (e.g. H_3O^+) to the crack-tip region.
2. Reduction of the hydrogen-containing ions to give adsorbed hydrogen atoms.
3. Absorption of hydrogen adatoms followed by interstitial diffusion or dislocation transport of these hydrogen atoms to a „process" zone at a distance, X, in front of the crack-tip.

Each of these steps may be rate controlling. In most models it is assumed, that once the hydrogen concentration in this „process" zone has reached a critical level, C_{crit}, over a critical volume, d_{crit}, then localized crack initiation within this zone followed by rapid crack propagation back to the main crack-tip. The fine details of micromechanims of crack initiation and advance are often not considered at all. Quantitative modelling is generally based on one of the above mentioned three rate limiting steps. So far it is not possible to estimate the distance X and the critical concentration/volume required for HE from first principles and they are primarily inferred from experimental observations.

In the last decades it has been increasingly proposed that hydrogen embrittlement may be also operating in lower strength alloys having many active slip systems and where creation of stress triaxiality is not a prerequisite for this mode of failure. The experimental evidence for this has been reviewed by Thompson and Bernstein [160] who indicate, for instance, that hydrogen diffusion can be markedly accelerated by dislocation transport thereby leading to hydrogen supersaturation under suitable dynamic equilibrium conditions at various hydrogen trapping sites.

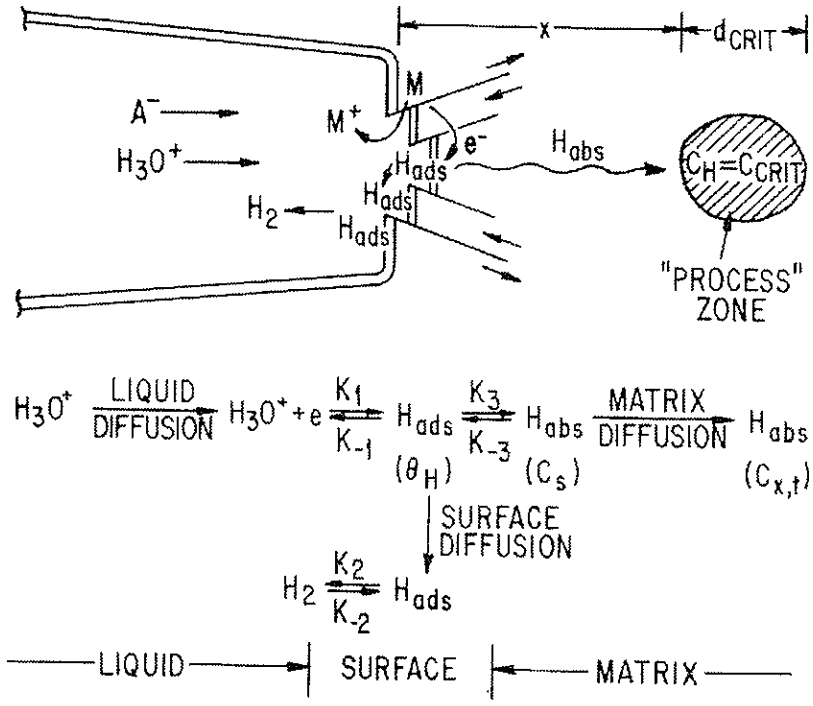


Figure 23: Interactions at crack-tip advancing by a hydrogen-embrittlement mechanism.

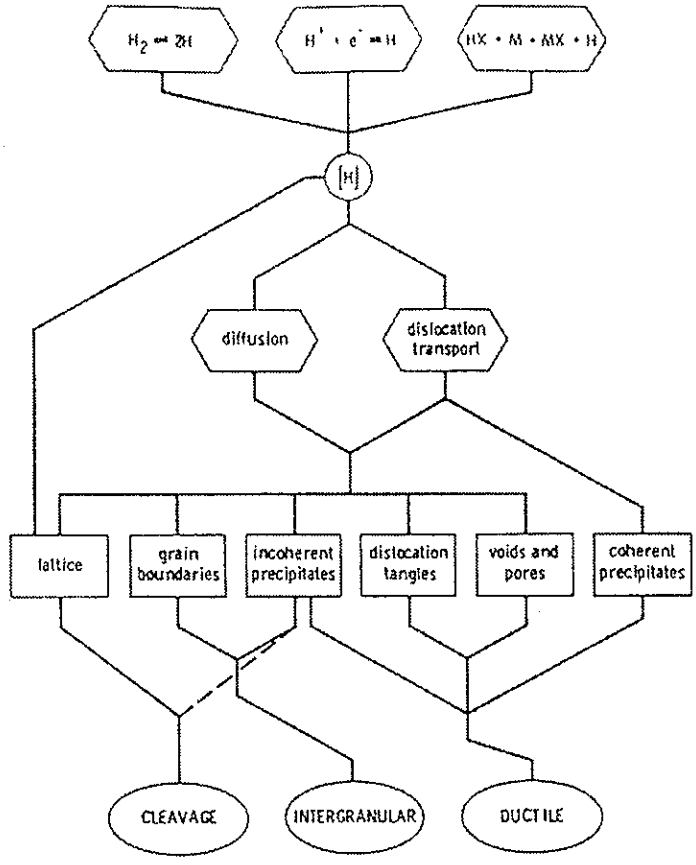


Figure 24: „Roadmap" of possible transport and trapping mechanisms for hydrogen embrittlement in ductile alloys.

4.1.2.4 HAEAC Model for LAS under LWR Conditions

Hänninen et al. [161, 162] have suggested that a hydrogen embrittlement mechanism is operating in the relatively ductile pressure vessel steels in water at 288 °C. The prime experimental evidence for such a suggestion is the fractographical observation of „brittle" cracks in corrosion fatigue tests (>10^{-3} Hz), which are associated with elongated MnS stingers ahead of the main crack-tip [164]. Moreover, the degree of environmental enhancement in fatigue crack growth rates could be directly correlated with the extent of these „brittle" fracture areas on the fracture surface. When environmental enhancement was observed in the cyclic crack growth rate, brittle features in fracture morphology (brittle striations, or striationless cleavage-like fracture) were always seen to be associated with MnS-inclusions; brittle crack often spreads like a fan from inclusion colony. The occurrence of EAC was accompanied by a transition from ductile to more brittle like fracture, whereas the corresponding striation spacing increased with this transition. Moreover, the quasi-brittle features observed were similar to the microscopic appearance of fracture generated in H_2 gaseous atmospheres at lower temperature e.g. at 95°C [164].

The most relevant model of hydrogen-assistance in EAC of LAS in high-temperature water has been qualitatively described by Hänninen [161, 162]:

The series of steps hypothesised to occur in this system are (see Figure 25):

- Enhanced oxidation (anodic dissolution and oxide reformation) at the strained crack-tip after oxide film rupture (1) (similar to FRAD).
- Hydrolysis of the metal cations and generation of H^+ together with a corresponding acidification of the crack-tip environment (2).
- Liquid phase transport (3)
- Dissolution of exposed MnS-inclusions intersected by the crack plane, leading to the creation of H_2S and HS^- and incorporation of sulphur into the reforming oxide (4)
- Creation of adsorbed hydrogen atoms due to the local hydrogen ion reduction reaction, followed by absorption. The kinetics of these reactions are believed to be accelerated by both the necessity to balance the enhanced oxidation reactions and by the presence of the sulphur-containing species in the crack-tip environment (4).
- The hydrogen absorption kinetics into the metal lattice is enhanced by the bare metal surface at crack-tip and by adsorbed HS^- (5).
- Hydrogen transport in the lattice (6).
- Hydrogen trapping at MnS-inclusions (7).
- Recombination of hydrogen atoms at MnS inclusions in front of the crack-tip leading to the formation of brittle cracks at the inclusion/matrix interface, which propagate under the action of hydrogen gas pressure and triaxial tensile stress (8).
- Linkage of these microcracks to the main crack to give a discontinuous crack propagation over and above that due to „mechanical" fatigue (9).

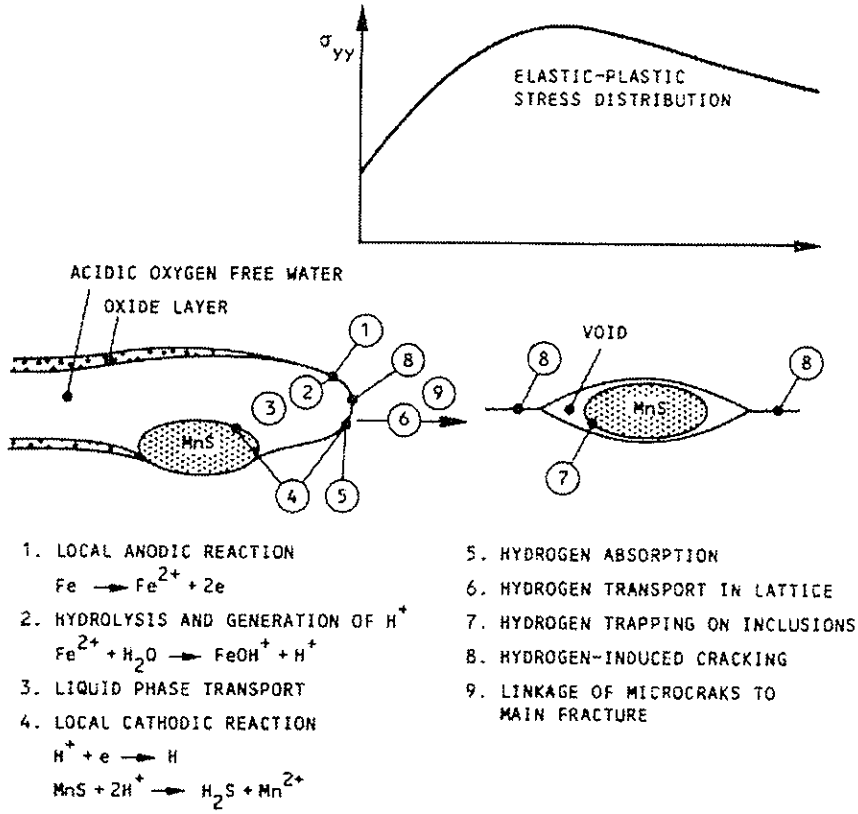


Figure 25: Schematic illustration of hydrogen assistance during cyclic crack growth of pressure vessel steel in high-temperature water according to Hänninen [162, 163].

Hydrogen transport in the electrolyte and in the metal lattice are believed to be fast. Therefore, the generation of bare metal surface by film rupture and the film reformation may be rate controlling steps in the cracking process and explain the strain-rate dependence of EAC.

The contribution of MnS-inclusions to EAC is rationalised in two ways:

a) The dissolution of MnS intersected by the crack plane leads to an additional source of hydrogen by generation of H_2S and subsequent dissociation to HS^- and H^+. Furthermore H_2S and HS^- enhance hydrogen absorption through their adsorption on the bare surface. Furthermore, they may retard repassivation and increase the hydrogen absorption.

b) MnS-inclusions located in the plastic zone ahead of the crack are supposed to act as an strong trapping site for absorbed hydrogen. At a location near to the maximum hydrostatic stress this process aids in micro crack formation.

4.1.2.5 HAEAC vs. FRAD

Under crack-tip conditions (ECP, pH, anion content) relevant for LAS under LWR conditions, hydrogen-assisted EAC and film rupture/anodic dissolution mechanism are both thermodynamically and kinetically viable and may therefore be simultaneously active [161 - 163]. Both mechanisms may be dependent on oxide film rupture rates, repassivation rates and liquid diffusion rates, since these factors affect the charge transfer per time in the FRAD and the hydrogen ad-atom coverage and hydrogen evolution rate in HAEAC models. Furthermore, since both mechanism may be controlled by the same rate limiting steps (for

example oxide film rupture rate, repassivation kinetics, ...), it is very difficult to experimentally differentiate between these two mechanism.

Both mechanism are able to explain the experimentally observed dominant effect of strain-rate and of the MnS-inclusions on the EAC cracking behaviour. The HAEAC model may better explain some special fractographic features but in contrast to the FRAD model no quantitative predictive formulation exists. In contrast to intergranular SCC, for example in sensitized stainless steels, there is no simple reason for the directed, anisotropic dissolution behaviour of LAS assumed in the FRAD models.

To date there is a lack of direct experimental evidence for distinct hydrogen effects in low-alloy primary pressure-boundary component steels under LWR operating conditions. Therefore it is difficult to isolate a distinct microstructural hydrogen mechanism, which could be active in the corrosion-assisted cracking. There is no evidence for brittle hydride formation in low-alloy steels. At typical LWR operating temperatures, the diffusivity of hydrogen is very high and because of thermal activation trapping (at carbides, grain boundaries, dislocations, ...) is not enough efficient that decohesion might be active. To date there is no experimental evidence for hydrogen-deformation interactions above temperatures of 150 °C which relevantly affect the cracking behaviour.

The most striking argument against relevant hydrogen effects in EAC at temperatures above 150 °C is, that HAEAC should be enhanced by increasing the hydrogen fugacity of the environment, by decreasing the corrosion potential to lower more cathodic potentials and by catalytic surfaces, which is obviously not the case. In all these cases cracking susceptibility and EAC crack growth rates in low-alloy steels with moderate strength level (300 - 600 MPa) is decreasing and not increasing.

In high strength low-alloy steels (> 800 MPa, turbine discs) HAEAC has been observed in high-temperature water up to temperatures of 200 °C [40, 165]. The crack path is often intergranular (along the former austenite grain boundaries) but may also be transgranular. Susceptibility is generally increasing from ferritic-pearlitc to bainitic to martensitic microstructure and with grain size. Susceptibility is generally increasing with increasing yield strength level. K_{ISCC} thresholds were often decreasing and crack growth rates increasing with yield strength level. Often lower K_{ISCC} thresholds have been observed under plane strain than plane stress and under mode I than mode III. The role of hydrogen has been clearly established for this high strength low-alloy steels at lower temperatures, with the kinetics of crack advance increasing with temperature up to about 60 to 100 °C, then rapidly falling of. This is consistent with the energetics of both decohesion and enhanced plasticity, which predict a lesser role of hydrogen at higher temperatures. In many cases crack growth rate is increasing again above 150 °C with a different activation energy than in the low temperature regime indicating a change in cracking mechanism from hydrogen-induced cracking to anodic dissolution.

In low-alloy LWR primary pressure-boundary component steels no distinct effect of yield strength on SCC susceptibility has been observed. The threshold under plane stress seem to be lower than under plane strain. The crack growth rate is increasing with increasing temperatures above 150 °C, which is hardly consistent with a hydrogen mechanism.

From a pragmatic perspective, there is no detrimental role of hydrogen at temperatures above 150 °C. At lower temperatures (< 150 °C) hydrogen effects may relevantly contribute to EAC growth, especially with increasing yield strength level and decreasing temperatures, or in the coarse grain zone of weld HAZ.

4.1.3 Dynamic Strain Ageing (DSA)

4.1.3.1 Background

Atkinson et al. [132 - 134] have suggested recently that dynamic strain ageing (DSA) in steel may be very influential in determining both EAC cracking strain-rate sensivity and its temperature dependence [135]. It provides an alternate possible explanation for strain-rate thresholds and more significantly, it may offer an explanation for the cracking peak at intermediate temperatures and rationalize the scattered data in this temperature range (see also Section 3.3.1). Furthermore it may provide a possible explanation for the observed quasi-cleavage fracture surface observed in EAC.

There is now increasing experimental evidence that DSA may play an important role on EAC under certain conditions:

Coincidence of temperature and strain-rate between DSA hardening and susceptibility to EAC of RPV steels in SSRT and SRL tests under low flow oxygenated high-temperature water conditions has been observed [132- 135] (see Figure 26 and 27).

The loss of ductility (RA) in SSRT tests in low flow oxygenated high-temperature water and in air increased with increasing free nitrogen content, confirming that DSA may be further contributing factor for EAC [132 -135].

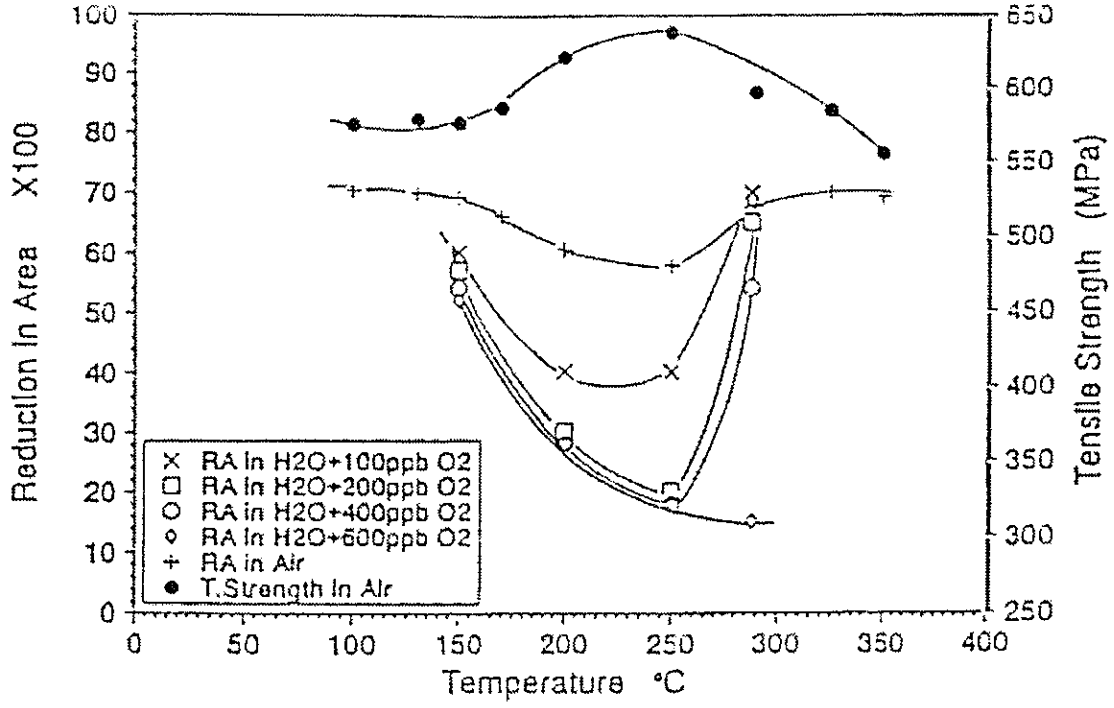


Figure 26: Coincidence of susceptibility of LAS to SICC in SSRT-tests (minimum in reduction of area) in high-temperature water with DSA behavior (maximum of tensile strength) in air in terms of temperature and strain-rate [133 -135].

4.1.3.2 Phenomenological and Microscopical Features of DSA

DSA may be observed in susceptible LAS during plastic straining at sufficiently slow strain-rates ($< \approx 10^{-2}\ s^{-1}$) in the temperature range from 100 °C to 350 °C. DSA in LAS is associated with diffusion of interstitial species such as C and N atoms to the core region of dislocations and their immobilization. The DSA effects increase with increasing concentration of free, interstitial N and C and are most pronounced if the diffusion rate of C/N and the dislocation

velocity are similar. Parameters, which affect the concentration of free C and N and their diffusion rate have therefore a strong effect on the DSA-behaviour of LAS.

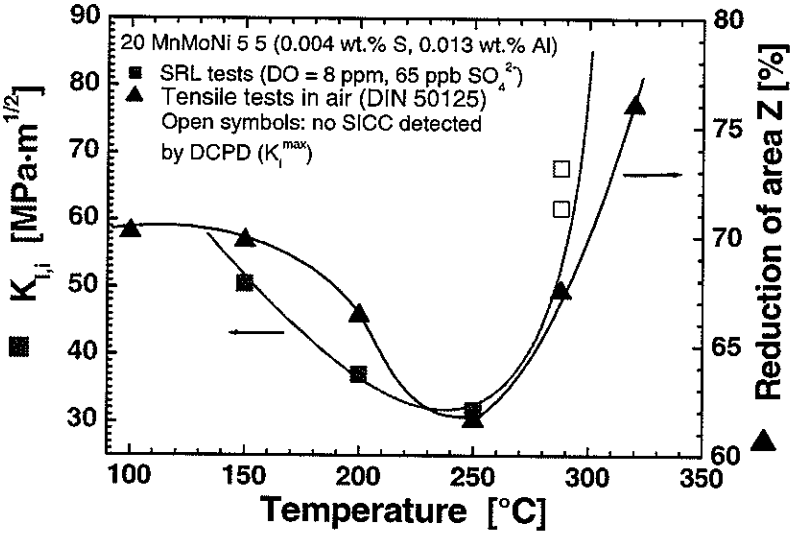


Figure 27: Coincidence of susceptibility of LAS to SICC in SRL-tests (minimum in $K_{I,i}$) in high-temperature water with a pre-cracked specimen with DSA behavior (minimum in reduction of area Z) in tensile tests in air in terms of temperature at a strain-rate of ca. 10^{-5} s^{-1} [217].

Dynamic strain ageing has some detrimental effects on LAS. Phenomenologically, it results in a peak in ultimate tensile strength (UTS), hardness, and strain hardening rate in the DSA temperature range, a minimum of ductility (elongation to fracture, A and reduction of area, Z) and results in negative strain-rate sensitivity (Figure 28). Yield strength is affected by static strain ageing rather than DSA resulting in plateau or a small peak in yield strength in the temperature range of DSA. The temperature of the peak effect decreases with decreasing strain-rate. Microscopically, DSA results in an inhomogeneous localisation of deformation, an increase of dislocation density and in deformation bands.

4.3.1.3 Physical Metallurgy of DSA

DSA in carbon and low-alloy steels is an elastic interaction between the strain fields of solute interstitials as nitrogen and carbon and moving dislocations with edge-character. The elastic interaction leads to the diffusion of interstitials towards the dislocation and to the formation of increased interstitial concentrations in the vicinity of the dislocation core in the region of maximum dilatation (Cottrell atmosphere) and results in a overall decrease of the total strain energy. Consequently dislocations can be locked in position by strings of C or N atoms along the dislocations, thus substantially raising the stress, which would be necessary to cause dislocation movement. Only very small amounts of interstitials are necessary to lock dislocations (less than 10 ppm). At higher temperatures (> 400 °C) thermal energy kT can overcome the elastic interaction or binding energy between the solute and dislocation and dislocations can escape form their atmospheres as a result of thermal activation.

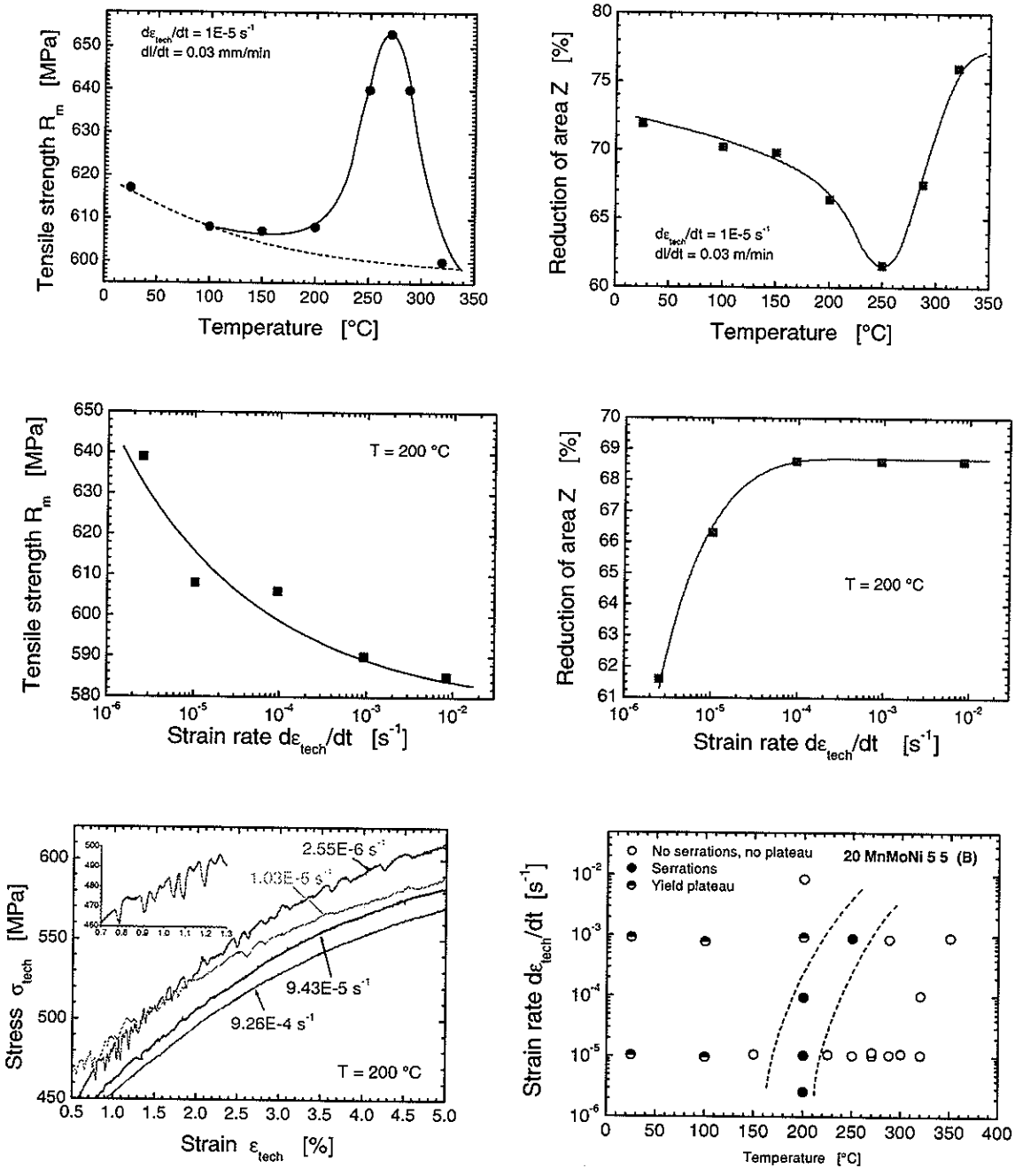


Figure 28: Typical features of DSA in tensile tests in air with a susceptible RPV steel (20MnMoNi 5 5 , 30 ppm N_{free}): Maximum/minimum in R_m/Z at intermediate temperatures, negative strain-rate sensivity, serrations in stress strain curve [216].

When the temperature is raised into the DSA region (typically 100 - 350 °C), interstitials can diffuse during deformation and can form atmospheres around dislocations generated during deformation. The dislocations generated are quickly pinned so that others must be generated to allow deformation to continue. As a result, the dislocation density at a given strain is higher than when the straining is done outside the DSA range. The repeated breakaway and repining of mobile dislocations by the interstitials was the original explanation for the

serrations in the stress-strain curve. The alternate explanation is that once carbon and nitrogen atmospheres are formed, the dislocations remain locked, and the serrated yield phenomena arise from the generation and movement of newly formed dislocations, which are then suddenly pinned. The DSA effect respectively the pinning of dislocations is at maximum, if the diffusion rate (which is dependent on the temperature) of the free interstitials and the dislocation velocity (which is dependent on loading and strain-rate respectively frequency) are similar. This is schematically shown in Figure 29. At low strain-rate or frequency, diffusion of the interstitials is faster than the dislocations, at high strain-rates dislocations are too fast to be pined by the interstitials, so in both cases there is no significant DSA-effect. The maximum is a function of temperature or strain-rate. For higher temperatures maximum DSA-peak is shifted to higher strain-rates. With increasing strain-rate DSA-peak is shifted to higher temperatures.

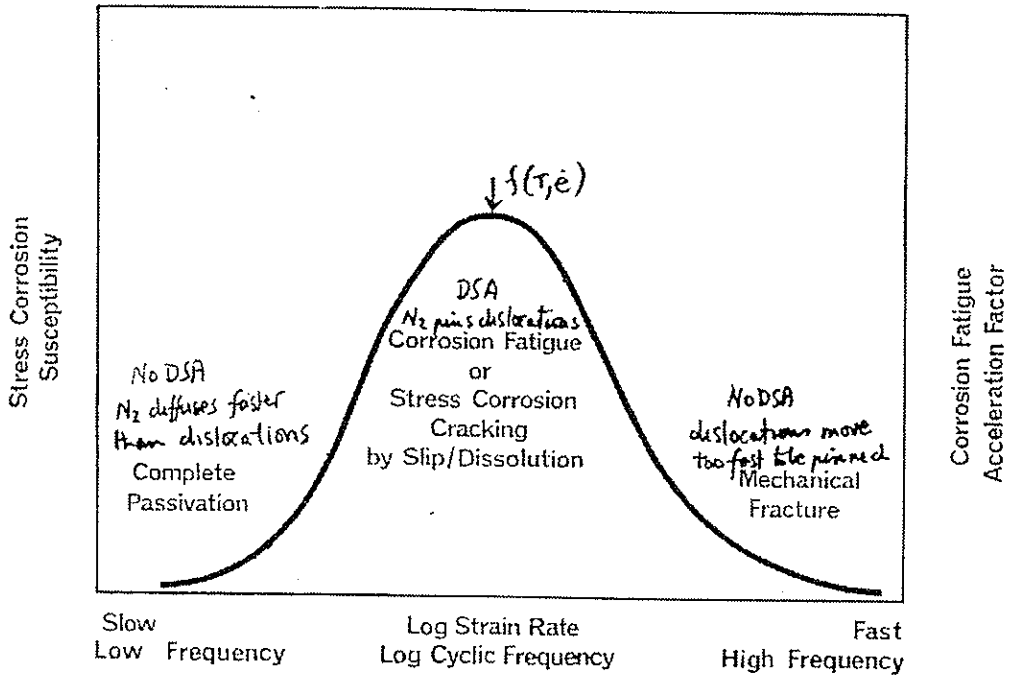


Figure 29: Correlation between frequency/strain-rate and DSA or EAC response.

4.1.3.4 The Metallurgy of DSA

In ferrite N and C have similar diffusion coefficients and they are producing a nearly identical lattice misfit strain, thus, these two elements are expected to produce nearly similar DSA effects in LAS. Therefore, in general, the effects produced by C and N can be considered as additive. At room temperature, the residual solubility of N in ferrite is about 100 times greater than that of C – N solubility in steel is higher at all temperatures than that of C. It is generally assumed that N, rather than C, is mainly responsible for DSA. However, at higher temperatures in the DSA range the increasing solubility of carbon may cause DSA even in the absence of N.

The concentration of free interstitial C and N strongly depend on the steel making (killing) or welding process, the thermal history or heat-treatment (annealing-, PWHT- or stress relieving temperature) and on the chemical composition (C_{tot}, N_{tot}, Al, V, Ti, Cr, Mo, O, Mn ...) of the steel. Alloying elements, which have a strong affinity to N or C, such as Al, Cr and Mo, and form nitrides or carbides may result in a reduction of the residual concentration of free C and N. Parameters, which would affect the interstitial diffusion in dilute alloys might also affect the DSA-behaviour of LAS. The measured activation energy for the onset of serrations in the

stress-strain curve is not sensitive to the microstructure or composition of steel. The exemption being the Mn content which seems to influence the diffusion process of N and C by forming Mn-N and Mn-C pairs increasing thus the activation energy for the diffusion process [135]. Large differences in the activation energy for the disappearance of DSA reported suggest that it is also a function of steel composition.

Silicon-killed vs. Al-killed low-alloy steels:

Silicon killed, air poured carbon or low-alloy steels show a much more pronounced DSA effect than aluminium killed vacuum ladle degassed steels, since in aluminium killed steels, aluminium nitrides are formed and the remaining free interstitial nitrogen content is very low. The Al/N-ratio is therefore an important parameter governing the free nitrogen content and the resulting DSA effect.

Weld material:

During the welding process uptake of small amounts of oxygen and nitrogen can occur. Weld metal often have a very little aluminium- but high oxygen-contents. Because of its very high affinity to oxygen, aluminium fist combines to oxygen (aluminium oxide precipitates) in welds, which reduces the beneficial effect of the aluminium. During fast cooling after welding, incomplete precipitation of carbides and nitrides occurs resulting in an increased or even supersaturated concentration of free C and N in the as-welded condition. The precipitation of carbides during PWHT further reduces the concentration of free C and N. The PWHT-temperature is detrimental. The free C and N decrease with increasing annealing temperature because of precipitation of carbides and nitrides.

Welds might reveal increased concentrations of interstitial N and therefore be more susceptible to EAC in the DSA-temperature /strain-rate range than generally thought so far. LFCF crack growth tests in high-temperature water with weld materials have been performed under temperature-strain-rate conditions (> 250 °C, > 10^{-3} Hz) where DSA is absent or only moderately active. The better resistance of the weld material under these conditions has been mainly attributed to the different morphology and chemical composition of MnS-inclusions in the welds (very small spherical inclusions).

Weld HAZ material:

The free carbon content in low-alloy steels can strongly vary depending on the heat treatment and on chemical composition (C_{tot}, Cr, Mo, V, ...). Alloying elements, which have a strong tendency to form carbides as Cr or Mo may also affect the residual interstitial carbon content. In the heat-affected zone near to the fusion line, with high peak temperatures slightly below the melting point (partial) dissolution of carbides and (incomplete) re-precipitation during subsequent cooling occurs, which can result in a supersaturated state. During the following PWHT (stress relieving) precipitation of further carbides occurs. The interstitial carbon is strongly dependent on the stability of the carbides (chemical composition), on the peak temperature, heating and cooling rates and on the PWHT-treatments applied. The most severe DSA-effects are expected for materials in the as-welded condition without PWHT (e.g. repair welding).

The free carbon and nitrogen content are not specified in the relevant nuclear guidelines and regulations (KTA, ASME BVP) for the low-alloy LWR primary pressure-boundary component steels and can strongly vary from steel to steel, steel to weld and within weld HAZ resulting in a different EAC response in the DSA-temperature/strain-rate range. The concentrations can vary between 0 ppm and a supersaturated state well above the solubility limit. Differences in free nitrogen and carbon content of otherwise identical or similar low-alloy steels may be one important further reason for the relevant scatter of EAC crack growth

rate data, and especially for the sometimes-observed different trends in temperature dependence of EAC.

4.1.3.5 Possible Interaction between DSA and EAC in LAS

The role of DSA in EAC has not been studied much. However, the EAC data strongly suggest that the susceptibility of LAS to EAC coincides with DSA behaviour, in terms of temperature and strain-rate [133 -135]. Environment-assisted cracking behaviour of LAS is controlled by various mechanical, environmental and material parameters. In EAC, DSA is especially important in dynamic crack-tip plasticity behaviour such as dynamic loading or development of creep strain. The crack-tip strain-rate is an important parameter in controlling EAC (see Section 4.1.1). DSA affects the yield strength, strain hardening exponent and creep rate, which are important factors affecting the crack-tip strain and strain-rate. DSA may result in a higher crack-tip strain and strain-rate than in a material, which is not susceptible to DSA. Microscopically, DSA results in an inhomogeneous localisation of deformation, an increase of dislocation density and increase in planar deformation [135]. These factors can result in reduction of the local fracture toughness and favour brittle crack extension, but also in the mechanical rupture of the protective oxide film and therefore crack advance by anodic dissolution/hydrogen embrittlement mechanism. Therefore DSA may synergistically interact with anodic dissolution and hydrogen embrittlement to increase EAC cracking susceptibility.

EAC in LAS has been observed under temperature/stain rate conditions or in materials, where no or only minor DSA-effects were present. DSA is therefore not a pre-requisite for EAC and best regarded as an additional contribution to EAC growth process.

4.2 Local Crack-Tip Chemistry and Mass Transport

EAC crack initiation and growth from incipient cracks are governed by the **local** mechanical, metallurgical and environmental crack-tip conditions, e.g. for a given material primarily by the crack-tip strain-rate and the activity of chloride and sulphur-anions and the pH in the crack-tip environment [48]. This local factors are governed by a system of interrelated corrosion system parameters such as the applied load and load ratio, strain/loading rate, the ECP or dissolved oxygen content, the flow rate across the crack mouth, the bulk concentration of specific anionic impurities as SO_4^{2-} and Cl^- and the steel MnS-inclusion content and morphology.

The local crack-tip water chemistry is normally more aggressive than the corresponding bulk water chemistry outside the crack. But generally, only the bulk water chemistry is known and direct information on crack-tip water chemistry arises primarily from modelling and from new in-situ experimental techniques (crack-tip microsampling, crack-tip ECP measurement).

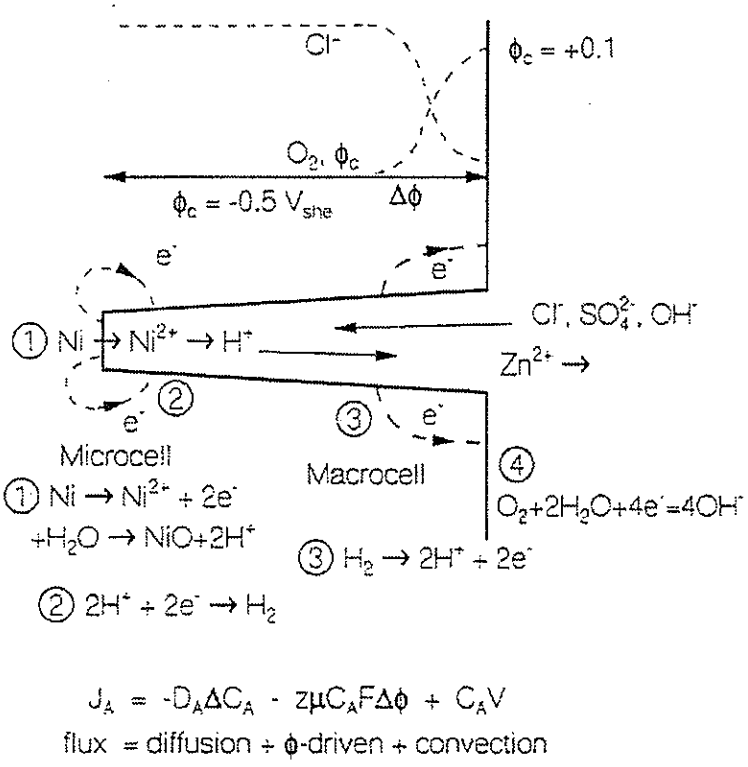
The following sections qualitatively outline, how the local crack-tip chemistry is related to the known bulk water chemistry outside the crack by mass transport mechanism and to local microchemistry by the dissolution of MnS-inclusions. The discussion is primarily focused to BWR conditions and is based on the film rupture/anodic dissolution mechanism. Crack and crevice chemistry have been the topic of many reviews [166 - 168]. Models for crack/crevice (electro-)chemistry and their potential application to LWR conditions have been recently discussed in [166, 168].

The basic concepts and fundamental processes for the evolution of the occluded crack chemistry are discussed in Section 4.2.1. Typical crack-tip conditions (potential, pH, conductivity, impurity concentrations) in LAS under LWR conditions are outlined in Section 4.2.2. Finally, some important aspects of crack (electro-) chemistry (ECP, impurities, MnS-inclusion, flow rate) are further discussed in Section 4.2.3.

4.2.1 Basic Concepts of Crack Chemistry in Low-Alloy Steels under LWR Conditions

Figure 30 shows the basic concepts of crack chemistry and electrochemistry for EAC in LAS under LWR conditions, which is based on the film rupture/anodic dissolution mechanism. This qualitative picture of crack (electro-)chemistry is primarily based on experimental observations. Currently, only very simplified and therefore limited models exist for LAS under LWR conditions [168].

Bulk and crack-tip environment are coupled by mass transport processes (diffusion, migration, convection) and charge conservation. The impurity concentration in the crack enclave is dependent on its bulk concentration outside the crack enclave, its production/depletion rate by homogeneous or heterogeneous reactions in the crack enclave (e.g. MnS-dissolution, hydrolysis of metal cations, precipitation reactions, electrochemical reactions at crack surface) and by its transport into or out of the crack enclave by diffusion, migration and convection. Many of these processes are dependent on one or several factors such as the potential, pH, concentration, which may be a function of location in the crack enclave.



$$J_A = -D_A\Delta C_A - z\mu C_A F\Delta\phi + C_A V$$

flux = diffusion + ϕ-driven + convection

Figure 30: Schematic of crack electro- and water chemistry showing the differential aeration cell at the crack mouth (reaction 3 and 4) that establishes the crack-tip chemistry and the local microcell (reaction 1 and 2) associated with metal dissolution and crack advance. Because of the high ohmic resistance of the electrolyte, there is no direct coupling of electronic currents between these two cells. The potential gradient between the aerated crack mouth (+ 0.1 V_{SHE}) and the de-aerated crack-tip (- 0.5 V_{SHE}) results in an additional flux of anions/cations into/out of the crack enclave and an enrichments of anions and pH-shifts in the crack-tip environment in the case of non-OH^- anions in the bulk environment. (In the case of low-alloy steels, Ni/Ni^{2+} has to be replaced by $Fe/Fe2^+$).

Even under relatively pure bulk water chemistry conditions, an aggressive occluded water chemistry can be formed in cracks and crevices under the action of concentration (differential aeration) or thermal cells or from outright boiling. Such occluded cells only require a restricted crevice geometry. For LWR low-alloy steel primary pressure-boundary components only the differential aeration cell is of relevance.

In oxygenated high-temperature water (BWR conditions) a differential aeration cell is formed in the crack mouth region, since oxygen reduction is faster than its diffusion. Dynamic crack-tip straining may additionally result in oxide film rupture and the formation of a dissolution cell at crack-tip. Both cells may exist without the existence of the other one. The evolution of the differential aeration cell, for example, only requires a restricted crevice geometry. Because of the limited conductivity under typical LWR conditions and the resulting high ohmic potential drops, the crack-tip (dissolution cell) and crack mouth electrochemistry (differential aeration cell) are only coupled by mass transport but not by direct electronic coupling.

4.2.2 Differential Aeration Cell at the Crack Mouth

Oxygen reduction kinetics on oxide films is fast with respect to oxygen mass transport by diffusion in high-temperature water. Therefore, in a high aspect ratio cracks with restricted mass transport, almost all oxygen is consumed over a short distance in the crack mouth region resulting in a built-up of a differential aeration cell (oxygen concentration cell). The resulting potential drop in this differential aeration cell and the additional mass transport by migration were important factors for the evolution of the corresponding crevice and crack-tip water chemistry. The potential drop in the crack mouth is acting as a pump for anionic impurities in the bulk environment towards the crack-tip and retains anionic impurities generated by (electro-)chemical reactions (dissolution of MnS-inclusions) in the crack-tip environment. If the bulk reactor water contains specific anionic impurities as SO_4^{2-}, Cl^-, the migration of these impurities can result in a pH-shift. The dissolution of MnS-inclusions and the hydrolysis of metal cations generated by anodic dissolution may be further reasons for pH-shifts under these conditions. The potential gradient and its effect on the evolution of the crack-tip chemistry is decreasing with decreasing bulk oxygen content. Under BWR/HWC or PWR conditions, there is only a small or virtually no potential gradient between the crack mouth and crack-tip and mass transport is governed by diffusion only.

4.2.3 Dissolution Cell at the Crack-Tip

Mechanical straining results in the rupture of the protective oxide film at the crack-tip and in exposure of fresh bare metal to the de-aerated crack-tip electrolyte and in crack growth by anodic dissolution. The crack growth is stopped by the reformation of the protective oxide film (repassivation). Because of complete oxygen depletion in the crack enclave, anodic dissolution current on the very localized anode is balanced by the reduction of hydrogen or water on the crack walls in the absolute vicinity of the crack-tip. Hydrogen is always present in the crack-tip environment because of corrosion processes (oxide film formation) and hydrolysis of metal cations generated by anodic dissolution. The limited conductivity results in high ohmic potential drops if currents were flowing and therefore strongly limits the spatial extension of local galvanic elements and is therefore avoiding direct electronic coupling between crack-tip and crack mouth electrochemistry.

The crack-tip sulphur-anion (SO_4^{2-}, HS^-, S^{2-}) activity and pH, by there strong effect on repassivation kinetics, control the anodic dissolution respectively EAC crack growth in LAS under LWR conditions. This is clearly confirmed by the mircosampling technique and by repassivation measurements under simulated crack-tip conditions [46, 50, 86, 147, 154, 163]. In LAS crack-tip sulphur-anion activity is governed by the dissolution of the MnS-inclusions intersected by the crack enclave and the bulk sulphur-anion concentration outside the crack and by their transport into or out of the crack enclave. Crack growth rate itself may have a strong influence on crack-tip sulphur content by the exposure of fresh new dissolvable MnS-inclusion. The type, size, morphology and spatial distribution of the MnS-inclusions are further important factors.

The migration of sulphur-anions in the potential gradient in the crack mouth region given by difference of low ECP inside the de-aerated crack and the high ECP under oxidising bulk conditions results in an enrichment of sulphur-anions in the crack-tip electrolyte and permits shifts in pH in acidic direction, although generally only by a small amount (< 1-1.5 unit) [46, 50, 86]. Apart from the dissolution of MnS-inclusions, hydrolysis of metal cations as well as the migration of other specific anionic bulk impurities were further causes for this slight acidification. Under PWR conditions there is virtually no potential gradient between crack mouth and crack-tip and the described sulphur enrichment mechanism by migration is absent.

4.2.4 Mass Transport Process in the Crack Enclave

The concentration of a specific species in the crack-tip environment is governed by its different source terms (homogeneous/ heterogeneous reactions) and the different mass transport mechanism. There are three different basic transport mechanisms, which can be simultaneously active:

- Diffusion of neutral and charged species due to their concentration gradients.
- Migration of charged species due to a potential gradient.
- Convection of neutral and charged species by water flow induced by external flow across the crack mouth or by fatigue pumping by the relative displacements of the crack flanks between the maximum and minimum stress portions of a fatigue cycle.

The presence of high convection generally dominates all other transport mechanism and homogeneous concentration and ECP conditions do generally exist in regions of high convection. Fatigue pumping becomes more important as cyclic frequencies are increased and as stress ratio is decreased. Under static loading and for long cracks convection can be neglected, and then mass transport is dominated by diffusion (reducing PWR and BWR/HWC conditions) respectively diffusion and migration (oxidizing BWR conditions). The complete flushing out or dilution of the aggressive crack-tip environment by convection may completely suppress or relevantly slow down EAC crack growth. Flow rate and convection effects will be discussed further in Section 4.4.5.

4.2.5 Critical Crack-Tip Sulphur-Anion Concentration for EAC

Based on experimental observations, several authors have proposed, that a critical crack-tip sulphur-anion concentration has to be achieved for the occurrence of EAC [84, 169, 170]. The crack-tip sulphur-anion activity is determined by synergistic system parameters such as the ECP (bulk DO) at the external surface in the crack mouth region, the flow rate past the crack mouth, the bulk concentration of sulphur-anions, the MnS-inclusion content of the steel and the crack growth rate itself. Suitable combinations of these parameters may help to exceed the critical crack-tip sulphur-anion concentration provided that there is at least one source of sulphur-anions (bulk-sulphur-anions or MnS-inclusions).

Based on the mentioned sulphur enrichment mechanism and different sulphur sources, a high crack-tip sulphur-anion activity > the critical concentration and high cracking susceptibility is therefore favoured by

- a high ECP (a high DO)
- a high bulk sulphur-anion activity
- an alloy with a high sulphur content
- a long pre-existing crack (→ large area of dissolvable MnS-inclusions, small flow rate effects)
- low-flow or quasi-stagnant conditions
- sufficiently high crack growth rate (exposure of new, fresh dissolvable MnS-inclusions)

The sulphur may be present either as MnS-inclusions in the steel or as an impurity in the bulk water. A high steel sulphur content or a high ECP are therefore not mandatory for EAC. SICC has been even observed in extremely low-sulphur steels at high ECP and/or high bulk sulphur-anion contents [97, 98, 138]. Otherwise, sustained, fast EAC may be observed at very low ECP (PWR) under suitable cyclic loading conditions or at high bulk H_2SO_4 concentrations [86].

4.3.6 Critical Crack Growth Rate for EAC

Under reducing PWR conditions, the sulphur enrichment mechanism by migration is absent. In the absence of bulk sulphur-anions in relatively pure PWR water, the crack-tip sulphur-anion concentration is governed by the balance between competing processes of sulphur-anion supply by the dissolution of MnS-inclusion and the loss of sulphur-anions by the diffusion out of the crack. To maintain a high crack-tip sulphur-anion activity, the growing crack has to expose a sufficient amount of new fresh dissolvable MnS-inclusion, otherwise the continuous diffusion will result in a continuous decrease of the crack-tip sulphur-anion activity and of EAC growth rate. The cessation of EAC in LAS under PWR conditions has been experimentally observed and recently discussed in two new papers [171, 172]. The idea of a critical crack-tip sulphur-anion activity for the occurrence of EAC has led to a new idea of a critical crack growth rate and critical crack extension length which have to be simultaneously exceeded that sustained EAC may be observed. If these conjoint conditions are not satisfied, cessation of EAC and crack arrest is observed. Time-domain EAC plots clearly reflect this behaviour (Figure 31). A sufficiently high a growth rate may be attained by suitable cyclic loading conditions with a relevant pure mechanical fatigue component for relevant environmental acceleration of crack growth. The critical crack growth rate is expected to decrease with increasing steel sulphur content and increasing ECP/DO.

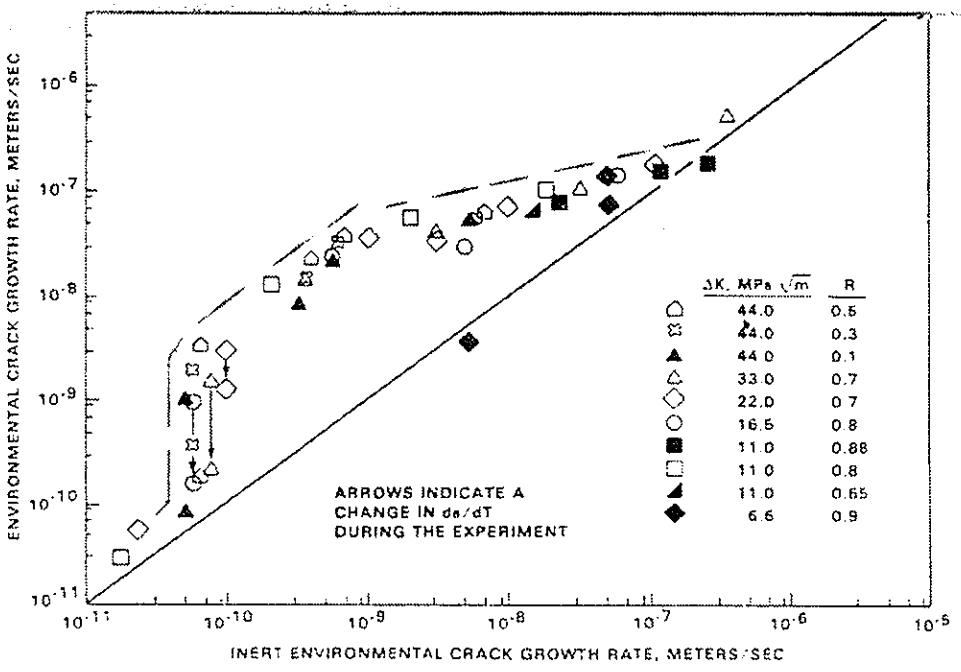


Figure 31: Time-domain plot of EAC crack growth rates from low-frequency corrosion fatigue tests with SA 533 B Cl. 1 material (0.025 Gew.% S) in oxygenated high-temperature water (200 ppb DO, 288 °C) under different loading conditions revealing a critical crack growth rate for the onset of EAC of ca. 10^{-10} m/s for a DO of 200 ppb [218].

The crack-tip sulphur-anion activity and strain-rate seem to be more fundamental than the other system parameters. Several thresholds may be related to the critical crack-tip sulphur-anion activity, like the critical cracking potential ECP_{crit}, steel sulphur thresholds or a critical bulk sulphur-anion concentration, which all are variable system parameters. Most EAC cessation and crack arrest phenomena in the system LAS/high-temperature water may be attributed to the requirement of dynamic crack-tip strain-rate and high crack-tip sulphur-anion content and their interrelation to crack growth and mass transport.

4.3 Crack-Tip Electro- and Water Chemistry in LAS under LWR Conditions

4.3.1 Crack-Tip ECP

The ECP at the crack-tip is always low (typically around - 500 mV_{SHE}) even at extremely high bulk DO of 42 ppm and/or high n/γ radiation levels and is similar for oxidizing BWR and reducing PWR conditions. The crack-tip ECP is governed by the H_2/H_2O-line, since oxygen is completely consumed in the crack enclave. This is confirmed by the low crack-tip ECP [148, 149] close to the equilibrium potential for H_2/H^+ reaction measured under aerated bulk conditions. Because of the lack of excessive hydrogen overpressure and LiOH under BWR bulk conditions, crack-tip ECP under BWR conditions are slightly more positive (100 - 250 mV) and crack-tip pH at temperature slightly more negative (1 - 2 units) than under PWR conditions [173]. In BWR, the nominally pure water provides no pH buffering capability, and the differential aeration cell that results from the oxidizing bulk conditions causes anion enrichment in the crack and pH-shifts. In PWR, there is essentially no differential aeration cell, and many components are not subjected to differential thermal cells or local boiling. Thus the main difference between PWR and BWR is the difference in operating temperature (315 - 320 °C compared to 270 - 290 °C), pH, Hydrogen fugacity and impurity level [173].

Under oxidizing BWR conditions, the ECP on the external surface outside the crack is high (typically - 50 to + 200 mV_{SHE}) and governed by the O_2/H_2O-line. The potential difference between the deaerated crack-tip and the oxygenated crack mouth region typically amounts 500 - 700 mV [50]. Under reducing PWR conditions there is virtually no potential gradient between crack mouth and crack-tip. In oxygenated high-temperature water, the potential gradient depends on the dissolved oxygen content and flow rate and increases with increasing DO. There is a large shift in ECP between 10 to 100 ppb DO and a high flow rate may produce relevant positive shifts in ECP in this region. Above 200 ppb DO, the ECP only slightly increases with increasing DO and flow rate has only a small effect [170].

4.3.2 Crack-Tip pH and Crack-Tip Sulphur-Anion Concentration

A slight acidification of the crack-tip environment with respect to the near neutral bulk reactor water is generally observed under BWR conditions, but the pH-shift is generally limited to maximal 1 - 2 units [50, 173]. Dissolution of MnS-inclusions and hydrolysis of metal cations as well as the migration of specific anionic bulk impurities were the cause for this slight acidification. In PWR, there is essentially no differential aeration cell and the PWR water provides a pH buffering capability, therefore the crack-tip pH at temperature is slightly more positive (1 - 2 units) than under BWR conditions.

Under aerated BWR conditions, crack-tip sulphur activity is typically 20x - 30x the bulk sulphur-anion activity. Under de-aerated PWR (or BWR/HWC/NMCA) conditions, where the mechanism of anion enrichment is not active, crack-tip sulphur activity is approximately 2x - 3 x higher than the bulk sulphur-anion activity and 10x lower than under aerated bulk conditions under otherwise identical testing conditions [46, 86].

4.3.3 Crack-Tip Conductivity

The solubility of corrosion products in near neutral high-temperature water is very limited and only slightly changing for the observed small pH-changes [50, 173]. Precipitation reactions and the small solubility of most ionic impurities limit the concentration of cationic and anionic impurities respectively of the conductivity at the crack-tip. Crack-tip conductivity is probably at maximum 100 to 1000 x higher than in the bulk environment outside the crack, but still very small [50, 173].

4.4 Discussion of some Specific Aspects of Crack Chemistry and EAC

4.4.1 ECP and Dissolved Oxygen Content

The ECP is more fundamental for EAC than the direct absolute concentration of oxydizing and reducing species, since it is primarily the potential drop in the crack mouth region which governs the evolution of the crack-tip water chemistry for given conditions [50]. In good conducting electrolytes (PWR) a similar EAC behaviour was observed under nominal identical conditions independently if ECP was controlled potentiostatically or by O_2 or H_2O_2 -addition [14, 16,]. ECP can encapsulate to a certain extend, radiolysis and flow rate effects as well as the effect of oxidizing and reducing impurities other than oxygen.

In contrast to the ECP, dissolved oxygen content itself does not necessarily reflect the real local electrochemical conditions near to the specimen or component surface. Similar oxygen concentrations do not necessarily result in similar ECP. Significant ECP shifts of up to 300 mV can be observed for example in the transition range from 10 - 100 ppb oxygen (transition from oxygen to hydrogen or water reduction), if flow rate is changed from quasi-stagnant to turbulent conditions.

4.4.2 Impurity Content and Conductivity

The exact composition of the electrolyte respectively the type and concentration of ionic impurities which determine the conductivity were much more important than the conductivity per se. Conductivity can have a little effect on crack growth rate to a certain extend, but it is primarily the concentration of specific anionic impurities as sulphate/sulphides and chloride which have a strong influence on crack-tip repassivation kinetics and pH which govern the SCC susceptibility or accelerate EAC crack growth of these steels. It is widely known that certain species (NO_3^-, BO_3^-, F^-) have a strong effect on conductivity but little or no effect on crack growth rate [50]. More importantly, it has been shown that increases in conductivity can also reduce the crack growth rate, e.g. in cases where bulk pH is shifted / buffered to slightly alcalic $pH_{288\,°C}$ of about 6.5 to 8 [50].

There is strong experimental evidence, that the crack growth and the cell current in the dissolution cell is rather limited by the repassivation kinetics (which is governed in particular by the activity of sulphur-anions and crack-tip pH) after oxide film rupture than by cathodic reactions. Tests with microsampling [46, 86] with and without bulk H_2SO_4- addition under aerated (+ 150 mV_{SHE}, 10 ppm O_2) and de-aerated (-500 mV_{SHE}, 0 ppm O_2) bulk conditions and with variation of the microsampling rate clearly indicate, that it is not the potential gradient, per se, which enhances crack-tip dissolution, but the aggressive chemistry in the crack (activity of sulphur-anions and crack-tip pH). Under de-aerated conditions high EAC growth rates may be observed at high bulk H_2SO_4 concentrations and crack-tip microsamples collected during bulk H_2SO_4-addition under de-aerated conditions showed higher crack-tip concentrations than that expected from a simple addition of the crack-tip value in pure de-aerated water plus the bulk H_2SO_4-addition. These two findings confirm that neither the external corrosion potential nor potential gradient directly controls the dissolution rate, but the presence of sulphur species in the crack-tip (probably the acidic shift in pH) enhances both the MnS-dissolution and dissolution rates. At high crack-tip microsampling rates, flushing, dilution and aeration of crack-tip electrolyte crack occurred by convection. The crack growth slowed down or was completely suppressed under these conditions demonstrating that crack growth is not controlled by the crack-tip potential (which significantly increased) but primarily by the activity of sulphur-anions and crack-tip pH.

4.4.3 Effect of MnS-Inclusions

The dissolution of MnS-inclusions to H_2S respectively HS^- and S^{2-} may contribute to EAC in the following ways:

Sulphur-anions as HS^-, S^{2-} and SO_4^{2-} may significantly retard repassivation after oxide film rupture and therefore increase crack advance by anodic dissolution in the FRAD-model (Section 4.1.1) and the HAEAC-model (Section 4.1.2). The retarded repassivation by the film-free surface and the adsorbed HS^-, S^{2-} or H_2S increase the hydrogen absorption to the metal lattice, and favour therefore HAEAC. Furthermore, the dissolution of MnS is a further potential source of hydrogen and MnS-inclusions in the region of maximum hydrostatic stress ahead of the crack-tip may act as strong hydrogen traps and HAEAC initiation sites (Section 4.1.2).

The following factors are important parameters for the dissolution behaviour of MnS and for the crack-tip sulphur-anion activity:

- The dissolution behaviour is dependent on the type, size, morphology and spatial distribution of MnS-inclusions in steel [120 - 124]. The area fraction of MnS generally corresponds well to the observed EAC susceptibility [128]. The steel making and manufacturing process and the product form (hot rolled plate, forging, weld), which affect the distribution (segregation) and morphology of MnS-inclusions, are further influencing factors. Therefore origin and orientation of specimen with respect to their location in the plate may affect EAC susceptibility and is an important source of scatter of EAC data.
- The crack growth rate, which governs the intersection rate of new dissolvable MnS-inclusions.
- Temperature, pH, potential, which govern dissolution kinetics and solubility.

Post-test fractography and metallography [161, 164], crevice experiments [174] and tests with microsampling [46, 86] indicate, that dissolution of MnS-inclusions, which are intersected by the crack plane can and does occur under deaereated crack-tip conditions. The detail of reaction mechanisms and kinetics are not known. The following reactions for the dissolution of the MnS-inclusions have been proposed:

$$MnS \leftrightarrow Mn^{2+} + S^{2-}$$

$$MnS + H_2O \leftrightarrow Mn^{2+} + HS^- + OH^-$$

$$MnS + 2\,H^+ \leftrightarrow Mn^{2+} + H_2S$$

$$MnS + 4\,H_2O \leftrightarrow Mn^{2+} + SO_4^{2-} + 8\,H^+ + 8\,e^-$$

$$MnS + 4\,H_2O \leftrightarrow Mn^{2+} + HSO_4^- + 7\,H^+ + 7\,e^-$$

$$2\,MnS + 3\,H_2O \leftrightarrow 2\,Mn^{2+} + S_2O_3^{2-} + 6\,H^+ + 6\,e^-$$

$$Fe + 2\,HS^- + 2\,H^+ \leftrightarrow FeS\downarrow + 2H_{ad}$$

$$Fe + H_2S \leftrightarrow FeS + H_2$$

The MnS-dissolution kinetics and type of reaction may depend on the temperature, pH and potential. Under typical deaerated crack-tip conditions (low ECP of ≈ - 500 mV_{SHE}, slight acidic pH shift of 1- 2 units from neutral) H_2S respectively HS^- and S^{2-} seem to be the thermodynamically stable dissolved sulphur products. SO_4^{2-} added to the bulk water outside the crack might be kinetically stable under crack-tip conditions, since reduction to H_2S is kinetically inhibited.

The dissolution rate would be an important parameter in EAC modelling. The kinetics of dissolution is not known. It might be reaction or diffusion controlled. pH, potential, solubility and size of the inclusion may affect its dissolution behaviour. Based on microsampling [46, 86] tests and other investigations, it seems that MnS-dissolution is rather slow.

Under typical deaerated crack-tip conditions (low ECP of ≈ -500 mV_{SHE}, slight acidic pH shift of 1 - 2 units from neutral) Fe_3O_4 respectively FeS and FeS_2 are stable corrosion products, which can form films. Depending on crack-tip sulphur-anion activity, the stable film on surface is either Fe_3O_4 or mixed Fe_3O_4/FeS/FeS_2. In fact, FeS and FeS_2-films respectively increased sulphur concentrations in the oxide films have been observed by post-test fractography in specimens which have shown fast EAC during the test. But it was not clear if precipitation of iron sulphides has occurred during the test or during cooling down. The iron sulphides and sulphur built-in the oxide film may act as a trap for sulphur-anions but also as a possible source of sulphur-anions and could eventually cause distinct hysteresis effects and an asymmetric transient behaviour in LAS.

The incorporation of metallurgical sulphur effects into the crack-tip chemistry models requires assumption regarding the rates sulphur-anion generation and transport within the crack. Assumptions are necessary since insufficient data are available to adequately characterize the rate of sulphur-anion generation which is a function of the distribution of MnS-inclusions (length, aspect ratio, ...), of the intersection rate (which is proportional to the crack growth rate) and of the kinetics of dissolution (e.g. extent and rate of dissolution, which eventually depends on pH, potential, temperature, size, solubility,...). So far only a semi-empirical model exists to incorporate the metallurgical sulphur effects [157, 175]. In this model, the crack-tip concentration C_{CT} is correlated with the bulk concentration C_{EXT}, the potential gradient $\Delta\Phi$ in the crack enclave, the steel sulphur content S and crack growth rate da/dt by an equation of the following type:

$$C_{CT} \approx C_{ext} \cdot A^{\Delta\Phi} + B(S) \cdot da/dt \quad (11)$$

where A and B(S) are constants, the later being dependent on the steel sulphur content.

4.4.4 Asymmetry of Transients and Hysteresis Effects

As already pointed out in the preceding Sections, EAC growth form incipient cracks is governed by the crack-tip strain-rate and the sulphur-anion activity and pH in the crack-tip environment. A slow, positive tensile strain-rate and a high sulphur-anion activity in the crack-tip environment have to be simultaneously maintained for sustained, fast EAC growth with high sulphur rates. The threshold condition for EAC is directly related to crack-tip chemistry (critical sulphur-anion concentration) and crack growth rate, not to loading parameter or bulk environmental per se. The synergistic interrelation and interdependence between crack growth rate and crack-tip chemistry and crack growth rate and crack-tip strain-rate and the important effect of time-dependent mass transport process (migration) on the evolution of the crack-tip chemistry in the crack enclave are the major reasons for hysteresis and retardation effects. Most EAC cessation and crack arrest and local crack pinning phenomena in the system LAS/high-temperature water may be attributed to the requirement of dynamic crack-tip strain-rate and high crack-tip sulphur-anion content and their interrelation to crack growth and mass transport.

The GE model inherently predicts hysteresis effects as shown in Figure 32 based on equation (11). To sustain high-sulphur crack growth rates, a high sulphur-anion activity has to be maintained in the crack-tip electrolyte. If such a high sulphur-anion activity cannot be sustained, the crack growth rates drop down to low-sulphur rates. The exact location of the

transition curve between the low and high sulphur line depend on the exact value of ECP, steel sulphur content, bulk sulphate concentration and the flow rate across the crack mouth, but also on the history of the specimen/component. Under oxidizing conditions, the crack-tip sulphur-anion concentration is governed by the balance between competing processes of sulphur-anion supply by the dissolution of MnS-inclusion (which is dependent on the crack growth rate by the MnS intersection rate) / retention of these anions and transport of bulk sulphur-anions towards the crack-tip by migration on the one hand and the loss of sulphur-anions by the diffusion out of the crack on the other hand (see Section 4.1.1). Compared to an initially "high sulphur crack-tip condition, starting from low sulphur condition requires a higher crack-tip strain-rate, stress intensity or loading frequency to achieve the critical crack-tip chemistry / crack growth rate, because the higher crack growth rate under high sulphur conditions itself provides a higher crack-tip sulphur-anion content and the crack-tip strain-rate. In fact, such a behaviour has been observed by van der Sluys [218] in tests with increasing/decreasing frequencies/stress intensities.

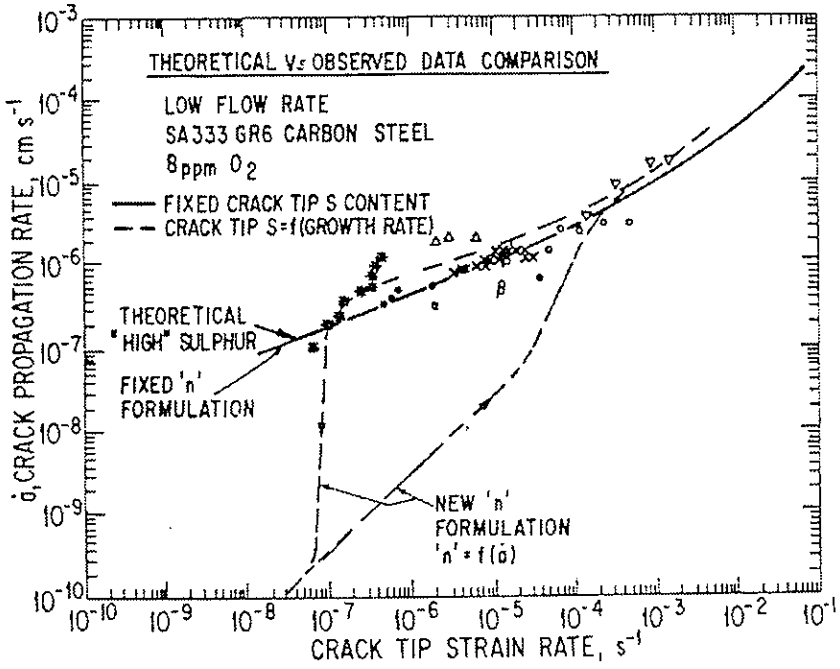


Figure 32: Corrosion fatigue crack growth rate vs. crack-tip strain-rate according to the GE-model [157, 175] showing a distinct hysteresis loop under strongly oxidizing conditions. Different crack growth rates are predicted depending on the starting condition of the test.

The hysteresis loop is more pronounced under oxidizing BWR/NWC than under reducing PWR or BWR/HWC conditions. Within the limited range of the transition lines for increasing/decreasing conditions, different crack growth rates may be observed depending on the start conditions of the test.

Asymmetry of water chemistry and potential transients (dissolved oxygen) transients:

The effect of water chemistry and ECP may have either a strong or no effect on EAC crack growth depending on the exact value of the other system parameters (loading conditions (crack-tip strain-rate), steel sulphur content, ...). A relevant effect of sulphate or ECP on EAC growth is only observed in the transition region between the low and high sulphur line. If high/low sulphur crack-tip conditions are achieved, a further increase/decrease in sulphate or ECP does not result in a further increase/decrease of EAC crack growth rate. The EAC

growth rates are then bounded by the high/low sulphur growth rates and the effect of sulphate and ECP saturate.

Apart form the interrelation between crack growth rate and crack-tip chemistry and crack growth rate and crack-tip strain-rate, the mass transport process in the crack enclave is an important reason for hysteresis and retardation effects, e.g. in the case of water chemistry or potential transients. Water chemistry and potential transients are best viewed from the perspective of "transport symmetry". For the sake of simplicity, the effect of convection is neglected (good approximation for deep cracks, static or low-frequency loading, low flow) in the following discussion. Looking only at mass transport or crack chemistry three important practical cases can be differentiated:

1. Impurity transients under reducing PWR conditions or BWR/HWC/NMCA conditions:

Under PWR conditions or BWR/HWC/NMCA conditions, there is virtually no potential gradient between the crack mouth and crack-tip and in the case of the absence of convection mass transport is governed by ordinary diffusion. Here the things are pretty symmetrical, thus, the transient or response time for rising impurities is similar as for falling impurity levels.

2. Potential transients:

Potential transients (controlled by the dissolved oxygen content) are also fairly symmetrical. A sudden return to low potentials is only possible in LAS, which have been treated by NMCA, otherwise the return to low potentials itself requires a lot of time. The transient or response time for rising ECP is slightly larger than for falling ECP.

3. Impurity transients under oxidizing BWR conditions:

If the impurity level is changed at high potentials, the things are not symmetrical, because there's an additional driving force (migration of ions by the potential gradient) for moving anions into the crack (and shifting pH). For increasing bulk impurity levels starting from high purity water, the concentration-driven (diffusion) and potential-driven (migration) flux of anions both have the same direction towards the crack-tip and the effects are additive. After the transient, when the bulk impurity level is reduced again to high purity water, the concentration driven and potential driven flux have opposite directions. The overall concentration-driven flux of anions from the crack-tip towards the crack mouth is reduced by the potential-driven flux which is still towards the crack-tip, resulting in a reduction of the overall flux out of the crack and longer response times when returning to high purity water. Thus, the transient/response time for rising impurities is faster than for falling impurity levels.

With regard to EAC growth (not just crack chemistry) there is the potential for a further non-symmetry for the following reasons:

1. The relationship between chemistry and EAC is not simply a "linear proportionality". On a somewhat different issue, there are also strong non-linearity's between dissolved oxygen and potential, and between potential and growth rate.
2. Another non-symmetry occurs when the sulphate/sulphide level (in the crack) is high enough to precipitate metal sulphides. The external environment (especially at high potential) can keep pumping in sulphate, but if it is "consumed" in forming metal sulphide precipitates then the crack-tip sulphur-anion content is limited by the solubility limit and the crack never reaches equilibrium with the bulk chemistry. When the bulk chemistry is cleaned up, the sulphide precipitates represent a huge reservoir of sulphur-anions and the

driving force for the transport of sulphate/sulphide out of the crack is lower, both because of the potential gradient (assuming it still exists) and because the dissolved S concentration in the crack is at a lower level (limited by the solubility of the metal sulphide). When this occurs, it can be a huge non-symmetry.

3. With low-alloy and carbon steels, another important factor must be accounted for, i.g. the dissolution of MnS:

   As already mentioned, the crack chemistry is strongly affected by the dissolution of MnS and by the crack growth rate itself by the intersection rate of MnS. This produces a hysteresis (non-symmetry) in response in pure water i.e., the steel exhibits "low sulphur" response initially, and the K_I (or K_I/frequency) must be raised substantially until it finally produces a sufficiently high growth rate that enough MnS is intersected and their dissolution gives rise to a "high sulphur" crack chemistry and EAC rate. If K_I (or K_I/frequency) is now decreased, the "high sulphur" response is able to maintain a high growth rate (and MnS intersection rate) to much lower K_I values than before, but eventually a critical growth rate is achieved and the EAC rate falls dramatically. This behaviour is not seen in stainless steels. For sulphate transients under oxidizing conditions under specific combinations of test parameters starting from low sulphur crack-tip conditions, it is even feasible that high-sulphur crack-tip conditions and growth rates achieved during the transient may be sustained after returning to high purity water, since the high crack growth rate itself may be sufficient to maintain the high sulphur crack-tip conditions.

Hysteresis and retardation effects may be a further reason for the large scatter of literature EAC crack growth rate data. The discussion above shows that test results may be strongly dependent on the applied test procedure and the starting conditions. Multi-parameter tests with changes of system parameter or unintended transients should be analysed very thoroughly. It is also stressed that no crack growth rate results under highly oxidizing conditions should always be treated with caution, since there are many experimental reasons for crack arrest/pinning or cessation of crack growth because of the conjoint requirement of dynamic crack-tip strain-rate and high crack-tip sulphur-anion content and their interrelation to crack growth and mass transport. No crack growth results are often an experimental artefact and should not be regarded as a definite evidence for a low EAC susceptibility under these conditions until it has been independently verified by several suitable tests (long-term tests, periodical partial unloading, test start with actively growing EAC crack, ...).

4.4.5 Effect of Flow Rate

4.4.5.1 Experimental Observations and Phenomenological Aspects

Possible flow rate effects are briefly discussed and reviewed in [47, 170]. High flow rates may be beneficial for both EAC initiation at smooth surfaces and EAC growth of mechanically long cracks in LAS under LWR conditions. EAC initiation may be significantly retarded or even completely suppressed (under static load) and EAC growth may be stopped or significantly slowed down by turbulent high flow rates (see Figure 29 and 30) [43, 176 - 184]. Studies by Lenz et al., for example, suggest that, to some degree, EAC crack growth rates under cyclic fatigue loading and BWR conditions appeared to be inversely proportional to the water velocity past the crack mouth [176].

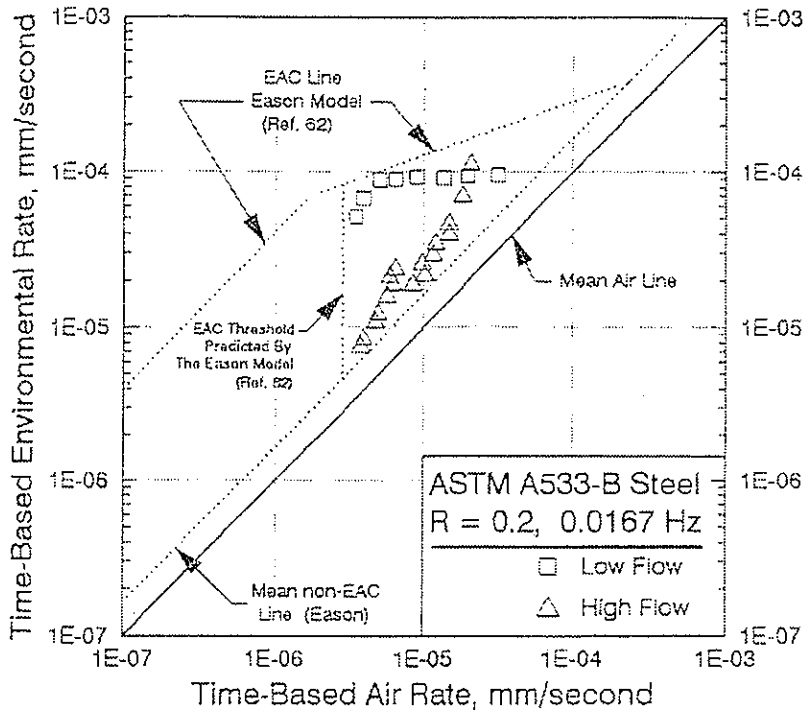


Figure 33: Effect of water flow rate upon the corrosion fatigue crack growth rate response of a 0.014 wt.% S SA 533 B Cl. 1 steel in a BWR environment (200 ppb DO, 288 °C) in a time-domain plot [170].

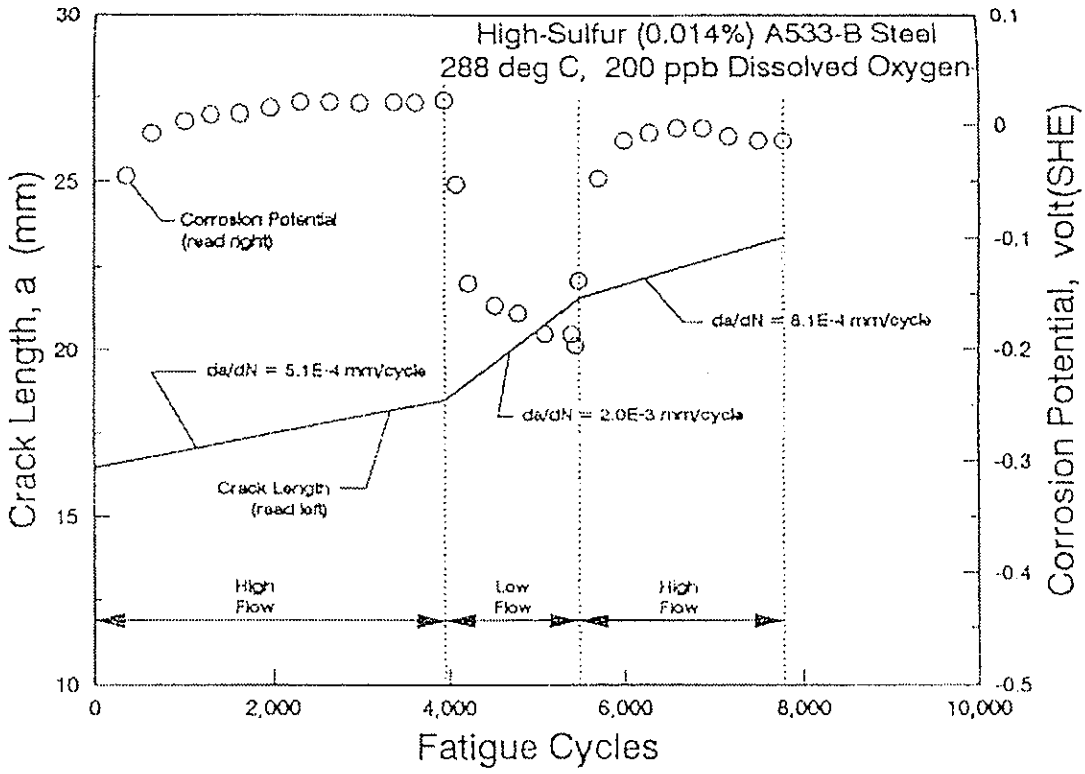


Figure 34: Crack length (and corrosion potential) vs. time for low-alloy steel tested under cyclic load in 288 °C water containing 200 ppb oxygen. Higher flow velocity increased the corrosion potential, but reduced crack growth rate [179].

A beneficial effect of high flow rate probably only exists for good bulk water chemistry quality (low level of specific anionic impurities as Cl^-, SO_4^{2-}, H_2S, HS^-, S^{2-}) but not for aggressive environmental conditions. The high turbulent flow rate, mitigates or avoids the evolution of an aggressive occluded water chemistry in small surface defects and pits, which seems to be a necessary pre-requisite for accelerated EAC initiation at smooth surfaces. The crack growth of long cracks may be relevantly slowed down or even stopped if relevant dilution or complete flushing out of the aggressive chemistry formed in the crack occurs.

The flushing of crack-tip electrolyte is more efficient for small cracks and under cyclic loading conditions and depends on factors such as the crack surface roughness, crack path, oxides in the crack, ratio of CMOD to crack length respectively on the crack opening angle, on the flow rate, on the orientation of flow and on (cyclic) loading conditions (frequency, R-ratio). No negative effect of high flow rate on EAC in LAS under LWR conditions has been observed so far. The beneficial effect of high flow rate on EAC growth is generally slightly overestimated, especially for static loading conditions and for deep cracks. Most investigations on the effect of flow rate have employed cyclic loading conditions with relative high frequencies ($\geq 10^{-3}$ Hz) and specimens with through-thickness cracks, e.g. compact tension-type specimen. The higher CMOD of these specimens compared to more realistic and more tight surface cracks for similar crack lengths and K_I-levels and the fact that the crack enclave is open to three sides make crack-tip flushing more favourable in this specimen type. Experiments with tight relatively deep (up to 15 mm) semi-elliptical surface cracks under cyclic fatigue loading clearly demonstrated, that for high flow rates of several m/s could mitigate EAC growth rates [180, 181]. The case of a tight surface crack penetrating the cladding and reaching to the RPV base metal has not been investigated so far. It is expected that intergranular respectively interdentritic crack path by SCC in the stainless steel or Alloy 182 cladding could relevantly reduce the interaction between fluid flow past the crack mouth and the crack-tip environment.

There are two major reasons for effects of convection in EAC, the convective flow induced within the crack due to fluid flow past the crack mouth and due to „fatigue pumping". „Fatigue pumping" results from the relative displacements of the crack flanks between maximum and minimum stress portions of a fatigue cycle. A certain volume of water could therefore be pumped into, an out of, the crack during each fatigue cycle. This can result in a dilution of the crack electrolyte. Such a process would be become of greater importance as cyclic frequencies increased and with lower stress ratio and higher flow rates across the crack mouth.

Most of the experimental studies have been performed under „quasi-stagnant" or low flow conditions (< cm/s). Since the formation of an aggressive occluded water chemistry is favoured in creviced regions under these conditions, they are generally regarded to be conservative. As noted in the review of service experience in Section 5, several number of service failure have been associated with low-flow or stagnant conditions, apparently confirming this aspect. In most regions of the rector turbulent conditions with comparably high flow rates in the range of several m/s exist.

4.4.5.1 Discussion of Different Types of Flow Rate Effects

The high flow rate generally causes a distinctive rise in mass transport by convection, whereby this rise may lead to a flushing out of the aggressive crack environment and to flow induced rise in surface corrosion potentials which have to be taken into account if discussing the effect on flow rate to EAC susceptibility [47]:

Type A: Crack-tip flushing

Depending on both length, geometry of crack and level of flow rate, there is an opportunity for properly oriented flow to dilute or completely flush out of the aggressive chemistry formed in the crack. This is relevant to PWR conditions, where dissolution of MnS-inclusions in the crack can produce an aggressive chemistry and accelerate crack growth rates. It has been demonstrated by many independent tests that crack-tip flushing by high flow rates may relevantly slow down EAC crack growth rates in LAS under these conditions [181, 182, 185, 186].

Type B: Crack-tip flushing with increase of crack-tip corrosion potential

In oxidizing BWR environments, crack-tip flushing is related to a large increase in corrosion potential at the crack-tip from the presence by convection of high oxidant levels. Experiments by Lenz et al.[176] and Katada [179] have demonstrated, that even under BWR conditions high flow rates may mitigate EAC growth rates. In experiments in oxygenated high-temperature water with crack-tip microsampling with very high sampling rates, where flushing of the crack-tip electrolyte occurs, EAC growth rates have been relevantly slowed down, compared to low sampling rates [46, 86]. As noted in Section 4 EAC growth in LAS is primarily governed by the crack-tip pH and activity of specific anionic impurities but not by the crack-tip corrosion potential.

Type C: Flow induced increase rise in surface corrosion potential

At low bulk oxygen concentrations (10 - 100 ppb), high flow rates can produce a significant increase in the external (crack mouth) corrosion potential (up to 400 mV). At low DO and low flow conditions, oxygen reduction and ECP is controlled by the diffusion of oxygen through the diffusion layer to the steel surface. The DO concentration at the steel surface is lower than in the bulk environment and results in a low ECP. An increased flow will reduce the thickness of the stagnant boundary layer and increase the DO concentration and ECP at steel surface. At very high flow rates oxygen reduction kinetics is controlled by the reduction reaction itself (activation polarisation) but not by mass transport. The oxygen concentration at steel surface and in the bulk environment are identical. Under these conditions, ECP is ca. independent on flow rate and has reached its highest value for a given DO.

The higher ECP at crack mouth would result in an increase in potential gradient between crack mouth and deaerated crack-tip, which is at rest, and in the potential gradient driven migration of specific dangerous anions towards the crack-tip. Because corrosion potential and SCC growth rates are strongly correlated, there has been a sensible concern that this will produce substantially increased SCC susceptibility and crack growth rates.

While the effect of flow-induced elevation of corrosion potential has traditionally been viewed as promoting SCC, it has been recently proposed by Andresen that the deleterious effect of flow rate can be ignored, and the corrosion potential relevant to EAC advance is the „low flow" potential (see Figure 35). This view is based on recognition that the effect of corrosion potential can be understood in terms of the role of the potential-driven ion migration in mass transport (i.e. in crevice differential aeration cell). The kinetics of mass transport is such that convection completely overwhelms (by many orders of magnitude) the contributions of ordinary concentration gradient driven diffusion and potential gradient driven ion migration. The presence of high convection prevents the formation of an occluded chemistry where convection exists, thus eliminating any relevant concentration and potential gradient (concentration or flow-induced) in this region (see Figure 35). Thus, where convection is present, there is no relevant diffusion and migration. Occluded chemistry can only form near the point of „zero convection" in the crack, and the relevant potential is

associated with the low flow conditions at this location. This location referred to as the „electrochemical crack mouth". Between the geometrical crack mouth and the electrochemical crack mouth, any effect of potential gradient is overwhelmed by convection. Thus, while the corrosion potential at the free surface may be greatly elevated under high flow rate conditions, the flow merely acts to shift the electrochemical crack mouth into the crack. There are some few tests under conditions, where corrosion potential at external surface has been shifted by high flow rate [179]. The EAC growth rates have been slowed down at high flow rates under these conditions. The slow down of crack growth might be an effect of crack-tip flushing. Further critical experiments at low DO levels with low and high flow rate with long cracks where flushing of crack-tip environment can be excluded would be necessary to verify the hypothesis of Andresen.

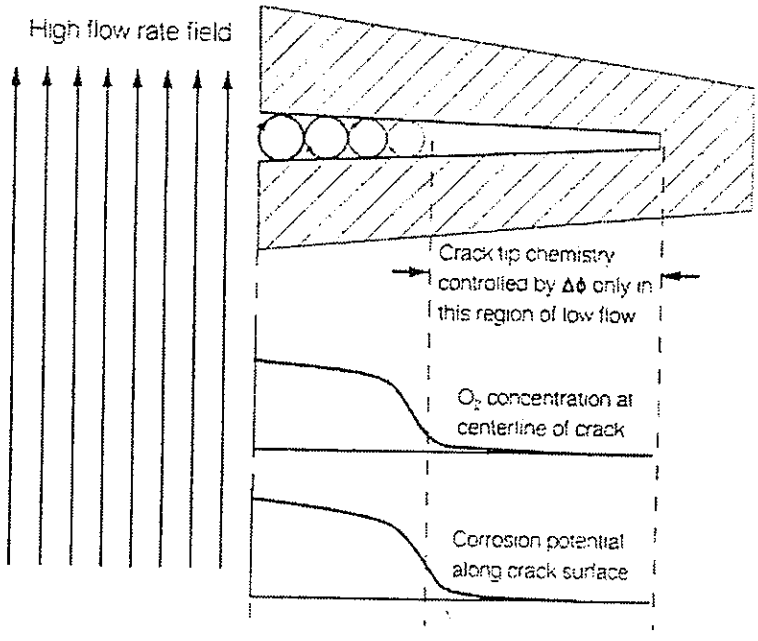


Figure 35: Schematic of the electrochemical crack mouth, which is defined as the location in the crack enclave where convective flow becomes small. Since convection dominates diffusion and migration, the electrochemical crack mouth is defined as the location where the contribution of the potential gradient can strongly influence mass transport and the crack chemistry. At locations toward the geometric crack mouth, the effect of any potential gradient is overwhelmed by convection. Thus, while the corrosion potential at the free surface may be greatly elevated under high flow rate conditions, the flow rate merely acts to shift the electrochemical crack mouth into the crack [47].

High flow rates may be beneficial for both EAC initiation and growth. High flow rates may significantly retard EAC initiation but not completely prevent it. High flow rates may relevantly slow down crack growth under cyclic fatigue loading conditions and/or under conditions where flushing out of the aggressive crack environment can occur. For static loading conditions and deep cracks, the beneficial effect of high flow past the crack mouth is generally overestimated and only a minor effect is expected here compared to low flow and quasi-stagnant conditions. The only case, where EAC might be significantly accelerated by high flow rates, is the situation in high-temperature water with low DO and high flow, where ECP is significantly shifted on the external surface, but the flow does not enter the crack, so that an occluded chemistry can form, a situation which seems not to be very realistically.

5. LWR Operating Experience and EAC Cracking Incidents

It is obvious from the accumulated experience of operating PWR and BWR that EAC of low-alloy pressure vessel and piping steels is not a major problem in the sense that it is clearly not widespread in occurrence. Nevertheless, rare instances of EAC in LAS have occurred, more often in pipelines than in pressure vessels and very rarely in reactor pressure (RPV) vessels themselves [16, 19, 89]. One reason for this is that low-alloy RPV steel does not come into contact with the liquid phase primary coolant since in common Western LWR designs most parts of the RPV are normally protected by a duplex or stabilised austenitic stainless steel weld overlay cladding providing a high stability against EAC and thermal fatigue.

Compared to fossil power plants, where corrosion fatigue continues to be the damage mechanism responsible for the largest percentage of availability loss, the world-wide accumulated operating experience and performance of low-alloy primary pressure-boundary components in LWR has been excellent. This is attributable to a relevant part to the quality and care with which the nuclear systems have been designed, built, maintained, and operated, in addition to the large conservatism introduced at the design stage, especially with respect to the known or anticipated mechanism of failures including fatigue. Thus the initial chance of occurrence was reduced through the design basis and, when indications were found or suspected at critical locations in some plants, augmented inspections and operational procedures were instituted to further reduce the chance of fatigue failures in service.

The high standards of safety and reliability on pressure-boundary components in NPP require that even very low probability failures must be understood to prevent recurrences by adequate countermeasures. Therefore it is essential to define the conditions under which environmentally-assisted cracking can occur in high-temperature water and to quantify margins between normal operating and upset conditions which can cause EAC.

5.1 EAC Cracking Incidents in LWR

Cracking incidents have occurred in BWR and less distinct in PWR. Carbon and low-alloy steel components [14, 16, 19, 26, 32, 89] being involved are pressure vessels [187], steam generators [188, 189], piping [190 – 194], deaerators [195 – 197], and steam turbine discs [198 –200]. Just in the latter situation intergranular cracking of prior austenitic grain boundaries in bainitic NiCrMo and CrMo steels (HAEAC) has been observed. In all other cases cracking has been predominantly transgranular in nature where carbon or low-alloy steels covered by the designations of SA 333Gr6, SA 106, SA 302GrB, SA 533 B, or SA 508 (and other national equivalents) have been involved. The following discussion is focused on low-alloy LWR primary pressure-boundary components.

5.1.1 Common Features of EAC Cracking Incidents

Most EAC cracking incidents have been carefully analysed and documented in literature. Notwithstanding that even similar components can significantly differ in design details, in design and material concepts, in manufacturing and fabrication process and in operation-related features and operation history, common features and similarities of these cracking incidents could be derived. These EAC incidents have been often associated with, and exacerbated by, various combinations of:

- severe dynamic straining, due to thermal stratification/stripping (e.g. during hot-stand-by at low feedwater flow rate) or due to thermal and pressurisation cycles (e.g. plant-start-up/shut-down, hot stand-by,...).

- an oxidizing environment due to e.g. oxygen (BWR pipe lines carrying stagnant steam or non-degassed condensate during normal operating, ...) or Cu^{2+}-cations (leakage from brass condensers, ...), sometimes in conjunction with unspecified anionic impurities (Chloride, ..).
- high local stress around or above the HT yield stress or high secondary or residual stress due to, for instance, localised post-weld treatment, fit-up deformation, local stress raisers, geometrical welding defects due to misalignment, excessive weld penetration (leading to root notches and lack of fusion or incipient cracking in the root region).

Instances of EAC have particularly occurred in BWR service, most often in LAS piping, and, very rarely in the RPV itself. EAC damage was usually detected by non-destructive examination and seldom led to through-wall penetrations with leakage [19, 32]. In many of the reported incidents, EAC in LAS has occurred as a result of substantial departures from either design intentions or normal operation practice, which are identifiable and can be therefore avoided [16]. Oxidising agents, usually oxygen, and severe dynamic straining were always involved [16, 32]. These cases could be attributed either to SICC or low-cycle corrosion fatigue. Several incidents were related to unanticipated sources, frequency, and/or severity of thermal stress cycles in critical locations, thus indicating design inadequacies [89]. In many cases fabrication or design deficiencies often favoured local plastification (e.g. welding defects) and dynamic straining (e.g. thermal sleeve with old slip fit design, see Section 5.1.2)) and sometimes resulted in an increased stress intensity (residual stress, welding hot cracks of the cladding) or increased EAC susceptibility of the material (e.g. excessive hardness of LAS weld HAZ, increased IGSCC susceptibility of SS cladding due to insufficient delta ferrite, martensite formation or extensive cold work due to grinding, ...) [16, 19, 32, 89]. By an improved design of the components or fabrication procedure and quality control during the fabrication process, reoccurrence of these cases could be avoided or significantly reduced [16, 19, 32, 89]. In some cases water quality outside current EPRI water chemistry guidelines (high level of aggressive impurities) has been a further contributing factor [16].

Cracks often initiated from geometric discontinuities (which result in local stress concentration and favour the formation of an aggressive, occluded water chemistry) and/or in regions, where the formation of an aggressive environment were favoured (stagnant flow, crevice,...). EAC cracks were mainly initiated from corrosion pits and/or at MnS-inclusions, which intersected the steel surface but rarely if ever from pre-existing large cracks. In general, crack initiation has been more affected by the high frequency, high-cycle fatigue due to local thermal stratification or thermal stripping action limited to near surface regions. The crack propagation was often dominated by the low-cycle fatigue from slower and less frequent transients due to global thermal stratification or operational power transients.

A complete root cause evaluation has not always been performed in all cracking incidents. Therefore, identification of cracking mode respectively the separation of the relative contributions of EAC (SCC or SICC/CF) or pure mechanical fatigue to the total crack advance has not always been completely clear. Minor contributions to crack propagation due to SCC can therefore not be completely ruled out for many cracking incidents, but cases with major or relevant contribution of SCC to the total crack advance in properly manufactured and heat-treated low-alloy primary pressure-boundary components are not known to the author. In contrast, certain cases indicate excellent SCC resistance of the base metal under stationary power operation conditions, since no corrosion damage in the form of cracks has occurred either as a result of extensive surface contact with the operating environment (e.g. for unclad reactor heads or nozzle bore radii) which exhibited extensive contact with the

operating environment, or at the tips of cracks ending through the cladding in the low-alloy base metal [187].

Some typical aspects for corrosion-assisted crack advance in low-alloy pressure-boundary components in the primary coolant circuit of BWR will be worked-out in more detail on the basis of two „classical" types of cracking incidents.

5.1.2 EAC of BWR RPV Feedwater Nozzles

EAC has been observed in some RPV feedwater nozzles in BWR [20, 187]. Cracking has been located in the bore and blend radius regions of the SA 508 nozzle (Figure 36) cladded by 308 (non-sensitised) duplex stainless steel. The corresponding thermal sleeve design allowed a leakage flow of cold feedwater in the annulus between the nozzle and the sleeve.

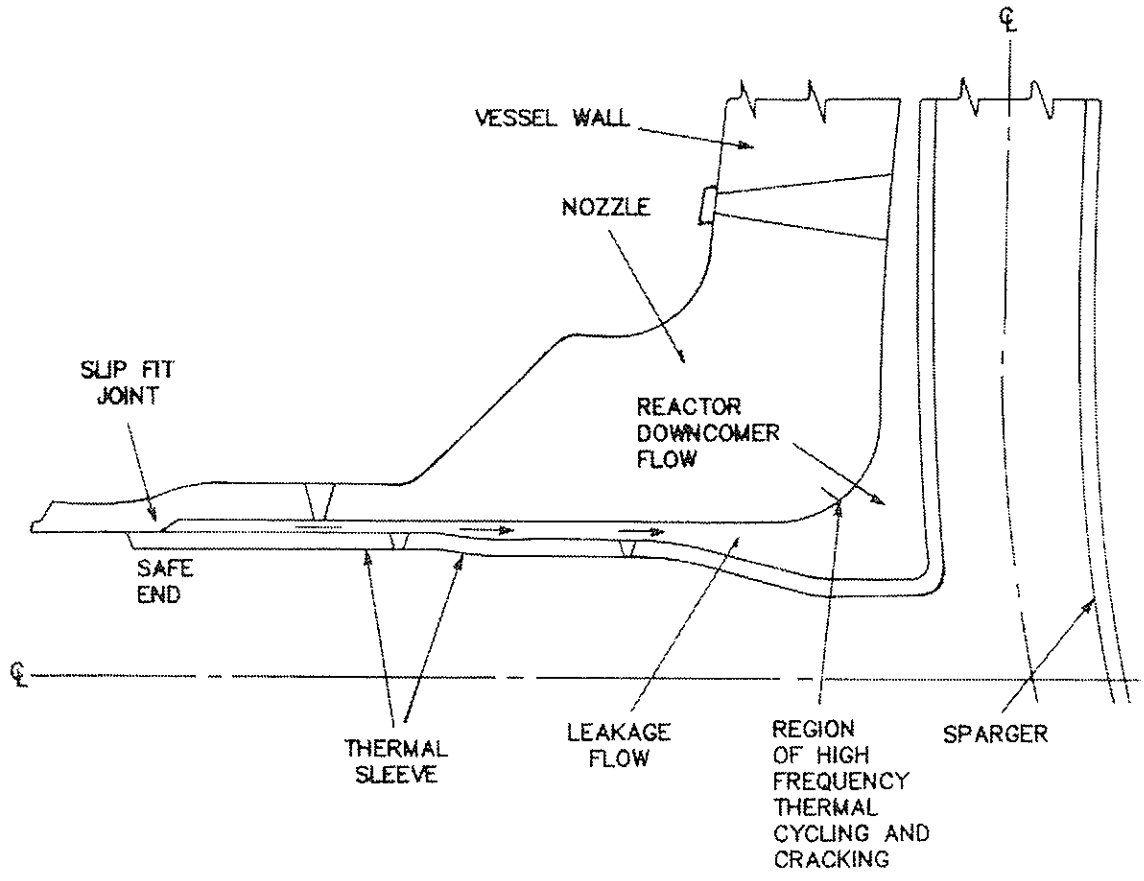


Figure 36: Cross section of BWR feedwater nozzle with cracking location [20, 187].

As a hypothesis, the cracking was due to a sequence of high cycle fatigue and EAC under low cycle conditions:

-A high frequency thermal fatigue mechanism (without relevant environmental contribution) initiated cracks in the stainless steel cladding, which subsequently propagated through the low-alloy steel. This mechanism [20, 187] was attributed to turbulent mixing of the cold leakage flow (220 °C), past the slip fit joint of the safe end, and the hot downcomer flow (280 °C). The mixing fluid impinges on the nozzle wall, causing thermal cycling at frequencies in the range of 0.01 to 1 Hz. The thermal stress amplitude from this particular source degrades to zero when the crack propagates to an approximate 6 mm depth. An

alternate thermal sleeve designs and removal of cladding by grinding, which minimise the high frequency thermal stresses, has been revealed as an adequate countermeasure.

- Further propagation of this crack in the LAS has been assigned to low frequency thermal and pressurization cycles associated with e.g., start-up/shut-down cycles, scrams, turbine rolls, etc. The cracking mechanism could be assigned to SICC or low-cycle CF with relevant environmental acceleration of crack growth. SCC under static load during steady-state power operation seemed not to relevantly contribute to crack advance in this case. This assumption is supported by the better correlation between the extent of cracking and the number of start-up/shut-down cycles than with the total operating period [20, 187].

5.1.3 SICC of Thin-Walled Pipings in German BWR

Relatively high strength fine-grained structural steels (WB 35) have been widely used in Germany, e.g. for the construction of pressure vessels and piping in BWR systems and for the fabrication of feedwater tanks and heat exchanger in the secondary circuit of PWR which enabled to manufacture relative thin-walled components. Cracking incidents have been occasionally observed in feedwater tanks of PWR but more often in thin-walled piping of BWR with stagnant steam or stagnant high-temperature water. Several of these cases were reviewed in [18, 32, 38, 201 -203] and possible mitigation remedial actions are discussed in [193, 204 - 207]. In all these cases oxidizing conditions and local dynamic straining were involved. The PWR cases cited above involved feedwater under operating conditions, for which the normally low contents of oxygen cannot be assumed.

The piping cracking incidents could be attributed to SICC (strain-rate-sensitive SCC) and in some few cases to corrosion fatigue at very low cyclic frequencies. The crack growth was rather intermittent and occurred during special operating conditions (start-up/shut-down, hot-stand-by at low feedwater rates with thermal stratification). Typical chemical and cyclic strain transients in LWR pressure-boundary components are specified in Table 5. The specified conditions fit excellent to the SICC susceptibility conditions observed in SSRT tests (see Figure 17 in Section 3.). There were no indications for relevant SCC crack growth under static loading during steady state power operation. The cracks often initiated in regions of increased local stress above the design level (for example at welding defects, pipe bends in conjunction with inadequate pipe support or restraints) or in horizontal pipe sections where thermal stratification could occur. The fact that frequently cracking occurred in lines with stagnant steam or non-degassed condensate, but not in comparable lines carrying flowing steam, is a indication that oxygen concentration/corrosion potential are a crucial parameters in respect to the occurrence of SICC, since such conditions are known to encourage the formation of a condensate rich in dissolved oxygen.

Many early SICC field incidents involved stagnant conditions, where the real conductivity of the water within the porous oxide/hydroxide layer immediately adjacent to the surface of the affected component might be expected to be much higher. Significantly, cracking has occurred in recent years in Germany in BWR feedwater lines, although the purity of the bulk medium was exceptionally high [209]. Geometrically, however, it was clearly associated with areas in the lower part of the horizontal piping where corrosion products (primarily rust) had formed from water residues during prior shut-down. Thus it is possible that a local, "micro-environment" of much higher conductivity had still existed during plant start-up, i.e. at the time when significant, dynamic straining at welds in the piping also occurred.

Component	Operation	O_2 (ppb)	Temp. °C	$\Delta\epsilon$, %	$\dot{\epsilon}$, 1/s
PWRSG FW Nozzle	Startup	5	230/RT	0.2–0.5	10^{-4}
BWRPV FW Nozzle	Startup	20/200	216/38	0.2–0.4	10^{-4}
BWR FW Piping	Startup	20/200	216/38	0.2 0.5	10^{-5}–10^{-4}
BWR FW Piping	Startup	20/200	288/38	0.067 0.1	4–8x10^{-8}
BWR FW Piping	Turbine Roll	< 200	288/80	0.4	3 6x10^{-5}
BWR FW Piping	Hot Stand-by	< 200	288/90	0.26	4x10^{-6}
BWR FW Piping	Cool down	< 20	288/RT	0.2	> 6x10^{-6}
BWR FW Piping	Stratification	200	250/50	0.2–0.7	10^{-6}–10^{-5}

Table 5: Typical chemical and cyclic strain transients in LWR pressure-boundary-components [208].

5.2 Operating Experience vs. Laboratory Background Knowledge

The results of root cause analysis of different cracking incidents fit well to the accumulated experimental and mechanistical background knowledge on the EAC and pitting behaviour in the system LAS/high-temperature water (see Section 3.2, Table 3 and 4). The operation experience confirms the high SCC resistance of quenched and tempered LAS under steady-state power operation and static loading conditions. Both operating experience and lab data clearly reveal that slow, positive (tensile) dynamic straining with associated plastic yielding and sufficiently oxidising conditions are essential for EAC initiation and subsequent growth in high-temperature water of high or moderate purity. Since primary design stress are generally limited to values below the elastic limit, (local) plastification at defect-free surfaces can only occur under special operation conditions with high secondary stresses (thermal stresses) or in regions of increased local stress (notches, residual stress,...). EAC cracks often initiated from corrosion pits or MnS-inclusions which intersected the steel surface. Pitting of LAS is strongly favoured under oxidising conditions (high oxygen concentration) especially at low and intermediate temperatures and by slow dynamic straining. Quasi-stagnant or low flow conditions are promoting the formation of an aggressive occluded water chemistry at the pit ground and therefore strongly promoting EAC initiation.

So far we could not find any major discrepancy between operating experience and trends in laboratory data. The following two major apparent disparities have been sometimes mentioned in literature:

- EAC is much easier to induce in laboratory specimens tested in autoclaves under simulated LWR conditions, particularly in steels with elevated concentrations of sulphur, than in operating components under comparable conditions.
- There is no evidence for a relevant SCC susceptibility of LAS base metal under stationary power operation condition. Here there seemed to exist an enormous discrepancy between operating experience and some very high SCC crack growth rate laboratory data under static loading under nominal BWR conditions reported in literature. This discrepancy was explained by crack initiation problems (low probability, extremely long incubation periods) under BWR power operation conditions (with high flow rate and high purity of the coolant) and there was a concern that, if crack initiation should occur, then high crack growth rates relative to operational time scales or inspection intervals might be observed.

5.2.1 Reasons for Higher EAC Cracking Frequency in Laboratory Tests

There are several reasons, why EAC is more frequently observed in lab tests than in operating components under nominally comparable conditions:

- For the occurrence of EAC initiation (and subsequent growth), several parameters such as the ECP, strain-rate, strain and temperature have to simultaneously exceed certain threshold values during a sufficiently long period (see Section 3.2). If one threshold condition is not satisfied, no relevant effect of the environment on fatigue initiation and growth is observed. The probability of EAC initiation is then extremely low and even an initially growing EAC crack will generally arrest. The probability that all these factors are simultaneously achieved is relatively low and for many component locations/operation conditions one or several of these factors are missing. A high EAC risk is therefore restricted to some few critical component locations and/or special operation conditions. Even if these conjoint threshold conditions are simultaneously fulfilled, crack initiation process may require a relevant time period and crack growth rates can be very slow.

- Furthermore, a high flow rate representative for most RPV locations may completely suppress or at least retard crack initiation by suppressing the evolution of an aggressive occluded water chemistry in pits or small surface defects by flushing the pit or defect environment. Even crack growth of deep cracks may be completely suppressed or relevantly slowed down if flushing of crack-tip environment occurs.

  Most laboratory experiments were performed under low flow or quasi-stagnant conditions, whereas most locations are subjected to turbulent high flow rate conditions.

- Most laboratory experiments start with a sharp and relatively deep fatigue pre-crack that is „ready" to propagate; most structural components do apparently not (see Section 5.1). In the absence of pre-existing defects or cracks, EAC cracks need to be initiated at the free surface before propagation can occur, and this process may consume a large part of the life time or many fatigue cycles.
  EAC initiation at fatigue pre-cracked specimens is facilitated with respect to defect free surfaces for the following reasons:
  Since primary design stresses are limited below the yield strength, plasticity at defect-free surfaces are restricted to regions of increased local stress (e.g. notches, weld defects and residual stress) or to special operation conditions with high secondary thermal stresses. The pre-requisite of plasticity is always given in pre-cracked specimens. In pre-cracked specimens, a large volume of MnS-inclusions is intersected by the pre-crack crack plane. The dissolution of these MnS-inclusion and the creviced geometry of the pre-crack (with high aspect ratio) favours the formation of an occluded aggressive EAC promoting crack-tip environment. At smooth defect-free surfaces, the evolution of an occluded aggressive environment in small corrosion pits and therefore the initiation and subsequent EAC growth may be completely suppressed by flushing of the environment at the pit ground. Flushing of crack-tip environment in deep surface cracks is more difficult.
- In western LWR most parts of the RPV are protected by a duplex or stabilised austenitic stainless weld overly cladding with a high stability against EAC. EAC in the RPV requires cracking of this cladding and direct access of the environment to the crack enclave.

5.2.2 Reasons for High SCC Cracking Susceptibility in Some Lab Tests

Reasons for the large scatter and for the very high SCC crack growth susceptibility sometimes observed under "nominal" BWR water chemistry conditions have been discussed in Section 3 and 4. Many tests revealing those high SCC crack growth rates plotted in Figure 20 have been performed under a combination of both gross yielding of the remaining specimen ligament which is not relevant to the thick-walled RPV structure and aggressive water chemistry conditions which are not representative for current BWR operation. Another important reason for high crack growth rates have been loading conditions significantly different from static loading, e.g. slow rising displacement tests or tests with periodical partial unloading with very short constant load periods in-between, where relevant dynamic crack-tip straining by external loading occurs. In many older investigations, system parameters having a strong influence on crack growth were neither sufficiently controlled and monitored nor documented. Thus, the transferability and relevance of these data to pressure-boundary components and to BWR power operation conditions cannot be evaluated. In those cases where enough information on testing characteristics were available to the author, either no or very slow SCC crack growth rates were observed under simulated BWR conditions, or plausible reasons for the deviations form this behaviour based on the accumulated well accepted experimental and theoretical background knowledge for the system under investigation, could be given (see Section 3.6.3)

The high SCC cracking susceptibility observed in older tests could not be reproduced by recent reactor site testing [25, 26] and by recent experiments [28, 30, 138] in modern high-temperature loops with water refreshment, on-line crack growth monitoring and documentation of all relevant test parameter. From these investigations it is now more and more apparent that the „low sulphur line" can be regarded as an upper bound for possible SCC crack growth rates under current BWR operating practice. Relevant additional dynamic loading is necessary to maintain low sulphur crack growth rates if water chemistry conditions were maintained within current BWR operation practice to some extent. Otherwise crack arrest occurs under purely static loading.

The high crack growth rates down to small stress intensity factors are in clear contradiction to the world-wide accumulated RPV operation experience. Clearly, if there would be a practical problem of that magnitude occurring generally under conditions relevant to power operation, then no low-alloy steel vessel used in high performance steam production plant, nuclear or non-nuclear, and especially those vessels, where EAC cracking has been observed through the cladding down to the unaffected base metal, could survive, which is manifestly not the case.

5.2.3 Summary

LAS pressure-boundary components in nuclear RPVs had an excellent service record. Nevertheless, rare instances of environmentally-assisted cracking have occurred, more often in pipework than in pressure vessel and very rarely in reactor pressure vessels themselves. Components in BWR have been involved much more than in PWR. Oxidising agents, usually oxygen itself, and relevant dynamic straining were always involved in these cracking incidents. They could be attributed to SICC or low-cycle CF, but hardly if ever to SCC.
Incidents in PWR did generally occur under operation conditions, where the presence of oxidising agents cannot be excluded and/or the concentration of specific impurities did clearly exceed current water chemistry guidelines. Under reducing conditions characteristic for the primary coolant circuit of PWR under steady-state power operation, the LAS are not

susceptible to SCC. Compared to BWR, the susceptibility to SICC and low-cycle CF is drastically reduced.

As long as water chemistry is maintained within current BWR/NWC operation practice to some extent, properly manufactured and heat-treated LAS pressure-boundary components seem not be susceptible to sustained, fast SCC growth under static load. Therefore, relevant SCC crack growth under transient-free steady-state BWR/NWC power operation appears to be highly unlikely. In contrast to their high stability against SCC, the LAS show a distinct susceptibility to SICC/low-cycle CF in oxygenated high-temperature water, even at very low impurity levels, if suitable slow dynamic/cyclic loading conditions do occur during operation.

5.3 Possible EAC Prevention Strategies and Mitigation Actions

The common SCC/SICC mitigation strategy is to exclude large pre-existing defects by adequate non-destructive examination and quality assurance measures during and after fabrication of components before they were put in operation and to avoid during operation those water chemistry/stress or strain combinations, which could lead to crack initiation. This procedure is applied for primary pressure-boundary components in nuclear power plants. The current LWR operation practice, EPRI water chemistry guidelines and the applied design codes are successful in avoiding most critical conditions for EAC initiation. The current fatigue design rules have been successful in preventing cracks in carbon and low-alloy steel and are very conservative and adequate under most circumstances. As revealed by the operation experience, it is very likely that SICC, or very low-cycle CF behaviour, that covers the most important gap in the design rules and fatigue usage methodologies. The short-lived plant transients (start-up/shut-down, hot stand-by, turbine trips, with temperature/ pressurization cycles, thermal stratification,...) have been identified as periods when SICC is most likely to occur.

Nevertheless, cracking in operating components may be induced by (unanticipated) transient or faulted operation conditions or may be (and has been) observed by ND-inspection during service. Furthermore, ND inspection methods have a limited resolution, sizing probability and reliability, therefore reactor safety analysis is primarily based on crack growth evaluations of postulated pre-existing cracks. Therefore reliable data on the SCC/SICC crack propagation behaviour are necessary and essential for both safety considerations/structural integrity assessments and to set-up/adapt ND inspection intervals, especially for safety-relevant primary pressure-boundary components, e.g. the RPV. There is still a lack of reliable quantitative SICC crack growth rate data under short-lived plant transients (start-up/shut-down, hot stand-by, turbine trips, with temperature/pressurization cycles, thermal stratification, ...).

For safety-relevant LAS primary pressure-boundary components, only the combination of avoiding of water chemistry/stress or strain combinations which promote crack initiation with structural integrity/safety assessments based on fracture control (based on non-destructive-inspection, crack growth evaluations and fracture mechanics analysis) can be guaranteed to be effective, since crack initiation during service can never be completely ruled out and because rates of environmentally-assisted crack growth can be sufficiently high under certain critical conditions relative to plant operational time scales.
The LAS show a distinct susceptibility to SICC in oxygenated, high-temperature water, even at very low impurity levels, if suitable slow dynamic/cyclic loading conditions occur during operation. It is therefore important to systematically identify specific circumstances that challenge the conservatism in present design rules and the possible system conditions (operating conditions, critical components) where such conditions can or could occur.

5.3.1 Critical Components

Critical components in NPP are for example [32]:

- pipelines carrying nearly stagnant steam or non-degassed condensate during normal operation (or which are used only intermittently).
- feedwater nozzles and adjacent sections of horizontal piping, if thermal stratification can occur.
- components, which are likely to undergo significant localised mechanical loading over or above the design levels (e.g. thin-walled piping and pipe bends in conjunction with inadequate pipe supports or restraints).

5.3.2 Mitigation Actions

Based on the operating experience and laboratory background knowledge different short or long-term remedial measures have been successfully defined and applied [193, 204 - 207] for example by changing or optimising of manufacturing, processing, design and operation related features. In any sensitive preventing strategy risks from fabrication defects have to be eliminated (ND inspection, QA). Operating conditions and component designs should be optimised to avoid dynamic straining and highly oxidizing/ stagnant conditions.

In summary SICC/SCC risks can be minimised by (for technical details see [193, 204 - 207]):

- suitable selection of materials e.g. low sulphur steel (< 0.010 wt.% S) with high toughness.
- suitable selection of manufacturing and fabrication practice to avoid welding defects and HAZ with high hardness (< 300 VH by properly performed post-weld heat treatments) and to reduce residual stress (stress relieving).
- an improved design to reduce regions of high local stresses (by increased wall thickness, by internal flush grinding of joints and optimisation of welding technology)
- avoiding or reducing the number of thermal and pressurisation cycles (thermal-stratification during hot stand-by, start-up/shut-down) by optimised operating procedure or an improved design of the affected component (thermal sleeve of feedwater nozzle, feedwater sparger)
- avoiding stagnant conditions and reducing oxygen levels by optimised operation practice (for example modification of start-up procedures to reduce dissolved oxygen levels by better venting of piping, improvement of drainage in horizontal lines, ...)
- an adequate water chemistry control (EPRI or VGB guidelines), HWC/NMCA.

6. Open Questions and Needs for Future Work

As mentioned in the preceding section, the EAC cracking incidents can be readily understood and satisfactory be explained by the existing laboratory data base, and so far we could not find any fundamental discrepancy between the accumulated operating experience and laboratory background knowledge. A lot of different parameters affecting the EAC behaviour of low-alloy pressure-boundary component steels in oxygenated high-temperature water have been identified during the last decades and several of them are now well established and readily understood (see Table 6). This has allowed to define countermeasures and mitigation actions to avoid or significantly reduce reoccurrence of these cracking incidents.

well characterized and established	insufficiently characterized and understood
• oxygen content and ECP • steel sulphur-content, MnS-inclusion morphology, product form, orientation • sulphate-concentration of environment • susceptibility conditions (crack initiation) • strain/load rate effects • stationary conditions	• temperature • microstructure/micro-plasticity (ferritic-pearlitic, bainitic, martensitic, weld, HAZ, grain size, yield strength, heat treatment, ...) • dynamic strain ageing (DSA) • residual stress • crack initiation and growth mechanism • irradiation effects • transient conditions • flow rate

Table 6: Assessment of important parameters for EAC in LAS in high-temperature water.

The detailed, microscopic mechanism of the crack initiation and growth process are still under discussion and reliable mechanistic-based quantitative lifetime prediction therefore still remains a challenge. Structural integrity and safety assessments are therefore still based on (over)conservative empirical/phenomenological relationships. One of the most important remaining problem, is the large scatter of most EAC data which makes rational life prediction and verification of EAC models difficult. To reduce scattering and undue conservatism, further high quality tests, which fulfil recently formulated requirements for the generation of hard EAC crack growth rate data [138, 210] are required. Degree of conservatism might be significantly reduced by studying and reliably predicting the complex behaviour of early growth of short cracks, which may cover a significant part of the lifetime.

6.1 Corrosion Fatigue/ Strain-Induced Corrosion Cracking

The corrosion fatigue / SICC "engineering" crack initiation behaviour of low-alloy steels in high-temperature water has been investigated over a wide range of loading (strain, strain-rate), material (sulphur content) and environmental parameters (DO, temperature, conductivity), mainly by SSRT and LCF tests with smooth tensile specimens. Most influencing factors and conditions, which could lead to crack initiation are now well established. In the meantime, new proposals for the implementation of environmental effects on fatigue initiation to the ASME III code [211 - 213] have been established based on these investigations.

The corrosion fatigue crack growth behaviour of LAS in high-temperature water is well established for temperatures in the range of 270 – 320 °C and loading frequencies > 10^{-3} Hz for PWR and to a lesser extent for BWR environments. The current reference crack growth

rate curves in the ASME BPV Code Section XI Appendix A are based on data obtained prior to 1980. They depend explicitly on ΔK and R-ratio, but not on other variables that are known to be important, such as loading frequency. In the meantime, several laboratories have conducted extensive testing programmes, including a wide variation of controlled variables. Based on this extended database, a proposal for new reference crack growth curves has been worked-out by Eason et al. [214, 215], taking into account the strong effect of strain-rate/loading frequency. The BWR database for this proposal was relatively small and mainly based on tests with an ECP of $\leq +50$ mV_{SHE}, temperatures around 288 °C and rise times $\Delta t_R \leq 1000$ s. There is still a relevant lack of experimental data for high ECP, low loading frequencies $< 10^{-3}$ Hz and intermediate temperatures, but also for very high R-ratios ≥ 0.95. This lack of data therefore results in a relevant uncertainty concerning the conservatism and adequacy of the proposed reference curve for these parameter combinations. Implementation of these proposals to the ASME III and XI codes and code upgrading are still under discussion. Practical application of these proposals is difficult and complex, since loading rate (strain-rate, rise time) is an important parameter.

The current fatigue design and evaluation codes (ASME III and XI) have been quite successful in preventing fatigue cracks and failures in low-alloy steel (LAS) components, and would therefore seem to be adequate or conservative under most operating circumstances. Despite the good record of current design rules in preventing cracks in carbon and low-alloy steel, a very few, do still occur. Thus identifying specific circumstances that challenge the conservatism in present rules is necessary. On the other hand, there is an obvious desire to eliminate overconservatism especially in the context of plant life extension assessments. Operational experience (Section 5) and laboratory background knowledge (Section 4) both indicate that the current fatigue design curves/codes and usage methodologies might be non-conservative for certain critical, short-lived, BWR plant transients (start-up/shut-down, hot stand-by, thermal stratification, ...) and that SICC, or very low-cycle CF behaviour covers the most important gap in the field of EAC of LAS. The changes of temperature and/or pressure (and of water chemistry) during such transients result in a complex load spectrum. The resulting loads may be out of phase or even in anti-phase with the temperature. The temperature/strain-rate combinations, which are relevant for these transients again draw the attention to possible DSA effects on EAC.

From a safety perspective, there is a relevant lack of quantitative SICC/low-frequency CF crack growth data under transient LWR plant conditions (i.e. at slow strain-rates/very low cyclic frequencies ($< 10^{-3}$ Hz), intermediate temperatures (100 to 300 °C) and high corrosion potentials (BWR)), where susceptibility to SICC/low-cycle CF is very high and the ASME XI wet reference curve may be significantly exceeded. The effect of specific impurities (Cl^-, SO_4^{2-}, ...), corrosion pitting and mean stress on SICC initiation, and the possible effects of flow rate and DSA on crack initiation and growth should be further investigated. Because of possible DSA effects, both, weld and weld HAZ have to be included in such investigations (see Section 4.1.3). The effects of random loading or overloads (e.g. hydrostatic test) on EAC initiation and growth have not yet been studied. The efficiency of HWC/NMCA on mitigation of SICC/LCF under transient operating conditions should be also clarified.

To evaluate real plant situations and for lifetime prediction flow rate effects and non-isothermal conditions should be further investigated including tests with surface-cracked specimens (also with cladding). Such tests might help understand some apparent discrepancy between operating experience and laboratory results and eventually to eliminate some overconservatism.

6.2 Stress Corrosion Cracking

Both, new laboratory investigations and operating experience are showing that relevant SCC crack growth does not occur under pure static loading, if water chemistry conditions are maintained within current BWR normal operation practice to some extent. Based on new results of qualified tests in simulated BWR environment interim disposition lines for SCC crack growth in low-alloy pressure-boundary component steels for BWR power operation have been proposed by an international group of experts within the BWR VIP project [25, 26]. This work has been recently accepted by the NRC as an interim position [25].

The quantitative data base for these disposition lines is still relatively small. Testing has been focused to water chemistry conditions representative for the bulk reactor water / feedwater under transient-free steady state BWR/NWC power operation and to material states representative for RPV/piping base metal. The disposition lines are primarily based on relatively short-term (typically around 1000 h) laboratory tests with respect to operational time scales. Most investigations under simulated BWR conditions were performed under stationary conditions in the temperature range of 270 to 290 °C at dissolved oxygen contents of 200 ppb to 400 ppb at relatively low ECP compared to the recently measured elevated in-pile values of corrosion potential.

There are many aspects of SCC which have not yet been sufficiently investigated (see Table 6). From a safety perspective and with regard to a reliable engineering judgement/assessment of the possible threat of SCC on the long-term structural integrity of the RPV and of other safety-related low-alloy steel pressure-boundary components, the following aspects should be further investigated to close the most important gaps:

- Long-term SCC cracking behaviour:

The disposition lines should be verified by some few long-term (> 1 a) SCC tests under constant active external load under BWR conditions. A part of these tests should start or include sequences with actively growing fast EAC cracks, which have been triggered by suitable cyclic loading, before switching to static loading conditions. Ideally, long-term tests could be combined with reactor site testing (in loop/autoclave systems attached to BWR coolant system).

- Effect of temperature:

The effect of temperature on SCC growth has not yet been systematically studied in high-purity high-temperature water. Because of possible DSA effects a higher susceptibility at intermedate temperatures cannot be excluded for susceptible steels [216].

- Effect of „ripple loading“:

Most SCC tests have been performed under pure static loading or with periodical partial unloading („gentle cyclic loading“). The effect of small stress or ΔK-fluctuations at high R-values ≥ 0.95 („ripple loading“) arising from small temperature or pressure fluctuations during steady state BWR power operation, is an aspect of EAC growth, which has not yet been studied for LAS under LWR conditions, but which might eventually significantly affect the cracking behaviour.

- Effect of water chemistry/loading transients:

The crack growth rate response during and after a water chemistry transient is of practical consequence because BWR system operation inevitably involves periodic, short-term variations in water chemistry (e.g. increased sulphate concentrations due to resin intrusions, condenser leackages, ...). Similar, ECP and dissolved oxygen transients occur during start-up

and occasionally during steady state power operation. Transients in ECP and dissolved oxygen occur with greater regularity with the implementation of HWC, since periodic shut-down of hydrogen injection is required. Since EAC may be controlled by the mass transport processes in the crack enclave (see Section 4.2), significant delay times might occur following a water chemistry transient and hysteresis and memory effects cannot be excluded under certain circumstances. During operation of a BWR, also loading transients (e.g. thermal/pressurisation cycles during start-up/shut-down, turbine trips, hot stand-by, ...) can and do inevitably occur. Information on the crack growth rate response during (incubation periods, response time, ...) and after water chemistry/loading transients (transition behaviour, delay times, hysteresis and memory effects, ...) are essential for an engineering judgement of these transients and for reliable structural integrity assessments of low-alloy pressure-boundary components concerning SCC.

Most of these transients are short-lived. Therefore, the main interest is not primarily in the transient itself, but in the transition behaviour following the transient: What are the CGR under transient conditions? Does the system return to same original state before the transient? How fast does the system return to the original state or to the new steady-state? Are there any hysteresis or memory effects after such transients? Which transients have to be considered in structural integrity assessments (thresholds for the amplitude /durance/frequency of transients)? May fast EAC crack growth, which has been triggered by transient loading (SICC, CF) or transient/faulted water chemistry conditions, be maintained after transition to static loading or to normal water chemistry conditions or does the crack growth slow down back to the very low values observed under these circumstances?

The results of PSI [138] and MPA [28] investigations indicate, that fast SICC/CF crack growth rapidly decays after the transition from monotonically raising/cyclic to static loading and crack arrest generally occurs a short period after this transition. This important preliminary result should be verified by further testing over a broader spectrum of environmental, material and loading parameters.

Effects of potential/DO transients on EAC crack growth in LAS have already been investigated by Andresen et al. in tests with periodical partial unloading [46, 86]. Relative short response and delay times of typically 10 to 100 hours are observed in the case of potential transients. The effect of sulphate and chloride transients at constant high corrosion potentials has not yet been studied for the case of LAS. Long delay times may be expected after such sulphate/chloride transients.

- SCC susceptibility of weld and weld HAZ:

The materials investigated so far, were mainly of base metal type in the quenched and tempered (bainitic) or in the normalised (equilibrium) state (ferritic-pearlitic). Welds and in particular weld heat affected zones have hardly been involved. Apart from the effect of sulphur other material parameters have not yet been systematically studied. Because of possible DSA-effects, a higher susceptibility of weld and weld HAZ material with respect to the base metal cannot be excluded under certain critical conditions. The coarse-grained and peak hardness zone of weld HAZ might reveal a higher SCC susceptibility than the unaffected base material [18, 48]. SCC testing with weld HAZ requires an appropriate modified specimen design (e.g. blunt notch C(T)).

7. Extended Summary and Conclusions

A literature survey on the SCC behaviour/mechanisms in low-alloy steels in high-temperature water with special emphasis to primary pressure-boundary components of BWR has been performed. The following conclusions could be derived from this work:

1. EAC susceptibility conditions:

Transgranular EAC in low-alloy RPV and piping steels in high–temperature has been observed both in laboratory experiments and in operating LWR. EAC initiation and growth are governed by a complex interaction of environmental, loading and material parameters. It is known from both experimental and field experience that EAC may occur in low-alloy pressure-boundary component steels in oxygenated, high-temperature water if the following conditions are simultaneously attained:

- Corrosion potential: $ECP > ECP_{crit} = -200\ mV_{SHE}$ (if $\kappa \leq 0.3\ \mu S/cm$)
- Strain-rate: $0 < \dot{\varepsilon}_{crit,min} \leq \dot{\varepsilon} \leq \dot{\varepsilon}_{crit,max} = 10^{-1}\ \%/s$
- Strain: $\varepsilon \geq \varepsilon_{crit} = 0.1 - 0.3\ \% >$ elastic limit ($\sigma_{crit} > R_p$)

In particular, slow, positive, dynamic tensile straining with associated plastic yielding (non-classical or Type II SCC) and sufficiently oxidizing conditions appear to be essential for EAC initiation and growth. The extent of EAC cracking is crucially dependent both on maintaining a positive crack-tip strain-rate and a high sulphur-anion activity in the crack-tip environment. Crack arrest can be expected if these two conjoint requirements were not met, which is generally the case under constant load for K_I-values $\approx \leq 60\ MPa \cdot m^{1/2}$ and for water chemistry conditions representative for stationary BWR/NWC power operating conditions.

A high sulphur-anion concentration at crack-tip and high cracking susceptibility is favoured by following factors:

- highly oxidizing conditions (high ECP, high DO)
- steel with high sulphur content, local increased sulphur content by segregation, long pre-existing crack with large area of dissolvable MnS-inclusions
- high bulk sulphur-anion concentration in the bulk water (e.g. sulphate from ion exchanger resin ingress, condenser leakage, ...)
- stagnant or low-flow conditions

Factors which promote a sustained dynamic crack-tip strain-rate under static loading conditions are:

- a high net section stress, gross ligament yielding
- superimposed periodical (partial) unloading
- DSA

2. Major influence parameters:

• Environmental parameters:

- corrosion potential ECP (dissolved oxygen content)
- temperature T
- concentration of specific (anionic) impurities: SO_4^{2-}, Cl^-, HS^-, S^{2-}, H_2S, ...
- flow rate

• Material parameters:

- sulphur content
- morphology, size, spatial distribution and chemical composition of MnS-inclusions
- free nitrogen and carbon content (DSA response of alloy) → nitrogen/aluminium-ratio, PWHT- or annealing-temperature, ...

• Loading parameters:

- loading or strain-rate: dK_I/dt, $d\varepsilon/dt$
- load, stress or strain level: K_I, σ, ε

The effects of the following parameters are well established/insufficiently characterized:

well characterized and established	Insufficiently characterized and understood
• oxygen content and ECP • steel sulphur-content, MnS-inclusion morphology, product form, orientation • sulphate-concentration of environment • susceptibility conditions • strain/load rate effects • stationary conditions	• temperature • microstructure/micro-plasticity • dynamic strain ageing (DSA) • flow rate • crack initiation and growth mechanism • transient conditions • irradiation effects

3. Main controlling factors:

EAC crack initiation and growth of incipient cracks are governed by the local mechanical, metallurgical and environmental crack-tip conditions, e.g. for a given material primarily by the crack-tip strain-rate and the activity of chloride- and sulphur-anions and the pH in the crack-tip environment. These local factors are governed by a system of interrelated corrosion system parameters such as the applied load and load ratio, strain/loading rate, the ECP or dissolved oxygen content, the flow rate across the crack mouth, the bulk concentration of specific anionic impurities as SO_4^{2-} and Cl^- and the steel MnS-inclusion content and morphology.

The corrosion potential in the crack mouth region (or more precisely the potential gradient in the crack mouth region) plays a dominant role in the evolution of an aggressive occluded crack-tip chemistry. Therefore, SCC susceptibility is strongly dependent on ECP and increases with increasing ECP.

4. Crack growth mechanism:

For the case of low-alloy steels in high-temperature water, the following potential cracking mechanism have been mainly discussed in literature:

- Film rupture/anodic dissolution
- Hydrogen-assisted EAC

The exact crack growth mechanism is still under discussion. None of the proposed mechanism can satisfactorily explain all experimentally observed cracking aspects. Currently, the observed cracking behaviour can be best rationalized by a combination of these two fundamental cracking mechanism. At lower temperatures (< 100 °C) and/or high strength levels (R_p > 800 MPa) hydrogen effects are more pronounced. At high-temperatures (≥ 150 °C) and/or lower yield strength levels (R_p < 800 MPa) anodic dissolution seems to dominate. Under certain combinations of temperature and strain-rate dynamic strain ageing may give an additional contribution to the crack growth in susceptible steels with a high concentration of free interstitial nitrogen and carbon.

5. Operating experience:

The worldwide accumulated operating experience and performance of low-alloy primary-pressure-boundary components is very good. Instances of EAC have particularly occurred in BWR service, most often in LAS piping, and, very rarely in the RPV itself. Oxidising agents, usually dissolved oxygen, and relevant dynamic straining (e.g. arising form thermal stratification, thermal and pressurisation cycles during start-up/shut-down, etc.) were always involved. These cases could be attributed either to SICC or low-cycle CF. Cases with major or relevant contribution of SCC to the total crack advance in properly manufactured and heat-treated low-alloy primary-pressure-boundary components have not been found in the literature.

6. Operating experience vs. laboratory background knowledge:

The cracking incidents can be readily understood by the accumulated experimental and mechanistical background knowledge on the EAC and on the pitting behaviour in the system LAS/high-temperature water. So far we could not find any fundamental discrepancy between operating experience and trends in laboratory data. Plausible reasons for the higher cracking frequency in lab tests compared to operating components have been given (fatigue pre-crack, conjoint requirements for EAC initiation, flow rate, stainless steel cladding). Most of the old lab data revealing very high SCC crack growth rates have been performed under a combination of both gross yielding of the remaining specimen ligament which is not relevant to the thick-walled RPV structure and aggressive water chemistry conditions which are not representative for current BWR operation.

7. SCC susceptibility under stationary BWR power operation conditions:

The high SCC cracking susceptibility observed in older tests could not be reproduced by recent reactor site testing (ABB, GE) and by recent experiments in modern high-temperature loops with water refreshment, on-line crack growth monitoring and documentation of all relevant test parameter (MPA, PSI, European Round Robin). From these investigations it is now more and more apparent that the „low sulphur line" can be regarded as an upper bound for possible SCC crack growth rates under current BWR operating practice. Relevant additional dynamic loading is necessary to maintain low sulphur crack growth rates if water

chemistry conditions were maintained within current BWR operation practice to some extent. Otherwise cessation of SCC crack growth and crack arrest occurs under purely static loading.

As long as water chemistry is maintained within current BWR/NWC operation practice to some extent, properly manufactured and heat-treated LAS pressure-boundary components seem not be susceptible to sustained, fast SCC growth under static load for K_I-values of ca. ≤ 60 MPa·m$^{1/2}$ at temperatures around 288 °C. Therefore, relevant SCC crack growth under transient-free steady-state BWR/NWC power operation appears to be highly unlikely. In contrast to their high stability against SCC, the LAS show a distinct susceptibility to SICC/low-cycle CF in oxygenated high-temperature water, even at very low impurity levels, if suitable slow dynamic/cyclic loading conditions do occur (e.g. transient BWR operation conditions).

8. Open questions and possible topics for further experimental investigations:

With regard to structural integrity/safety assessments and evaluation of plant lifetime extension the following aspects in the field of EAC of LAS are proposed for further investigations:

• All types of EAC:

- Role of DSA in EAC of LAS.
- EAC initiation and crack growth behaviour of weld filler and weld HAZ materials.
- Effect of flow rate on EAC initiation and growth.
- Effect of non-isothermal conditions.

• SCC:

- Effect of small load fluctuations at high load ratios ($R > 0.95$) near to fatigue thresholds ΔK_{th} on SCC growth ("ripple loading").
- Effect of lower and intermediate temperatures (100 – 250 °C) on SCC growth.
- Water chemistry transients: Effect of short-term SO_4^{2-}- and Cl^--transients on long-term SCC crack growth behaviour under oxidizing conditions (response times, asymmetry, memory and hysteresis effects?).

• CF/SICC:

- LFCF/SICC crack growth behaviour at lower and intermediate temperatures (100 – 288 °C) and at low loading frequencies ($\leq 10^{-3}$ Hz) under highly oxidizing transient BWR/NWC operation condition (ECP ≥ 100 mV$_{SHE}$).
- Effect of anionic impurities (Cl^-, SO_4^{2-}) on LCF/SICC initiation/growth.
- Effect of corrosion pitting and mean stress on LCF initiation.
- Effect of random loading and overloads on LCF initiation and LFCF growth.
- Mitigation effect of HWC or HWC/NMCA on LCF initiation and LFCF growth.

Investigations on flow rate effects may help to understand some apparent discrepancy between operating experience and laboratory results and also to eliminate some overconservatism. The degree of conservatism might be further reduced by studying the mechanism and improving the predicting of the complex behaviour of early growth of short cracks, which may cover a significant part of the lifetime.

8. Acknowledgement

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