B.8 "Stress Corrosion Cracking of Carbon and Low Alloy Steels,"

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Introduction

This background paper covers stress corrosion cracking of ductile carbon and low alloy steel components and their associated weldments. Stress corrosion cracking is part of a spectrum of failure mechanisms, including strain–induced cracking (SIC)[1] and corrosion fatigue. This background paper includes SIC. The topics of corrosion fatigue and stress corrosion cracking of higher strength steels used as bolting, for instance, are discussed in other background reports.

These ductile structural materials are used as pressure boundary materials in pressure vessels and piping in the RCS, ECCS, secondary water and service water systems of LWRs. The reasons for their use in LWRs are their combination of relatively low cost, good mechanical properties in thick sections and good weldability.

In components of the RCS, such as the pressure vessel, pressurizer and some piping, the carbon and low alloy steels are clad on the inside wetted surface with corrosion resistant materials such as austenitic stainless steels or nickel-base alloys. Thicker pads of alloy 182 have also been welded directly onto the pressure vessel steel in order to act as attachment points for internal structures. The higher yield strength of Alloy 182, its thicker section and its known SCC susceptibility raise special concerns for stress corrosion cracking of the underlying low alloy steel since it is possible that stress corrosion cracking or thermal fatigue of the austenitic alloy can occur such that the crack tip propagates to the interface between the austenitic and ferritic alloys. The practical questions in this case are "Will this crack propagate further into the underlying low alloy pressure vessel steel under constant load conditions?," and "What is the crack propagation rate vs. stress intensity factor (V/K) disposition relationship relevant to the material, stress and environment conditions?"

In cases where the ferritic steels are not clad, the relevant question is "Will a stress corrosion crack initiate (at, for instance, a pit), coalesce with nearby microcracks to form a primary crack, and then propagate to a significant depth?"

In general the resistance of the ferritic materials to transgranular stress corrosion cracking in LWR circuits has been very good, but isolated incidences have occurred. In order to understand the details of these observations, the mechanism of cracking and the associated corrosion system dependencies are discussed in order to (a) put this plant experience in the context of the conjoint conditions of environment, material and stress required to initiate and sustain cracking and (b) to define the predictive capabilities that are necessary in order to identify future areas of concern.

Mechanistic Understanding and Corrosion System Dependencies Governing Stress Corrosion Cracking of Carbon and Low Alloy Steels in LWRs

For a high-aspect ratio crack to advance in aqueous environments it is necessary that a mechanism exists to accelerate and focus the degradation at the strained crack tip. This degradation is generally related to localized oxidation processes at the crack tip, although historically there have been arguments that the degradation may be primarily associated with the production of hydrogen at the crack tip (which is, in turn, related to the crack tip corrosion rate) and its subsequent interaction with the microscopic deformation processes taking place there. There is a further factor, however, and that is that the crack sides must be protected by a film (oxide, salt, etc). If this latter criterion is not met then the incipient crack will degrade to a blunt notch [2-6]. Such requirements for a mechanically driven "electrochemical knife" [2] greatly limit the environmental conditions under which severe susceptibility is possible, and they provide a predictive capability for identifying the potential / pH regions where danger situations may occur in practice. For instance, cracking of carbon and low alloy steels in lower temperature aqueous environments (i.e. below 150°C) that might be representative of LWR service water or ECCS systems under faulted water chemistry conditions, is confined to potential / pH regions where a soluble species (Fe^{2+}, $HFeO_2^-$) can form when a protective magnetite, mixed oxide or salt film in hydroxide, nitrate, carbonate /bicarbonate or phosphate-containing solutions is ruptured. A relatively concentrated anionic solution is required for subsequent crack propagation to be significant under these conditions, thereby requiring precursor conditions of, for instance, crevice corrosion or localized boiling to create these high anionic activities. Thus the fact that there are these limiting criteria, indicate why transgranular stress corrosion cracking of carbon and low alloy steels in lower temperature LWR components are relatively rare. However, it should be noted that, in recent years, SCC has been observed in dilute solutions of molybdates and nitrites and in oxygenated water where the metal is cold worked in the 15-20% range or higher, and the temperature is in the range of 90-150°F and higher. As discussed below in relation to service experience, such failures have been observed in tertiary systems of nuclear plants.

In higher temperature PWR primary circuits, the oxide is protective magnetite (Fe_3O_4) but, as will be discussed below, the kinetics of crack propagation at static load of the carbon and low alloy steels under these low potential conditions will generally be low and of little practical importance. Under relatively high purity "normal water chemistry," (oxidizing), BWR water conditions the surface oxide at low temperature is less protective, and any incipient crack degrades to a non-propagating pit [5]. However at temperatures above approximately 150°C a highly protective, duplex oxide film of magnetite/hematite forms and allows the existence of a sharp crack, the propagation of which will depend on a variety of material, stress and environment conditions discussed below.

A considerable amount of attention has been focused internationally on the mechanism and kinetics of crack propagation in the carbon and low alloy steels used in, especially BWR, systems under at-power temperature and coolant chemistry conditions. Unfortunately there is a wide scatter in the stress corrosion crack propagation rate data (Figure B.8.1) [7,8], which poses a practical problem to the design or operational engineer who requires a specific life prediction or crack disposition algorithm (i.e. crack propagation rate (V) vs. stress intensity factor (K) relationship) that is technically sound and relevant to his particular plant.

The reason for the scatter in the stress corrosion data in Figure B.8.1 is associated with the fact that the crack propagation rate is controlled by interactions between various system parameters that are not always well defined or controlled in the plant or laboratory experiments. These factors include:

- Stress intensity and mode of stressing e.g., constant load, constant displacement, loading rate, periodic unloading etc.
- Test temperature
- MnS inclusion morphology and dispersion with respect to the crack plane
- Dissolved oxygen content (or, more accurately, corrosion potential as controlled by the coolant flow rate, alloy surface composition, dissolved hydrogen in the coolant, and oxidants such as oxygen, hydrogen peroxide, cupric cations, etc.)
- Solution flow rate past the crack mouth (or, more specifically, the extent to which hydrodynamic conditions permit flushing out of the internal crack environment)
- Solution conductivity (or, more accurately, anionic activity)
- Extent of crack tip constraint, i.e. plane stress vs. plane strain
- Yield stress of the material
- Testing time (and sequence of loading changes made during the test)

As a result there has evolved in the testing community a set of “quality control” criteria that can be applied to a given data set to assess their relevance to the conditions in operating Light Water Reactors. [8]

Coincident with these quality control actions, there has been a considerable international effort [7, 9-13] to develop a quantitative understanding of the mechanism of cracking, with the purpose of providing a sound basis for predicting and managing the cracking under the diverse corrosion system parameters listed above.

The hypothesis that has been most widely accepted for crack propagation in the carbon and low alloy steel /LWR water systems is the slip–oxidation mechanism. This mechanism relates crack advance to the enhanced oxidation rate that occurs at the crack tip when the thermodynamically stable and protective oxide film is ruptured by a strain increment in the underlying metal matrix. Once the protective oxide is ruptured, the crack will rapidly advance into the metal but will, within a matter of milliseconds, begin to slow down as the thermodynamically stable and protective oxide reforms at the crack tip. Continued crack advance depends, therefore, on maintaining a strain rate in the low alloy steel in the vicinity of the crack tip that will allow repeated rupture of the oxide film.

Thus the crack propagation rate, V, is governed by a relationship of the general form;

$$V = A\,(d\varepsilon/dt)_{ct}^{\,n} \qquad (1)$$

where the parameters A and n are related to the dissolution and passivation kinetics at the strained crack tip [11], and $(d\varepsilon/dt)_{ct}$ is the crack tip strain rate, which may be formulated in terms of "engineering parameters" such as stress, stress intensity, stress amplitude, loading frequency, etc. [11,12].

Both the dissolution and passivation kinetics on a bare low alloy steel surface depend critically on potential and the anionic activity in the crack tip environment [9,11,14] and these kinetics are bounded asymptotically by two limiting conditions associated [15] with the maintenance of either <20 ppb or >0.5 ppm S^{2-}. (Note that earlier investigations focussed primarily on the deleterious effect of sulfur-rich anions; more recent investigations indicate that chloride anions will also affect the crack propagation rate). This, in turn, leads to a predicted range in V vs.$(d\varepsilon/dt)_{ct}$ responses which are bounded by the "high" and "low" sulfur lines;

"High Sulfur" $\quad V = 2.25 \times 10^{-3}\,(d\varepsilon/dt)_{ct}^{\,0.35} \quad mm.s^{-1} \qquad (2)$

"Low Sulfur" $\quad V = 10^{-1}\,(d\varepsilon/dt)_{ct}^{\,1.0} \quad mm.s^{-1} \qquad (3)$

As can be seen in Figure B.8.2 the theoretical bounding crack propagation rates described by Eqn. 2 are not maintainable at the lower $(d\varepsilon/dt)_{ct}$ values, which are pertinent to creep rates under constant load or displacement conditions. The divergence from the maximum theoretical rates for these dissolved sulfur concentrations depends on the dissolved oxygen content and flow rate of the water. One reason for these divergences relates to the origin of the dissolved sulfur and other anions at the crack tip which can control the crack tip oxidation rate. As illustrated schematically in Figure B.8.3, the crack tip concentration of anions that originated in the bulk environment will be governed by the anionic concentration in the bulk environment and the mass transport mechanisms governed by convection, Fickian (i.e. concentration gradient) and potential gradient considerations within the crack. However, the concentration of sulfur-rich anions will be controlled not only by these specific mass transport mechanisms, but also by the rate of introduction of dissolvable MnS precipitates to the crack tip solution as the advancing crack tip exposes them to the crack tip solution. Thus it is predicted and observed that the crack propagation rate will be a sensitive function of, for example, the corrosion potential (Figure B.8.4), flow rate of the water past the crack mouth, the bulk anion concentration and, finally, the MnS size, shape and distribution. If the crack propagation rate falls below a critical value, such that a dissolved sulfur activity >0.5ppm S^{2-} cannot be maintained, then crack arrest may well occur, especially under the high water flow rate conditions expected in many plant conditions which tends to "flush" the aggressive anions out of short cracks, or in high purity water where there are no other non-OH anionic purities present.

The achievement and maintenance of crack propagation rates associated with the "high sulfur" rates depends not only on the maintenance of a high crack tip sulfur activity but also on the maintenance of a sustainable crack tip strain rate. The conjoint engineering system conditions that will achieve all these criteria will be met by combinations of:

- High sulfur content steels, mainly in the form of elongated MnS inclusions
- High corrosion potentials
- Stagnant or low flow rate water
- Highly impure water conditions, primarily chloride
- Unconstrained plane stress crack tip conditions

It is interesting therefore to note that the extremely high propagation rates that have been recorded by some laboratories [17-21] where combinations of the above system criteria have been met, are in agreement with the predicted "high-sulfur" rates (Figure B.8.1).

$$V = 9.6 \times 10^{-8} K^{1.4} \quad mm.s^{-1} \qquad (4)$$

with K in units of MPa√m

These "worst case" combinations of conditions do not exist generally in operating LWRs. For PWRs (and for the majority of the pressure vessel of BWRs on hydrogen water chemistry or Noblechem™) the low corrosion potential effectively preclude stress corrosion crack growth at rates that could be of any engineering significance. Under conditions more symptomatic of BWRs operating under "normal water chemistry" the crack propagation rates are generally below the "low sulfur" line; i.e.

$$V = 3.29 \times 10^{-14} K^{4} \quad mm.s^{-1} \qquad (5)$$

with K in units of MPa√m

The comparisons between observation and theory in this latter case are shown in Figure B.8.5 for an older data base [9] where a variety of loading conditions have been applied and in Figure B.8.6 [8] for a constant load data set from one laboratory [21-23] that has been screened for data quality. In these cases it is seen that, in general, the "low sulfur" line bounds the data sets, except at high stress intensity factors (a point that is addressed later).

It should be emphasized that the "low sulfur" propagation rates defined by Eqn. 5 are limiting values and the reason for this is that, in addition to maintaining a given dissolved sulfur activity at the crack tip, it is also necessary to maintain the crack tip strain rate. As discussed elsewhere [11, 12, 25-27], the formulation of the crack tip strain rate in terms of engineering parameters (stress intensity, yield stress, etc) has been the source of much international debate, which is still not finally resolved. However certain over-riding concepts are understood and accepted, and it is expected that, under constant load or displacement conditions, the crack tip strain rate will decrease according to a logarithmic creep relation of the general form;

$$(d\varepsilon/dt)_{ct} = B.(C\sigma^{m}).\ t^{-1} \qquad (6)$$

where σ is the tensile stress

Thus, there are two phenomena that indicate that the stress corrosion cracks may arrest under certain system conditions; the first is due to the lack of maintenance of a critical dissolved sulfur content at the crack tip, referred to earlier, and the second is the lack of

maintenance of the crack tip strain rate under constant load. In fact [27-29], crack arrest is frequently observed (Figure B.8.7) [27] and, as analyzed by Laepple [29], the crack propagation rate decelerates by approximately the predicted t^{-1} relationship in high purity BWR environments

Taking into account that there is an observed and understood tendency for crack arrest under closely controlled water chemistry purity (with no significant transients) and constant load conditions, the engineering judgment [30-33] is that, for disposition purposes, the average crack propagation under full power operations is given by;

$$V \leq = 2 \times 10^{-8} \quad mm.s^{-1} \qquad (7)$$

up to a stress intensity factor of 55 MPa√m . Above this K_1 level, but also below it (Figure B.8.8) in the case of either water chemistry transients or slight load variations, the low sulfur line of Eqn. 5 is considered more appropriate. It is also relevant to point out that the limiting nature of Eqn. 7 also applies (under the stated stressing and environmental purity conditions) to irradiated material and environmental conditions [23].

It should be emphasized that, although crack arrest is both predicted and observed, this may be counteracted by other material/environment/stressing factors and, thereby, may challenge the appropriateness of the disposition relations in Eqn. 5 and 7 when the strict water chemistry and loading caveats associated with these equations are violated [32]. Such factors may be categorized as those that increase the effective crack tip strain rate and/or markedly increase the crack tip anionic impurity concentration.

Examples of the effect of “inadvertent” increases in effective crack tip strain rate leading to increases in the crack propagation rate values in excess of those calculated by Eqn. 5 and 7 include;

- *Enhanced crack tip plasticity due to a loss of plastic constraint.* This concern is illustrated in Figures B.8.6 and 8 by the increase in crack propagation at stress intensity values beyond that where plane strain constraint to the crack tip plasticity is largely overcome. For the usual 25mmT fracture mechanics laboratory specimens this limit is defined as K values > 55 MPa√m. [22,23,24,28]. In large section pressure vessel components it is unlikely that this plane strain related criterion would be exceeded, but it may be a factor to be considered in thin section components.

- *Yield stress and dynamic strain aging.* Major increases in yield strength or hardness and/or in the degree of dynamic strain aging may increase the crack propagation rate of low alloy steels. The former effect has long been noted in the field of stress corrosion. As indicated in Figure B.8.9, the hardness effect on cracking susceptibility under constant load in oxygenated water is relatively minor over the hardness range associated with LWR pressure vessel steels, but a significant increase in susceptibility is observed should the heat treatment be such as to produce a (hard) martensitic microstructure [34]. On the other hand the effect of discontinuous yielding at a crack tip, which effectively increases the crack tip strain rate, and thereby the stress corrosion susceptibility, has been demonstrated in a variety of other cracking systems. The possibility of dynamic strain aging (DSA) having such an accelerating effect on the cracking of low alloy steels in LWR systems has been demonstrated by a number of investigators [34-39]. This opens

up the question of the definition of the allowable compositional limits for the low alloy steel, (mainly aluminum and nitrogen), and the resultant temperature ranges where the increase in cracking susceptibility is most marked. This latter aspect is of particular importance with respect to evaluating the susceptibility of, for example, feedwater piping which may operate in the temperature range 220-250^{0}C rather than at 288^{0}C where the majority of investigations have been focused. The cracking susceptibility can maximize in this lower temperature region under cyclic, monotonically increasing strain as well as static loading conditions. Historically this peak in the susceptibility has been attributed to a balance between the expected thermal activation of the corrosion processes fundamental to the crack propagation mechanism, and the changes in corrosion potential with temperature, especially at dissolved oxygen contents in the water less than 400ppb. This added contribution due to DSA is not yet fully evaluated

- *Transient or "ripple loading"* It has long been recognized that small repeated transients in loading (e.g. "ripple loading") can accelerate crack propagation due to the Bauschinger effect that leads to enhanced plasticity at the crack tip. This is illustrated in Figure B.8.10 for laboratory tests on low alloy steels in high temperature water involving high R (ratio of minimum stress intensity to maximum stress intensity) loading [34]

As emphasized earlier, the crack tip chemistry is of vital importance in defining the cracking susceptibility, and this impacts on the required degree of water purity control during steady state operation, and the control of the magnitude and duration of water chemistry transients. Of particular importance is the extent of chloride transients since, as illustrated in Figure B.8.11, chloride transients, in marked comparison with sulfate transients, may give extremely high sustainable crack growth rates approaching the theoretical maximum values defined by Eqn. 4; it should be noted that although the chloride transient (to 49 ppb) illustrated in Figure B.8.11 would be excessive for current BWR operating conditions and would have triggered an orderly plant shut down action, lower level transients (to10 ppb) also lead to significantly increased crack propagation rates [32].

Service History

In the 1970's there were numerous occurrences of *intergranular* stress corrosion cracking of low alloy NiCrMoV steels in steam turbine wheels (or discs) and, to a lesser extent turbine rotors. The specific cracking locations were primarily regions of high stress (due to wheel/disc shrink-on and centrifugal stresses) and creviced regions such as keyways or blade attachment where stress localization and contaminant concentration was possible. Initially these cracking incidents were primarily in fossil fired plant in low pressure turbine stages where steam condensation was possible and high alkalinity concentration could be attained due to the boiler water chemistries employed. However, since the mid to late 1970s cracking has been noted in lower temperature PWR and BWR driven turbines. These incidents have been widely reported and discussed [40-43]. It is significant, however, that many of the mechanisms-based concepts discussed earlier in this background report are of relevance. For instance, these concepts explain the narrow potential range for cracking associated with caustic cracking and the aggravating role vis à vis cracking susceptibility of contaminants such as chloride, sulfide (from lubricant), the presence of dissolved oxygen or other oxidants (e.g. Cu^{2+}), increased surface hardness due to abusive reaming of keyways and, finally, high yield strength associated with the bainitic or martensitic structures. Thus these earlier steam turbine experiences act as an historical guide to understanding service failures in the LWR systems of interest in this topical report that occurred in the late 1970s and early 1980s.

The accumulated operating experience and performance of the ductile carbon and low alloy steels in the majority of LWR systems has been very good worldwide and this is likely to continue. The reason for this optimistic statement is that the primary system in PWRs operates at low corrosion potentials because of the hydrogen overpressure, and the same observation applies to the vast majority of BWRs (in the US) that are currently operating under hydrogen water chemistry and/or noble metal addition (e.g., "NobleChem™") conditions; these factors ensure that there is a considerable margin in corrosion potential (see Figure B.8.4) before transgranular cracking would be expected.

There is cause for concern, however, in the PWR secondary systems for although they also operate at low corrosion potential (which is very strictly applied because of concerns that a more oxidizing potential will aggravate corrosion problems with Alloy 600 steam generator tube bundles), there is a higher risk of oxidizing corrosion potentials in the event of persistent leaks at interfaces with the environment, particularly in the condenser. There are also concerns for BWRs not consistently on hydrogen water chemistry, since cracking may be possible under more oxidizing conditions, especially if there are other aggravating factors. Indeed there have been two relatively major classes of cracking incidents of unclad carbon or low alloy steel components in operating LWRs that illustrate these concerns; cracking of carbon steel BWR feedwater piping due to strain-induced cracking, and cracking of PWR steam generator girth welds due primarily to water chemistry transients. These are discussed below in order to lay the basis for the next section that evaluates the potential erosion of margins due to evolving fabrication (or repair) and operational practices.

Strain-Induced Cracking of Steam, Feedwater and Condensate Piping

The cracking of steam, feedwater and condensate piping systems due to strain-induced stress corrosion has been extensively analyzed [1, 44-46] for German BWRs where these components have been fabricated with relatively fine-grained, higher-strength

steels (WB 35, WB36) that allow the use of thinner walled piping without stress relief treatment of the welds. The features that aggravated the cracking susceptibility in these incidents were;

- *Dynamic straining* associated with, for instance, reactor start-up or thermal stratification during low feedwater flow or hot standby conditions. Such operations lead to a wide range of applied strain rates [47] that may be as high as 10^{-4} s^{-1}, and would be expected to increase the crack propagation rate (see Figure B.8.2).
- *High local stress* at or above the high temperature yield stress, thereby giving a lack of plastic constraint at the incipient crack tip, and consequently an anomalous increase in crack propagation rate (see Figures B.8.6 and 8) due to the effective increase in crack tip strain rate. Such high local stresses were attributed in the failure analyses to weld defects (e.g. misalignment of weld edges, presence of root notches, etc), piping fit-up stresses and, in some cases inadequate pipe support at elbows. The combination of this high stress adjacent to the weld and the high applied strain rate led to a distribution of multiple cracks around the circumference of the pipe that was no longer confined by the asymmetric azimuthal distribution of weld residual stresses. These cracks propagated on separate planes and did not interlink, thereby potentially alleviating concerns about "leak before break" safety analyses that would be raised for a fully circumferential crack propagating evenly through the pipe wall.
- *Oxidizing* conditions, in conjunction with intermediate temperatures and potential anionic impurities. The affected piping generally operates in the temperature region 220^0C -250^0C where, as discussed earlier, the cracking susceptibility is at a maximum. Moreover, cracking was often observed in stagnant steam lines where. the dissolved oxygen concentration may be in excess of 100ppb, that is well in excess of the 30ppb quoted to be the "threshold" value above which strain-induced cracking is to be expected in these steels at 250^0C [48]; note that, as with the majority of EAC phenomena, the quotation of a firm "threshold" parameter (stress/strain rate, corrosion potential, anionic activity, temperature, etc.) is open to discussion, since the value defined will depend on the other relevant corrosion system parameters. This conjunction of environmental factors was further aggravated by the fact that during reactor shut-down stagnant water was sometimes left exposed to air in horizontal portions of piping; pitting and general corrosion occurred under these low temperature conditions, and these pits were observed to act as crack initiators during subsequent power operation conditions.

Stress Corrosion Cracking of Steam Generator Girth Welds

Very similar aggravating factors have been observed in transgranular cracking incidents in Model 44 and 51 designs of Westinghouse steam generators, starting with an isolated occurrence in Europe which was followed in 1982 with a well analyzed cracking incident at the Indian Point-3 PWR after approximately three effective full–power years. This cracking occurred at the upper shell to cone girth weld and was extensive with over a hundred circumferential cracks propagating to a maximum of 25mm. The cracking was attributed primarily to stress corrosion cracking with a component due to fatigue [49]. Similar incidents were subsequently observed at other US and European PWRs plants [50].

As with the case with the strain–induced cracking cases discussed above for the higher strength steels in German BWRs, the cracking in the PWR steam generator manufactured with lower strength SA 302 grade B weldments and SA 533 grade B plate steels, was aggravated by the fact that the weld was subjected to significant dynamic thermal stresses, in this case due to the fact that the incoming feedwater at 204-227^{0}C was impacting on the hotter steam generator shell before mixing with the steam generator recirculating water. Moreover in the affected plants this particular weld was the final closure weld, with a localized stress relief being applied; subsequent hardness measurements indicated that this stress relief had not been fully effective. Finally, with respect to the stress/strain rate conditions, there had been extensive weld repairs applied at Indian Point-3, an operation which has been widely associated with premature cracking in, for instance, nickel-base alloys in PWR primary components due to the attendant weld residual stresses.

Start-up operations in many of the cracking cases for this component involved the introduction of auxiliary feedwater from the condensate storage tank (CST) into the steam generator; unfortunately this water was aerated, since a nitrogen blanket was not applied to the CST. This deleterious oxidizing condition (Figure B.8.4) was exacerbated by the presence of Cu^{2+} associated with corrosion of the brass condenser tubes. Such oxidizing conditions promoted pitting, which, in turn acted as initiation sites for the stress corrosion cracks and poor chemistry control may also have increased the crack propagation rate.

Thus the unusual circumstances behind the cracking in these incidents were the conjoint presence of oxidizing secondary water conditions, high residual stress with a component of dynamic straining and a strong indication of high hardness due to inadequate stress relief.

Stress Corrosion Cracking in Tertiary Systems

Certain tertiary systems, which are fabricated of carbon steel such as the component cooling water system, have sustained SCC in the range of 90-150°F within times in the range of 5-10 years. Such SCC has perforated the walls especially at the higher range of temperature. These systems sustain such SCC in normal aerated chemistry with various inhibitive additives, within their nominal concentrations, such as molybdate and nitrite. Such SCC occurs where residual stresses are high due to fabrication, i.e. elbows, or at welds.

Observations of SCC in carbon steel in oxygenated water in this low range of temperature have been observed at least in six plants. However, these systems are not extensively inspected. Also, there are possibly ten different water chemistry treatment programs among the world utilities. There may be some interaction with MIC in some cases, but SCC can occur without the MIC and MIC does not always occur.

Other Cases

There have been other reported incidences of environmentally-assisted-cracking of carbon and low alloy steel in, especially, BWRs. The most significant of these have been cracks at nozzles associated with mixing of lower temperature water with hot water in a vessel, i.e., thermal fatigue cracks in BWR reactor vessel feedwater nozzles and control rod drive return line nozzles [51-55]. Although a component of SIC or stress corrosion cracking might be appropriate, it is apparent that the dominating degradation mechanism in these cases was corrosion fatigue, and discussion of these incidents is given in the fatigue background report.

Other potential cracking incidents have been reported but have been either isolated in occurrence or inadequately analyzed to allow a positive attribution to stress corrosion cracking. For instance, a through-wall crack developed in the low alloy steel wall of an early BWR (Garigliano) secondary steam generator channel head. The crack appeared to have grown due to SCC and was attributed to the presence of cracks in the Alloy 400 type cladding (Alloy 190 weld metal) that acted as initiating sites for the SCC in the base material, combined with high residual stresses due to an ineffective post weld heat treatment and, possibly, to an unusually high dissolved oxygen content in this unique BWR design.

In addition, a few flaw indications have been detected in vessel base materials by UT performed for baseline or in-service inspections, e.g., due to laminations or inclusions in the steel plates or forgings. The base material flaws have rarely if ever required repair. There appear to be no reported cases of service-induced growth of flaws present in the base plates or forgings. Finally, significant numbers of cracks have developed in the cladding of BWR reactor vessel heads. In some cases, the cracks have penetrated short distances into the low alloy steel base material. This cracking has required significant inspection and analysis to demonstrate the continued safe condition of the affected parts. In a few cases it has been concluded that the cladding cracks may have penetrated into the base material as the result of service, but it appears more likely that such ***penetration occurred during fabrication.***

Concerns Associated with Lack of Predictive Knowledge in Conjunction with Changing Operational Practices

There is no question that our capability to predict the changes in stress corrosion or strain-induced cracking of carbon and low alloy steels in LWRs due to the effects of materials, environment and stressing modes has significantly improved over the last 20 years. Prior to that time we would not have been able to quantitatively rationalize the cracking response of safety-related components and thereby define appropriate remedial actions beyond qualitative judgments to "reduce stress," improve chemistry control," etc. Consequently we understand in some quantitative detail the reasons why it is relatively hard to initiate and propagate stress corrosion cracks in carbon and low alloy steels in LWRs operating under good water chemistry control. We also understand many of the "upset" operating criteria necessary to give cracking, and these are generally met for the few instances where cracking in the plant has been observed.

However the bar is rising as reactors (in the US) apply for license renewal, power uprate, extended fuel cycles (and therefore increased time periods between inspection) and, possibly, limited load following. All of these changes potentially increase the danger of undetected stress corrosion degradation. Items of concern that need research attention in order to reduce that risk for stress corrosion (and strain-induced cracking) of carbon and low alloy steels include:

- A quantification of the sequential actions of pit formation, microcrack initiation and coalescence, followed by "short" and then "long" crack propagation. This sequence is well recognized in carbon and low alloy steels and has been quantified for gas pipelines. Such quantification has not been conducted for the nuclear systems. It is known that cracks may accelerate or arrest during this sequence; the quantification of this is inherent to the prediction of cracking of unclad ferritic piping

- The propagation rates are, in general, reasonably well understood; There are, however, some system parameters that can affect these rates, but which are insufficiently characterized at this time. Until this is done, the industry is open to unforeseen incidents. Prime examples include;

    - Ripple loading. As indicated in Figure B.8.10, ripple loading can significantly increase the crack propagation rate above the current disposition value, but we do not know the full extent (in terms of amplitude and periodicity) of these effects.

    - Dynamic strain aging. This is also a recognized effect, but insufficiently characterized. This has a direct impact on the definition of the maximum temperature for cracking degradation and on the compositional specifications for the steel. This latter aspect is of particular importance since steel manufacturers globally are modifying steel compositions (and in particular Al and N contents) in order to improve toughness together with higher yield stress. It imperative that such mechanical property driven changes also account for potential changes to the EAC resistance.

    - Heat affected zone (HAZ) anomalies. IGSCC in the weld HAZ is well recognized in austenitic alloys for a variety of material and local

stress/strain reasons. There is not a similar understanding of the potential increases in crack propagation rate in the HAZ of carbon and low-alloy steels.

- IGSCC of Carbon and Low Alloy Steels. IGSCC of higher strength bainitic steels used in steam turbines is a recognized phenomenon and has been related to the presence of grain boundary interstitials, which may also give rise to temper embrittlement. IGSCC in carbon and low alloy steels in the LWR systems has not, however, been widely observed, leaving the possibility that there may be unrecognized and potentially kinetically faster degradation modes under very specific operating and material conditions. There has been a recent isolated incidence of such cracking in a CANDU feeder elbow [56] that was associated with higher than normal hardness and residual stress associated with cold bending; flow assisted corrosion was also observed at the (assumed) crack initiation site. Moreover laboratory information [57] indicates that IGSCC is possible in higher hardness HAZs at temperatures < 265°C. It is necessary, therefore, to evaluate this degradation mode with respect to the relevant system variables, with some attention to potential synergisms with flow assisted corrosion and the associated hydrogen production.

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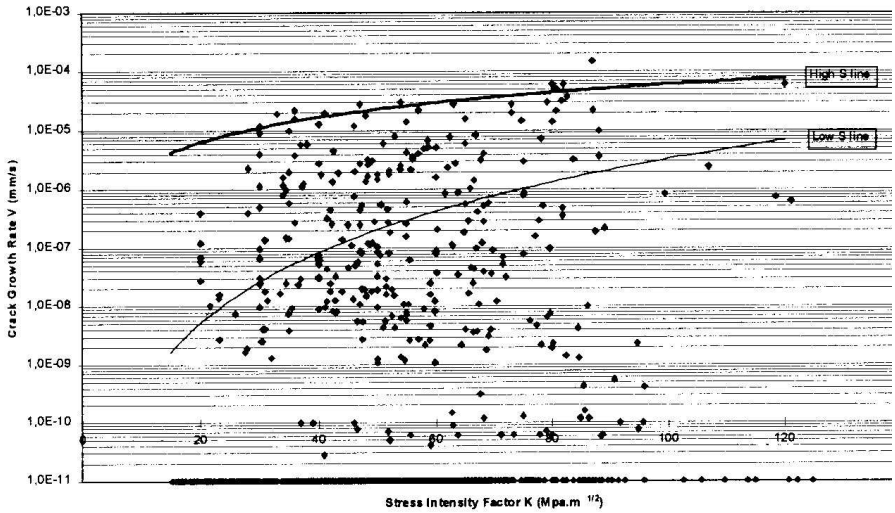

Fig. B.8.1 Crack propagation rate vs. stress intensity factor data for low alloy steels in "BWR" water at 288^{0}C [8]. Note that there must be a sound technical basis for the choice of the indicated disposition relationships.

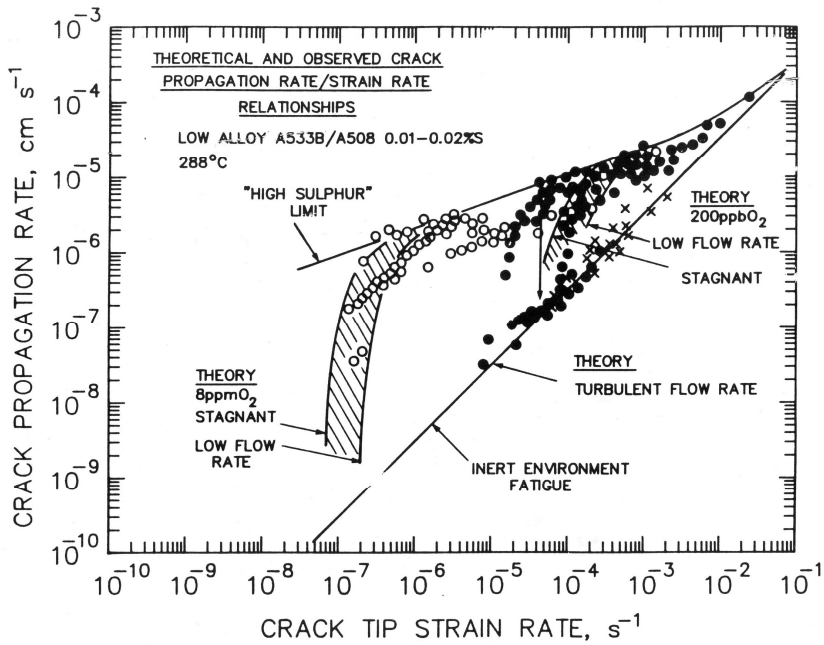

Fig. B.8.2 Observed and theoretical crack propagation rate / crack tip strain rate relations for low alloy steel in 288°C water at various corrosion potentials [9,12]. *(Used by permission of EPRI)* The strain rate values are pertinent to tests conducted under corrosion fatigue (at the higher end), slowly increasing applied strain, and constant load creep (at the lower end).

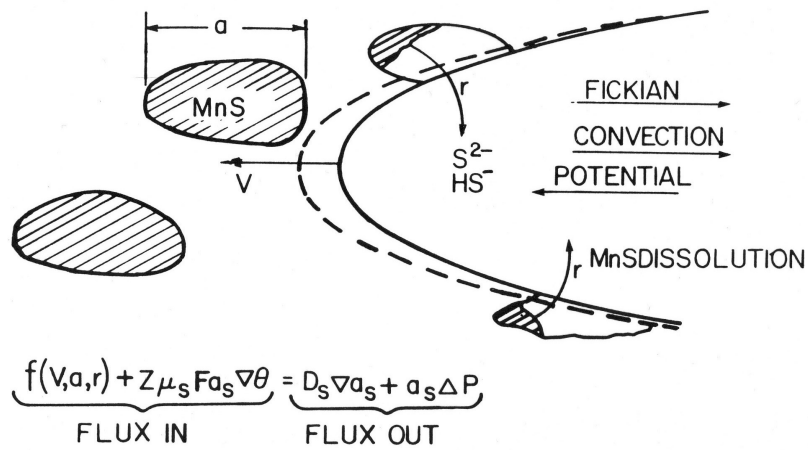

Fig. B.8.3 Schematic of crack tip illustrating the relationship between the MnS precipitate morphology and the advancing crack tip, and the various mass transport phenomena that will control the anionic activity at the crack tip.

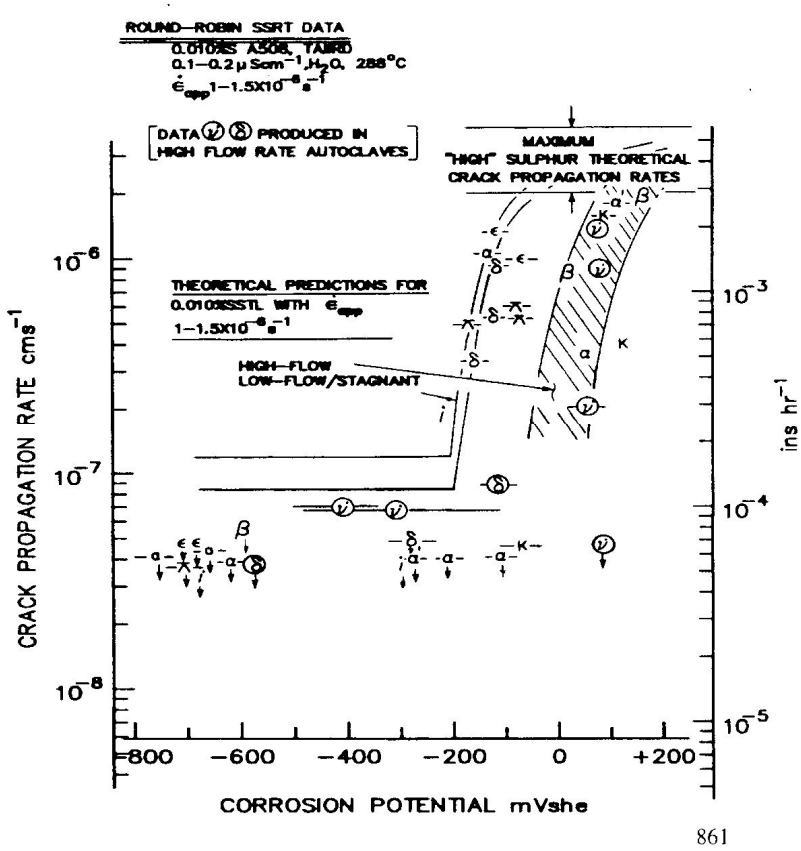

Fig. B.8.4 Observed (16) and theoretical (9) dependency of the average stress corrosion crack propagation rate on corrosion potential for 0.010% sulfur

A508 steel strained at 1-1.5 x 10 $^{-6}$ s.$^{-1}$ in 288°C water with conductivity of 0.02µS. cm $^{-1}$ *(Used by permission of EPRI)*

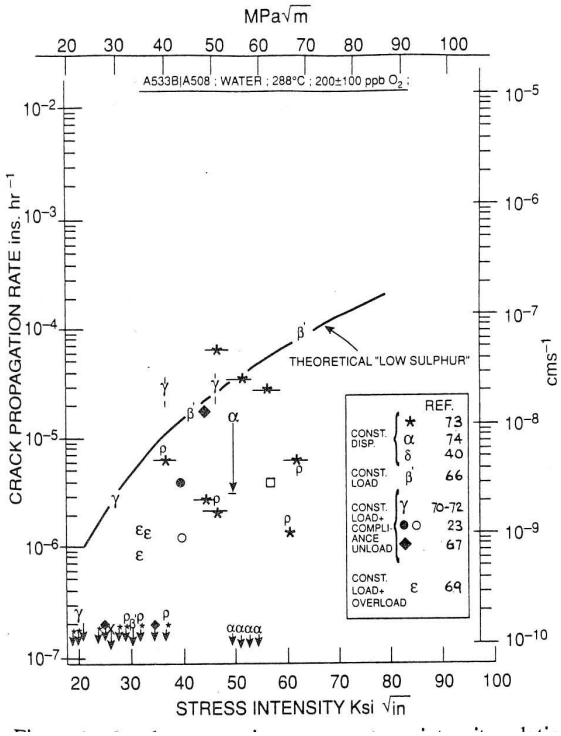

Fig. B.8.5 Theoretical "low–sulfur" crack propagation rate vs. stress intensity relationship (Eqn. 5) compared with selected laboratory data obtained in 288°C water containing 200 ppb oxygen, and stressed under constant load, constant displacement or constant load with periodic cycling conditions. [9] *(Used by permission of EPRI)*

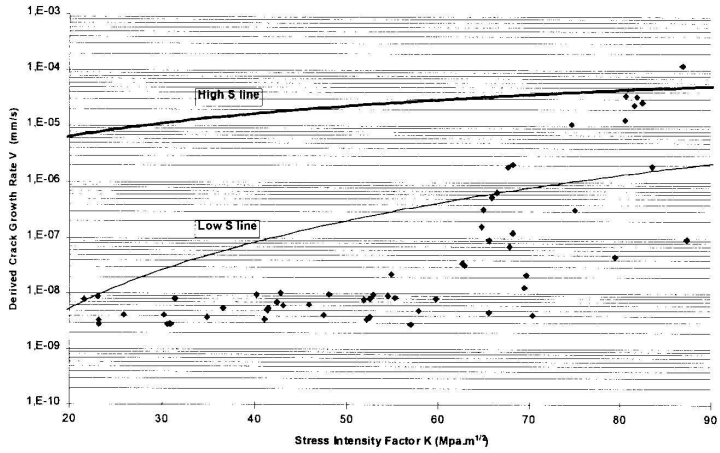

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Fig. B.8.6 Observed (21-24) crack propagation rates, screened for quality (8), obtained under constant load for low alloy steels in 240°C water with 0.4 or 8.0 ppm oxygen. These data are compared with the theoretical relationship in Eqn. 5.

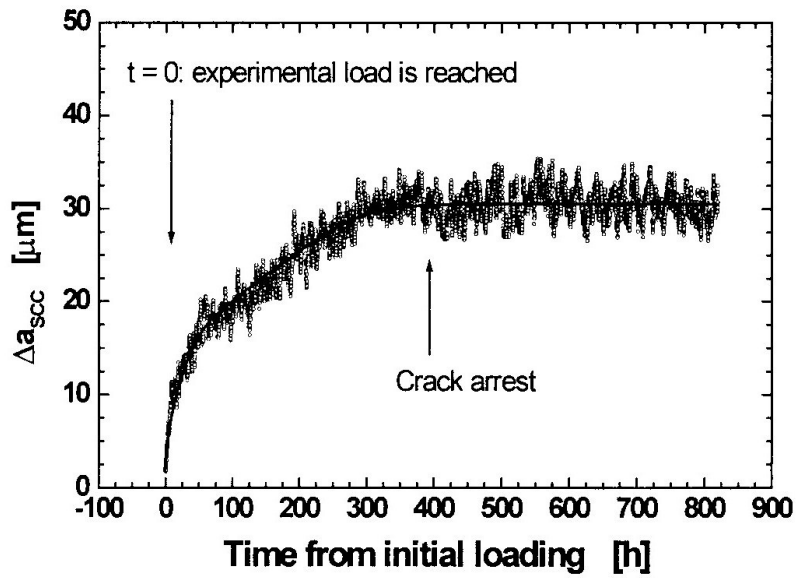

Fig. B.8.7 Crack length as a function of time for a low alloy steel specimen under constant load in BWR coolant. [27] *(Reprinted with permission from TMS)*

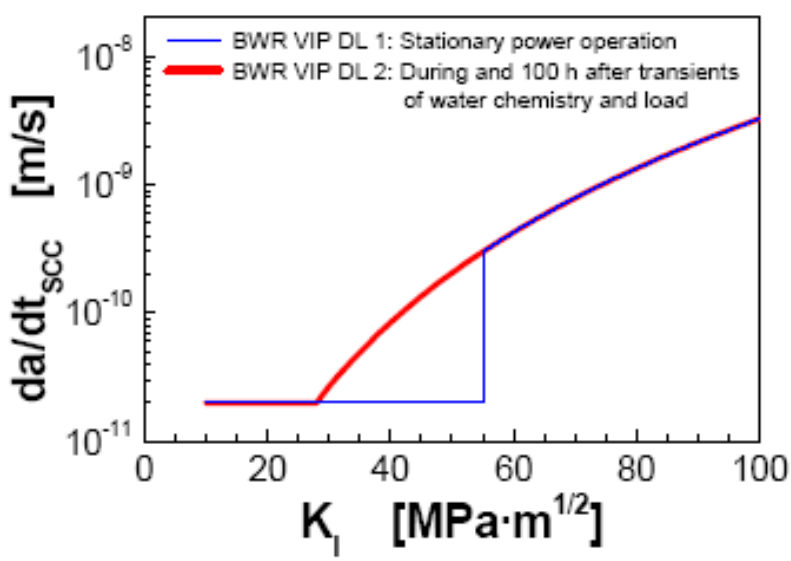

Fig. B.8.8 Propagation rate vs. stress intensity relationships for low alloy steels in BWR environments proposed by industry for disposition of cracks under stationary power operation (Eqn. 7), and during the 100 hours after limited water chemistry and load transients. (Eqn. 5). Also shown are relevant data obtained under unirradiated and irradiated (marked "IR") conditions. [23] *(© 2003 by The American Nuclear Society, La Grange Park, Illinois)*

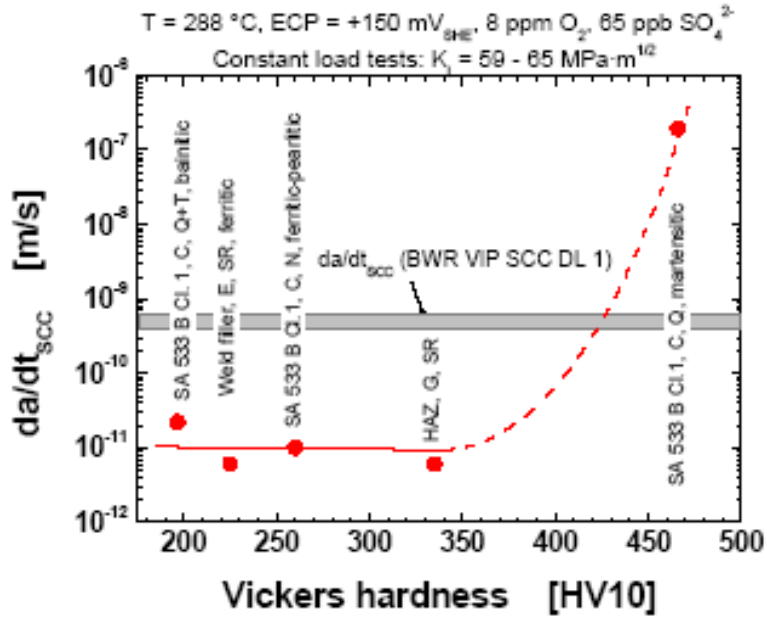

Fig. B.8.9 Effect of hardness on the crack propagation rate for various low alloy steel weldments, plate, etc. in 8 ppm oxygenated water at 288°C in comparison with the disposition propagation rate defined by Eqn. 5. [34] *(© 2003 by The American Nuclear Society, La Grange Park, Illinois)*

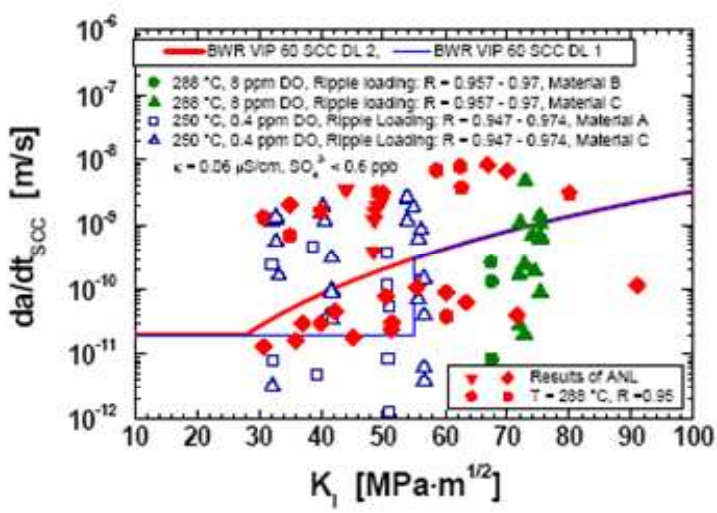

Fig. B.8.10 Effect of ripple loading (R>0.95) on the crack propagation rates for various low alloy steels in high purity, oxygenated water, indicating the possibility of exceeding the disposition propagation rates in Eqn. s 5 and 7 depending on the specifics of material condition. [34] *(© 2003 by The American Nuclear Society, La Grange Park, Illinois)*

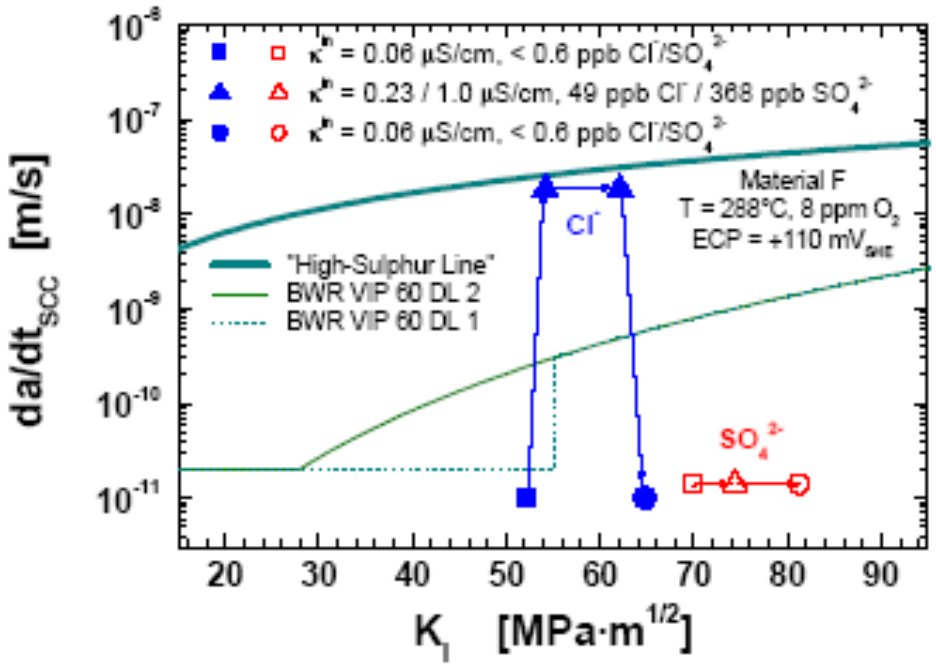

Fig. B.8.11 Effect of chloride and sulphate on the crack propagation rate of a low alloy steel in 8ppm oxygenated water at 288^{0}C. [34] *(© 2003 by The American Nuclear Society, La Grange Park, Illinois)*