

**BEFORE THE OFFICE OF ADMINISTRATIVE HEARINGS
FOR THE
MINNESOTA PUBLIC UTILITIES COMMISSION
STATE OF MINNESOTA**

IN THE MATTER OF AN APPLICATION
OF NORTHERN STATES POWER
COMPANY FOR AUTHORITY TO
INCREASE RATES FOR ELECTRIC
SERVICE IN THE STATE OF MINNESOTA

MPUC Docket Nos. E002/GR-12-961
E002/GR-13-868

IN THE MATTER OF THE REVIEW OF
THE ANNUAL AUTOMATIC
ADJUSTMENT REPORTS FOR ALL
ELECTRIC UTILITIES

E999/AA-13-599
E999/AA-16-523
E999/AA-17-492
E999/AA-18-373

OAH Docket No. 65-2500-38476

SURREBUTTAL TESTIMONY OF

DAVID G. DANIELS

On Behalf of

NORTHERN STATES POWER COMPANY

October 30, 2023

Schedules

Document	Schedule
Xcel Energy Response to DOC Information Request No. 51	Schedule 1
Xcel Energy Supplemental Response to DOC Information Request No. 51	Schedule 2
Xcel Energy Response to Information Amended Request No. 97	Schedule 3
DOC Response to Xcel Energy Information Request No. 34	Schedule 4

1 **Q. WHAT IS THE PURPOSE OF YOUR SURREBUTTAL TESTIMONY?**

2 A. In the four sections below, I respond to rebuttal testimony of Mr. Steve Klotz
3 regarding: (1) Cycle Chemistry Performance Review and Improvement Programs; (2)
4 Mechanical Carryover; (3) Sodium Monitoring; and (4) Makeup Water Quality.

5 **1. FORMAL CYCLE CHEMISTRY REVIEW AND IMPROVEMENT PROGRAM¹**

6 According to his own testimony, Mr. Klotz’s experience in the utility industry has
7 been as a corporate chemist for Consumers Energy (CE). It is therefore understandable
8 that he is a strong advocate of the programs he was paid to develop and maintain for
9 CE. However, what he developed for CE was not industry standard from 2000 to 2011.
10 In my experience during that time, the majority of the U.S. utility industry did not have
11 such a formal program. Even today, a “formal cycle chemistry review and improvement
12 program” as defined by EPRI, to which Mr. Klotz refers, is not industry standard
13 practice.

14 Mr. Klotz’s opinion also appears to be one based on semantics: whether the
15 program was formal rather than informal, without regard for the actual cycle chemistry
16 impacts of the program. He acknowledges that the Company had “informal evaluation
17 and communication processes,” including “logbook entries, chemistry monitor checks,
18 daily plant meetings” and other communications.² The Company therefore engaged in
19 regular, repetitive, and consistent processes led by an experienced chemistry lead and
20 supported by a chemistry laboratory that together were sufficient to identify and
21 respond to the presence of contamination in the steam cycle. Regardless of whether it
22 was a “formal” program to Mr. Klotz, the Company’s monitoring and review of Unit 3
23 cycle chemistry was reasonable and consistent with, if not better than, practices at other
24 utilities in those years.

¹ Klotz Rebuttal, p. 8-13.

² Klotz Rebuttal, pp. 9; *see also id.*, 39.

1 Although Mr. Klotz concluded that these “informal” processes were not sufficient
2 to avoid the 2011 Event,³ this is based on nothing more than speculation, as he also
3 admits that he did **not** “complete an analysis of the cycle chemistry compliance
4 performance of Sherco 3 prior to the 2011 SCC LP turbine failure.”⁴ His failure to
5 comprehensively review the available cycle chemistry data also undercuts Mr. Klotz’s
6 conclusion that “the cycle chemistry practices at Sherco 3 contributed to the SCC failure
7 of the LP turbine in November of 2011.”⁵ Mr. Klotz relies entirely on the analysis of
8 *other* experts to support this testimony.⁶ In contrast to Mr. Klotz, I have reviewed all
9 available data, and have found no evidence that the boiler and turbine were operated
10 with concentrations of sodium hydroxide that were excessive and outside of reasonable
11 and prudent practice. Fundamentally, as GE and industry experts acknowledge,⁷ if the
12 rotor design and operation generate sufficient stresses, there is no known level of
13 sodium hydroxide low enough to guarantee it will not “initiate and sustain SCC
14 damage.”

15 Finally, Mr. Klotz’s position that the data records provided are too incomplete to
16 make such a determination is untrue.⁸ Although the PI (plant historian) data cited by
17 Mr. Klotz is not complete by itself, when combined with other data sources and
18 laboratory records, a sufficiently complete picture can be produced to determine
19 whether cycle chemistry issues existed sufficient to warrant an inspection full blades-
20 off inspection of the turbine during the 2011 outage. I reviewed all of the available
21 information for Sherco 3, and found no evidence that the chemistry team or operators
22 ignored or continued to operate the boiler with contamination. They monitored the
23 system continuously and, when necessary, took action.

³ Klotz Rebuttal, pp. 9-10.

⁴ Klotz Rebuttal, pp. 10-11.

⁵ Klotz Rebuttal, p. 7.

⁶ Klotz Rebuttal, p. 7.

⁷ E.g., Daniels Direct, p. 13-14; Xcel Energy Resp. to IR 51 & Attachment A (see Exhibit____(DGD-3), Schedule 1); Xcel Energy Suppl. Resp. to IR 51 (see Exhibit____(DGD-3), Schedule 2); Tipton Direct, p. 16.

⁸ Klotz Rebuttal, pp. 10-11.

1 **2. MECHANICAL CARRYOVER⁹**

2 Mr. Klotz’s testimony acknowledges that “[t]here are several ways to monitor
3 mechanical carryover,” identifying both direct and indirect methods, and stating that
4 the direct method is more reliable than indirect methods.¹⁰ The cycle chemistry
5 monitoring at Sherco 3 indirectly monitored mechanical carryover. In finding the
6 Company’s practices insufficient, Mr. Klotz appears to be holding the Company to the
7 highest standard—not a prudence standard—when he criticizes the Company for not
8 monitoring mechanical carryover via a specific test protocol. Indeed, the testimony he
9 cites to from Duane Wold on this seems to be about a specific mechanical carryover
10 test set forth in an EPRI document, not about whether mechanical carryover was ever
11 monitored. However, consistent with Mr. Klotz’s testimony that “[c]ontinuous online
12 measurement of steam cation conductivity and steam sodium is an indirect way of
13 monitoring” mechanical carryover, the Company’s cation conductivity and steam
14 sodium monitoring confirms that mechanical carryover was not a significant¹¹ issue at
15 Sherco 3. Indeed, test results of the main steam chemistry do not show evidence of
16 abnormal carryover. Further, Mr. Klotz acknowledges that “visual inspection” is
17 another method to determine mechanical carryover.¹² Xcel conducted a physical
18 inspection of the steam drum every three years, which showed no indication of problem
19 with mechanical carryover.¹³ Evidence that the steam drum separation equipment was
20 working properly can be seen in the photos of the turbine inspections that were
21 performed, including the condition of other turbine blade surfaces after the event,
22 which were very well documented. The blades removed from around the failure were
23 clean, with very little operationally-related deposit on the blade surface. The formal

⁹ Klotz Rebuttal, pp. 21-23.

¹⁰ Klotz Rebuttal pp. 15-16.

¹¹ I say “significant” because, as Mr. Klotz acknowledges, “a certain amount of entrained water droplets will always exit the steam drum with the steam.” Klotz Rebuttal, pp. 14-15. So, it is not a question of whether mechanical carryover occurs, but whether the mechanical carryover is significant enough to cause caustic buildup on the turbine.

¹² Klotz Rebuttal, pp. 16-17.

¹³ Xcel Energy Resp. to Amended IR 97 (see Exhibit____(DGD-3), Schedule 3).

1 mechanical carryover test which Mr. Klotz cites is difficult to perform, and in my
2 experience, is not routinely performed by utilities after boilers are commissioned.

3 Finally, when I concluded that I “could find no evidence that the plant was
4 operated in a condition that would have sent contaminated steam to the steam
5 turbine,”¹⁴ this conclusion is based on EPRI’s boiler chemistry guidelines, which the
6 plant followed. EPRI takes total carryover into account when it generates these limits,
7 including limits on boiler sodium and boiler cation conductivity. In the extremely rare
8 instances when there were conditions in the boiler water that could have contaminated
9 the steam, the laboratory and operations personnel at Sherco 3 took immediate
10 corrective action to prevent contamination from reaching the turbine. I found no
11 periods where the plant ignored contamination in the boiler, which would have resulted
12 in significant contamination of the steam.

13 **3. SODIUM MONITORING**¹⁵

14 Mr. Klotz testifies that “Xcel followed some of EPRI’s recommendations but
15 not all of them,”¹⁶ implying that by failing to follow all of them, the Company was in
16 some way operating imprudently. I strongly disagree. *First*, EPRI produces
17 recommendations, not requirements, for their member utilities, stating very clearly that
18 their recommendations must be “adapted and customized,” supporting plant-specific
19 and experience-based modifications.¹⁷ Yet without considering plant-specific or
20 experience-specific application of the given EPRI standards to Sherco 3, Mr. Klotz
21 incorrectly claims that Sherco 3 “failed to meet EPRI recommendations.”¹⁸ *Second*, in
22 my work, the best power plants do exactly what EPRI recommends by adapting the
23 published chemistry guidelines to their particular situation, meaning there are some
24 sample points or on-line chemistry instruments which are in the EPRI guidance

¹⁴ Klotz Rebuttal, p. 23 (citing Daniels Direct, p. 24).

¹⁵ Klotz Rebuttal, pp. 23-29.

¹⁶ Klotz Rebuttal, p. 28.

¹⁷ See Daniels Rebuttal, pp. 16-17.

¹⁸ Klotz Rebuttal, p. 24.

1 document that they may not have or where modifications are made consistent with
2 plant experience. This is what the Sherco plant did. *Third*, when asked if Mr. Klotz’s
3 own “formal program” followed each and every EPRI recommendation, Mr. Klotz
4 admitted that it did not, but aligned “whenever practical and to address gaps based on
5 an evaluation of risk and cost.”¹⁹ Again, this is what the plant chemist at Sherco 3 did.²⁰

6 *Fourth*, as to Mr. Klotz’s specific criticisms of the Sherco 3 continuous sodium
7 monitoring, the monitoring in place was more than sufficient to identify contamination.
8 For example, while Sherco 3 did not have a redundant sodium analyzer at the
9 Economizer Inlet sample point, it did monitor sodium continuously at the Condensate
10 Pump Discharge sample point—the first place that contamination would be detected
11 from either the condenser or the water treatment area. That was reasonable.²¹ While
12 they did not continuously monitor sodium directly in the Main Steam sample until after
13 2008, they did continuously monitor it in the boiler (or drum water), which was
14 reasonable. But most importantly, the Company paid attention to the output of the
15 continuous monitoring instruments they had and took action if there was
16 contamination. Again, evidence of this was the condition of the blade surfaces after the
17 Event: the blades remote from the area of failure were clean, with very little if any
18 operationally-related deposit on the blade surface.

19 *Finally*, Mr. Klotz claims that because the Company did not monitor Main
20 Steam sodium prior to 2008, “Sherco 3 was blind to intermittently excessive mechanical
21 carryover of sodium hydroxide from the steam drum into the steam path to the turbines
22 during this timeframe”²² stating that there was “excessive mechanical carryover” as if it
23 were a known fact. However, nowhere does he provide evidence that such “excessive
24 mechanical carryover” existed during the 11 years prior to the Event. A lack of

¹⁹ See DOC Resp. to IR 34(e) (see Exhibit____(DGD-3), Schedule 4).

²⁰ See, e.g., Daniels Rebuttal, p. 12.

²¹ See Klotz Rebuttal, p. 26.

²² Klotz Rebuttal p. 31.

1 monitoring at a specific sample point cannot be equated with the presence of sodium
2 hydroxide in the steam. For the reasons given above, other data would have indicated
3 an issue, and I have seen nothing to indicate excessive mechanical carryover at Sherco
4 3—and Mr. Klotz has not presented any evidence otherwise. It is also important to note
5 that mechanical carryover is not selective to just sodium salts. Any other contaminants
6 in the boiler water would have likewise been carried over into the steam, producing an
7 elevated Main Steam cation conductivity reading, which Sherco has monitored
8 continuously since 1987. The data does not show cation conductivity levels which
9 would indicate “excessive mechanical carryover.” In addition, had there been “excessive
10 mechanical carryover,” it would have shown up when the Main Steam sodium
11 monitoring was started in 2008. But that monitoring showed very low levels of sodium
12 in the steam.

13 The question is whether the Company had a chemistry program that was
14 reasonable, and it did. Mr. Klotz has only argued that the Company’s program did not
15 perfectly align with every one of EPRI’s Steam Cycle Chemistry recommendations—a
16 standard his own “formal program” failed to meet and that EPRI itself does not require.

17 4. MAKEUP WATER QUALITY MONITORING²³

18 There are a number of issues with Mr. Klotz’s testimony on this issue. *First*, for
19 Sherco 3’s purported makeup water limits, Mr. Klotz is referencing a chemistry manual
20 produced prior to the plant commissioning in **1987**. This document is outdated and
21 does not reflect the sampling or testing practices of Sherco Unit 3 between 2000-2011.
22 *Second*, Mr. Klotz acknowledges that, regardless of the limits, actual data does not
23 show that Sherco 3 exceeded the applicable EPRI recommended levels.²⁴ As to chloride
24 and sulfate, it is generally accepted by EPRI and the industry that if the water had a
25 specific conductivity of <0.1 µS/cm, (which the Sherco demineralizer produced) it also

²³ Klotz Rebuttal, pp. 33-38.

²⁴ Klotz Rebuttal, pp. 36.

1 contained less than 3 ppb chloride and sulfate. Besides conductivity, the demineralizer
2 effluent was continuously monitored for sodium and silica. *Finally*, Mr. Klotz's
3 inference that a low pH of the demineralized water somehow indicated chloride and
4 sulfate contamination is technically flawed.²⁵ As anyone who has measured the pH of
5 demineralized water can attest, the measurement of a grab sample pH is always
6 depressed to about 5.5-6.0 due to the absorption of carbon dioxide gas from the air.
7 The grab sample pH values of demineralized water reported by Sherco are precisely
8 what would be expected and is not evidence of contamination. In sum, there is no
9 evidence that the plant fed contaminated demineralized makeup water to the Sherco 3
10 boiler.

11 **CONCLUSION**

12 In his rebuttal, Mr. Klotz understandably tries to find areas where there was
13 potential for sodium hydroxide contamination of the steam. Ultimately, his testimony
14 regarding contamination of the steam with caustic during the period between 2000-
15 2011 is all presented in the context of hypothetical risk factors and conjecture.
16 Importantly, consistent with my testimony, he does not present evidence of a single
17 specific event that demonstrates levels of sodium hydroxide contamination in the steam
18 which would have been a significant contributor to the Event in 2011.

²⁵ Klotz Rebuttal, pp. 36-37.

- Not Public Document – Not For Public Disclosure
 Public Document – Not Public Data Has Been Excised
 Public Document

Xcel Energy Information Request No. S51
Docket No.: E002/GR-12-961, E002/GR-13-868; E999/AA-13-599;
E999/AA-14-579; E999/AA-16-523; E999/AA-17-492;
E999/AA-18-373
Response To: Department of Commerce
Requestor: Michael Zajicek
Date Received: July 7, 2023

Question:

Topic: Sherco 3 operation and maintenance
Reference(s): Daniels Direct Testimony

In his direct testimony at page 13, Mr. Daniels states that “While it has been shown time and again that elevated concentrations of sodium hydroxide in steam have contributed to turbine rotor failures by SCC, the literature also states that, in the presence of sufficiently high stresses, SCC can occur in ‘pure water’” With respect to this testimony:

- a. Please produce all documents on which Mr. Daniels relies to support the statement that “it has been shown time and again that elevated concentrations of sodium hydroxide in steam have contributed to turbine rotor failures by SCC.”
- b. Please produce all documents on which Mr. Daniels relies to support the statement that “in the presence of high stresses, SCC can occur in ‘pure water.’”
- c. Please explain the mechanism that would cause corrosion of the finger-pinned dovetail joints in pure water and result in SCC and the amount of time in a pure water environment that it would take to result in the type of cracking found in the Sherco 3 L-1 LP finer (sic)-pinned joints.
- d. Is it Mr. Daniels opinion that corrosion in the L-1 finger-pinned joints is not accelerated by the presence of sodium hydroxide in steam? If so, please produce all documents that support that opinion.

Response:

- a. Xcel Energy objects to this information request as overly broad. However, see ASME Handbook on Water Technologies for Thermal Power Systems, Paul Cohen, Editor-in-Chief, Chapter 9 Corrosion of Steam Cycle Materials, by Digby D. Macdonald and Gustavo A. Cragolino, Section 9-5.5 Stress Corrosion Cracking. More particularly section 9-5.5.2 Stress Corrosion Cracking of Low-Alloy Steels, pg. 850-856. A copy of Chapter 9 is produced contemporaneous with this request, as Attachment A to this response.
- b. See response to subpart a. (The ability of SCC to form in pure water, pure steam, or pure condensate is mentioned in this section of the referenced handbook.) However, the statement taken from Mr. Daniels' testimony cited at the beginning of this document is misrepresented. The sentence quoted continues ... "where the concentration of sodium hydroxide is so small that it could not be measured." Thus, the theoretical concept of "pure water or pure steam" is here defined as water or steam in which the sodium hydroxide concentration is too low to be analytically determined. Intergranular stress corrosion cracking in low alloy steel has always been associated with the presence of some concentration of caustic. This is well documented in the above referenced material. The question here is whether this particular GE turbine design, (specifically the finger dovetails) can operate with prudent chemistry control without developing SCC. Furthermore, Mr. Daniels' statement is consistent with GEK-25407c, wherein GE states that the state of knowledge regarding SCC in turbine rotor material does not allow GE to establish a safe level caustic in the steam for their turbines.
- c. Experts, such as Mr. Macdonald, cited above, agree that the mechanism for stress corrosion cracking is not fully understood. However, Mr. Daniels has no reason to expect that the mechanism in this failure would be any different than for any other caustic SCC corrosion. Namely, it is a combination of a susceptible material, environmental conditions, stresses (design and operating stresses), and time.
- d. No, the presence of caustic in the steam would find its way into the high-stress areas of the finger dovetails, and would accelerate caustic stress corrosion cracking in this area.

Witness: David Daniels
Preparer: David Daniels
Title: Senior Principal Scientist
Department: Acuren Inspection, Inc.
Telephone: 512-407-8598
Date: July 19, 2023

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PAUL COHEN
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United Engineering Center 345 East 47th Street New York, NY 10017



CHAPTER 9

annealed Alloy 600. The authors observed that the attack occurs at both the outer and inner surfaces of the C-ring specimens used in their tests, suggesting that tensile stresses were not required to induce intergranular corrosion. However, deep fingers of extremely branched intergranular cracks were observed to extend well beyond the intergranularly corroded area. These observations suggest that high applied stresses (~ 150% yield strength) may also play a role in the propagation of the cracks. Other authors [42-46] have reported the occurrence of intergranular corrosion on stressed specimens of Alloy 600 when exposed to 10 w/o NaOH solutions containing various impurities, such as carbonate, sulfate, etc., at temperatures of about 300-320°C under various applied cathodic and anodic potentials. However, the morphology of the intergranular attack for some potentials resembles intergranular stress corrosion cracking, rather than a purely intergranular corrosion phenomenon. It has also been reported [47] that concentrations of NaOH equal to or greater than 10 w/o are needed to develop measurable penetrations of the attack along grain boundaries (capsule tests) in testing times of the order of 10 days at temperatures well above 300°C. The estimated rate of intergranular attack was about 0.48-0.72 μm/day in 25 w/o NaOH solution at 330°C.

Similar results have been reported by other authors [44], but they claim that the presence of magnetite is required to enhance the attack, because this oxide sets the potential close to the reversible potential for the hydrogen evolution reaction; the potential region in which IGC is severe. Furthermore, it was suggested [48] that the release of sulfur species from contaminated magnetite is the necessary condition for intergranular corrosion to occur at a high, easily detectable rate.

In model boiler tests, severe intergranular corrosion of Alloy 600 has been observed [40] in the presence of simulated sludge (Fe₃O₄) and low concentrations of NaOH in the recirculating water. It should be noted that IGC was accompanied by the occurrence of nearly through-wall cracking in many tests.

From the available information, it is apparent that intergranular corrosion in the absence of tensile stresses and caustic stress corrosion cracking of Alloy 600 are closely related phenomena. Therefore, a more detailed discussion on the effect of alloy microstructure and environmental variables is presented in Section 9-5.5.4.

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9-5.5 Stress Corrosion Cracking

For almost a century one of the more insidious forms of alloy failure in industrial applications has been stress corrosion cracking (SCC). This term defines a phenomenon by which many ductile metals and alloys fail by the concurrent action of a tensile stress (applied and/or residual) and a specific corrosive environment. An important observation is that SCC can occur at stresses that may be far lower than those required for macroscopic yielding. Cracks, which are initiated by the specific action of the corrodent at the metal/solution interface, can propagate through the material with velocities ranging from 10⁻¹² m/s to 10⁻³ m/s, depending upon the alloy/environment system. These velocities are significantly lower than the rates of crack propagation associated with brittle failure of high-strength steels, which are of the order of several thousand meters per second, corresponding to the propagation rate of elastic waves in solid materials. However, when stress corrosion cracks have propagated to a depth at which the remaining load-bearing section of the material reaches its fracture stress in air, the material fails by normal overload fracture, usually

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by microvoid coalescence in ductile alloys. The fracture surface, which in general is approximately perpendicular to the direction of the tensile stress, contains areas with the morphological characteristics of SCC, as well as areas exhibiting the dimples associated with coalescence of microvoids.

According to the path followed by the cracks, two different modes of propagation can be distinguished. One is termed transgranular, because the cracks run across the grain, in some cases according to preferential crystallographic planes (cleavage planes). The other mode is known as intergranular because the cracks propagate along grain boundaries. Either mode of propagation can be observed, depending upon the alloy/environment system, but in many circumstances both modes may occur simultaneously or consecutively. Eventually, a change from one propagation mode to the other may occur by small variations in the composition of the environment (i.e., pH or concentration of ionic species), in the potential, or in the microstructure of the alloy.

It should be noted that SCC generally occurs in ductile alloys that are extremely resistant to general corrosion due to the presence of a passive film on the metal surface. This is one of the reasons that SCC is so difficult to predict, because premature and unexpected failures may occur in a material that otherwise is not uniformly corroded to an extent that the load-bearing capacity is lost.

During recent years, a tendency has evolved to consider (in addition to SCC) other forms of failure under the simultaneous presence of stress and a corrosive environment, such as corrosion-fatigue and hydrogen embrittlement, as environmentally-assisted cracking. Despite the similarities these phenomena show substantial differences, thereby justifying a separate discussion (see Sections 9-5.6 and 9-5.7). At the same time, the concept that prevailed for many years that a single mechanism can be applied to explain all the cases of SCC, has been abandoned. Parkins [1] proposed that a continuous spectrum of mechanisms can account for the variety of alloy composition and environments that lead to SCC failures.

The subject of SCC has been extensively covered in many books and conferences [2-7] and probably is one of the most researched areas in corrosion science and engineering. This is without doubt a consequence of the extremely large number of SCC failures that have been observed in many industries, including the power-generating industry. It is interesting to note that in 1973 Bush and Dillon [8] reviewed 88 cases of SCC in nuclear reactors. A survey of this nature is an almost impossible task today. However, it is possible, using the approach of Parkins shown in Table 9-18, to present the full range of SCC mechanisms that are currently accepted for the combination of alloys and environments employed in thermal-power systems in which failures have been reported in service. It should be noted that for some alloy/environment systems, like turbine steels, the location in Table 9-18 is rather arbitrary, because the true mechanisms are not known. However, certain similarities with the SCC of carbon steels in caustic solutions indicate that the environment plays an important role. On the other hand, these alloys are known to be susceptible to intergranular cracking in high purity water or steam and therefore, can also be located at the far right side of the spectrum. The fact that high-strength steels are not generally used in contact with aqueous environments in the steam-water cycle of thermal power generating systems yields few examples of failures in these materials. However, generator rotor retaining rings have failed by SCC in many power stations, probably due to hydrogen embrittlement caused by the presence of moisture in the air or by the hydrogen gas used for cooling purposes [9]. Before discussing in some detail

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TABLE 9-18
 STRESS CORROSION CRACKING SPECTRUM

Failure Mode	Intergranular Corrosion	Corrosion Dominated (Environment Requirements Highly Specific)					Stress Dominated (Environment Requirements Less Specific)			Brittle Failure
		Sensitized austenitic stainless steel in BWR piping	Alloy 600 in PWR steam generators (1ary and 2ary side)	Plain carbon steels in boilers	Low alloy steels in low pressure turbine rotors	Admiralty brasses in condensers (steam side)	Austenitic stainless steels in heat exchangers	Admiralty and aluminum brasses in condensers (water side)	Low alloy steels in low pressure turbine rotors	
Alloy component system	Sensitized austenitic stainless steels									
Environment	Acid Solutions	H ₂ O + O ₂	H ₂ O, (+H ₂), OH ⁻	OH ⁻	OH ⁻	NH ₃ + O ₂	Cl ⁻ + O ₂	NH ₃ NO ₃ ⁻ NO ₂ ⁻ SO ₄ ²⁻	Steam + H ₂ O	H ₂ O H ₂
Main characteristics		Intergranular fracture along preexisting active paths					Transgranular fracture along strain generated paths			Mixed transgranular or intergranular crack paths by adsorption or decohesion

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each of the alloy / environment systems presented in Table 9-18, it is advantageous to first consider some of the variables influencing SCC.

As schematically illustrated in Fig. 9-99, stress is one of the three major factors required for SCC. The influence of applied stress on the time to failure for smooth specimens is shown in Fig. 9-100 for several stainless steels exposed to boiling 42 w/o MgCl₂ (154°C). It is apparent that the time to failure increases with decreasing applied stress (α), and that a threshold stress value (σ_{th}) exists below which SCC does not occur. The threshold stress in these examples varies from 50 to 100% of the 0.2% yield strength ($\sigma_{0.2}$), but in many alloy / environment systems, threshold stresses as low as 10% of the yield strength have been measured. Although, for practical purposes, the threshold stress value is important, the resistance of these alloys to SCC should be properly ranked by using the ratio $\sigma_{th} / \sigma_{0.2}$. Moreover, the time to failure includes the time for crack initiation and the time for crack propagation. Thus data of the type shown in Fig. 9-100 do not permit separation of the initiation time from the total time to failure. Consequently, crack propagation rates can not be accurately measured with this method, unless the propagation time is determined independently. In addition, the stress acting at the tip of the advancing crack increases with crack length (and time), even though the nominal applied stress is constant.

As discussed in Section 9-4.4.1, the application of linear elastic fracture mechanics to SCC testing overcomes some of these problems. The determination of crack growth rates on precracked specimens under well defined stress conditions is now possible. Although this approach has traditionally been applied to high-strength materials, such as high-strength steels, aluminum alloys, and titanium alloys [10], during recent years its application has been extended to ductile alloys, such as those employed in thermal power systems. This is illustrated in Fig. 9-101 for sensitized AISI 304 SS exposed to a simulated BWR environment at 250°C [11]. The main variable in this figure is the stress intensity factor (K_I). Two regions of K_I -dependence can be identified. At low K_I values, the crack growth rate is very dependent on K_I (Region I), whereas at K_I values greater than 20–25 MPa·m^{1/2} the propagation rate is almost independent of K_I (Region II). It is also apparent that a minimum value of K_I exists below which the crack growth rate becomes smaller than 10⁻¹¹ m/s. This value, usually identified as a threshold stress intensity for SCC, K_{ISCC} , seems to decrease with increasing applied potential. For many alloy / environment systems, in particular high-strength materials, a third region exists at very high K_I values (Region III). In this region very high crack propagation rates are observed. The upper limit is the critical value of K_I (usually designated as K_{IC}), at which critical crack growth rates, associated with mechanical overloading, are observed in inert environments (dry argon, vacuum). Crack propagation at stress intensities lower than K_{IC} is considered to be environmentally-assisted subcritical crack growth.

Using this approach, it is possible to select an alloy for a specific application in a given environment, in which the applied stress intensity, assuming a certain initial flaw size, is lower than K_{ISCC} . The application of this criterion to design has been addressed by several authors [12–14], and its limitations (discussed in Section 9-5.6) have been pointed out [15–16]. A second aspect, the prediction of crack growth rates in service to estimate component life, has also been discussed at length [14] (see also Chapter 20).

The principal purpose of this discussion, however, is to emphasize the important role of stress in SCC. It should be noted that, in many cases, the stresses involved

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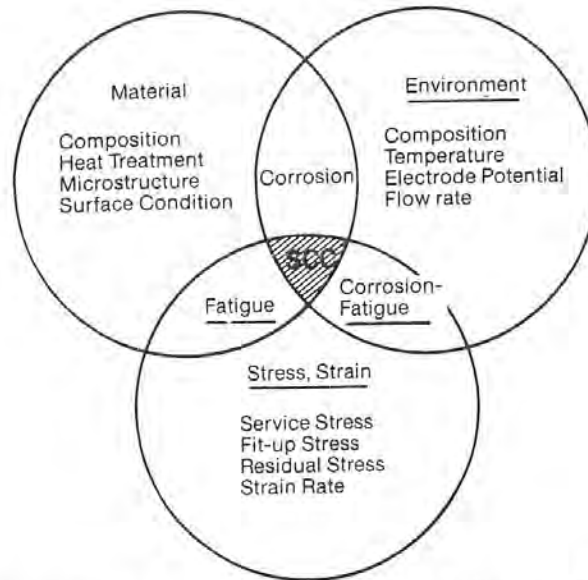


FIG. 9-99 THREE GROUPS OF MAJOR FACTORS DETERMINING SUSCEPTIBILITY TO STRESS CORROSION CRACKING (SCC). SPECIFIC VALUES ARE REQUIRED WITHIN EACH GROUP FOR SCC TO OCCUR. IN CONTRAST, CORROSION, FATIGUE, AND CORROSION-FATIGUE REQUIRE SPECIFIC VALUES IN ONLY TWO GROUPS OF FACTORS [14]

in service failures are residual stresses, caused by manufacturing processes, specific designs of components, welding operations, etc. In addition, thermomechanical service stresses caused by startup and on-load operations may play important roles. Although the previous discussion was essentially confined to sustained loading conditions (constant load), many components of power stations are subject to dynamic straining or vibrational stresses superimposed on a monotonically increased or constant mean stress. Proper consideration of this latter aspect will be given in the section on corrosion fatigue (see Section 9-5.6). The increasing acceptance of slow strain rate or constant extension (or deflection) rate tests, besides their mechanistic utilities, resides precisely in the fact the many structural components are subject to slow dynamic straining. It has been suggested [16] that slow strain rate conditions are established at the crack tip during crack propagation under constant load or constant strain.

As illustrated in Fig. 9-99, material variables are also extremely important in determining the susceptibility to SCC. The list of alloys that may experience SCC in a specific environment has grown with time and encompasses almost all the commercial alloys currently available. Even the concept, prevailing over a long time, that

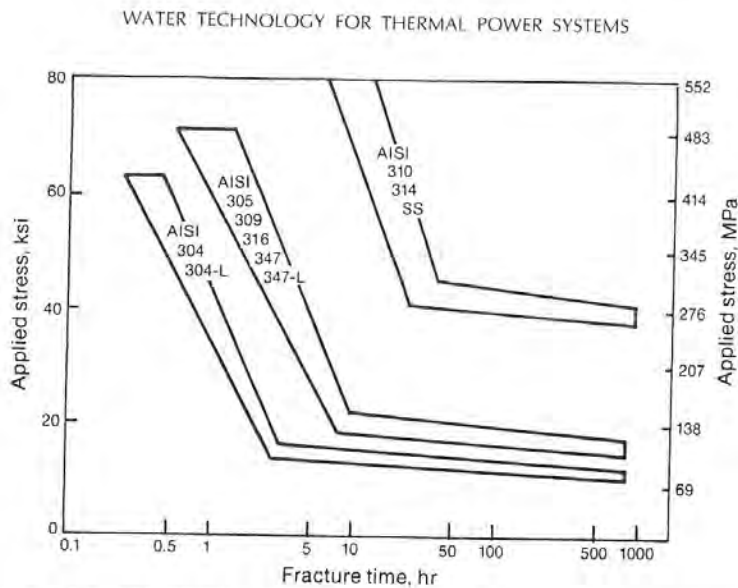
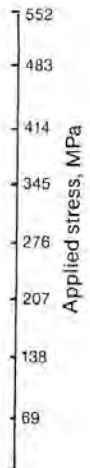


FIG. 9-100 COMPOSITE CURVES ILLUSTRATING THE RELATIVE STRESS-CORROSION-CRACKING RESISTANCE FOR COMMERCIAL AUSTENITIC STAINLESS STEELS IN BOILING 42% MAGNESIUM CHLORIDE [31]

pure metals are not susceptible to SCC has been proven to be wrong [18, 19]. This statement does not mean to imply that for certain environments of interest it is impossible to find an appropriate alloy resistant to SCC. However, in many circumstances, alloys that were assumed to be immune to SCC we found to be susceptible in some other, apparently innocuous, environment.

Alloy composition is one of the many factors that should be considered responsible for SCC resistance. This is clearly illustrated in Fig. 9-102 from the classical work of Copson [20], where the time to failure of Fe-18Cr-xNi alloy wires, exposed under stress to boiling 42% MgCl₂ solution (154°C), is shown as a function of nickel content. It is evident that in this environment the minimum time to failure corresponds to the composition of the more widely used austenitic stainless steels. On the other hand, nickel contents above 40% render the alloys resistant to cracking. On the basis of results of this type, austenitic nickel base alloys, such as Alloy 800 and Alloy 600 were adopted for steam generator (SG) tubing in PWRs. The possibility of chloride contamination of the secondary side of the SGs, as a consequence of condenser leakages, and the associated risk of SCC of AISI 304SS, led to the choice of nickel-base alloys for avoiding the so-called "transgranular chloride cracking."

Many other examples of compositional effects are documented in the literature. Even minor variations in the content of an alloying element may introduce dramatic variations in the SCC resistance, in many cases associated with the appearance of a second phase. Also, the presence of impurities may significantly alter the resistance



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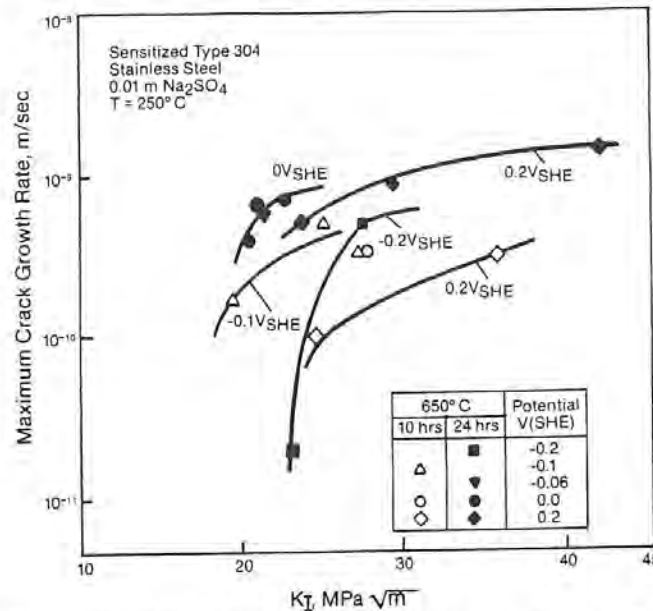


FIG. 9-101 MAXIMUM CRACK GROWTH RATE (Measured on Modified WOL Specimens) AS A FUNCTION OF STRESS INTENSITY (K_I) AT VARIOUS POTENTIALS FOR SENSITIZED AISI 304 SS IN 0.01 m Na_2SO_4 SOLUTION AT 250°C [11]

to SCC. This is precisely the case for austenitic stainless steels, such as Fe-16Cr-20Ni and Fe-18Cr-14Ni, in boiling $MgCl_2$. For the latter alloy, material prepared by plasma furnace melting [21] with a total metallic impurity content of 1 ppm and a total nonmetallic impurity (oxygen, nitrogen, sulfur, and phosphorus) content lower than 10 ppm was found to be extremely resistant to chloride cracking. Clearly, this is not always a practical approach for all commercial alloys because in many cases it is uneconomical to substantially reduce the level of impurities. However, improvements in steel making processes have made this approach practicable, in particular for high-strength, high-fracture-toughness steels.

The influence of heat treatment in relation to microstructural effects deserves special consideration. In Section 9-5.4, the problem of sensitization regarding intergranular corrosion cracking of austenitic stainless steels was discussed at length. The close relationship of this phenomenon with the intergranular stress corrosion of AISI 304SS in BWR environments will be the subject of Section 9-5.5.3. It should be noted, however, that heat treatment may not only induce the formation of precipitates (e.g., $Cr_{23}C_6$ in AISI 304SS) it may also lead to the development of a second phase (e.g., ferrite in AISI 308SS) or to the segregation of impurity elements to grain

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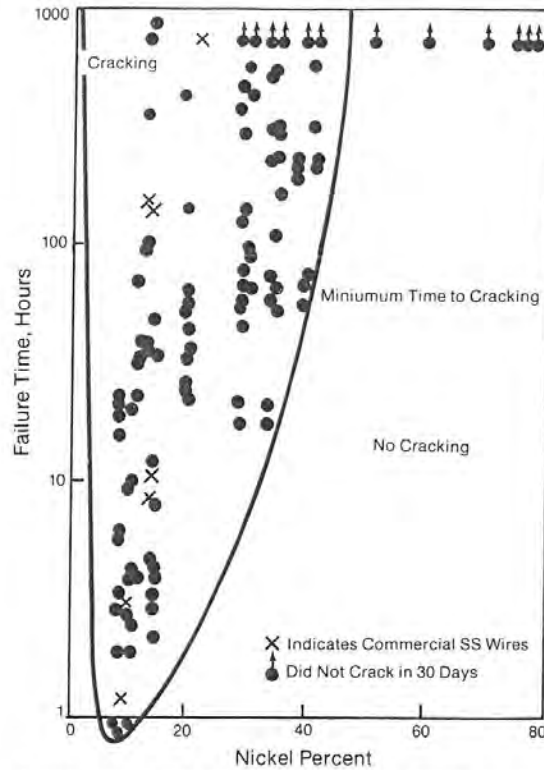


FIG. 9-102 EFFECT OF INCREASING NICKEL CONTENT ON THE SUSCEPTIBILITY OF Fe-18Cr-xNi ALLOYS TO SCC (Wire Specimens) IN BOILING 42% MgCl₂ [20]

boundaries. It is well known that low-alloy, medium-strength steels used as turbine materials may become susceptible to temper embrittlement when quenched and subsequently tempered. This is a phenomenon characterized by an upward shift in the brittle-ductile transition temperature, produced by heating within or slow cooling through the temperature range of 350–575°C. It is now recognized that segregation of impurities, such as antimony, phosphorus, tin and arsenic, along prior austenite grain boundaries is the cause of temper embrittlement. Although it is still disputed that impurity segregation is a requirement for SCC of turbine steels in wet steam, it has been found that steels with equivalent mechanical properties, such as yield strength, are more susceptible to cracking in the temper-embrittled condition than in the deembrittled condition.

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For many alloys, the effect of cold work is of paramount importance. For example, annealed AISI 304SS does not crack intergranularly in oxygenated high purity water. However, when the material is heavily cold-worked, transgranular stress corrosion cracking occurs in pure water with both 0.2 and 200 ppm oxygen at 288°C [22]. The susceptibility of cold worked stainless steel to SCC seems to be associated with the presence of deformation-induced martensite. In addition, as discussed in Section 9-5.4, cold work up to 5-20% prior to sensitization increases the degree of sensitization and therefore the susceptibility to intergranular corrosion. For similar reasons, the susceptibility to intergranular SCC in high temperature oxygenated water also increases.

Finally, the surface condition, as affected by local work-hardening, phase transformations, residual stresses, embedded material from abrasives and machining equipment, etc., also has a significant influence on the susceptibility to SCC. However, the precise effect is difficult to evaluate. Deep grooves or notches provide local stress raisers and hence are obviously detrimental. On the other hand, compressive stresses, introduced in surface layers by using shot-peening, are beneficial. Nevertheless, if phase transformation occurs as a consequence of shot-peening (i.e., formation of martensite in metastable austenitic stainless steels), the procedure can be detrimental in terms of SCC resistance.

The last group of major influential factors concerning SCC is that associated with the properties of the environment. It has often been stated that the environmental requirements for SCC are highly specific. However, the number of environments known to induce SCC in a given alloy has increased substantially during the last three decades and the concept of solution specificity is not as firmly based as before. As an example, Table 9-19 shows the environments known to induce SCC in carbon steels and austenitic stainless steels in 1950, as compared to those reported in 1985. The list does not pretend to imply that, for both types of alloys, SCC will occur independently of other environmental variables, such as temperature, pH, solution composition, etc. On the contrary, the requirement of a specific environment for the occurrence of SCC, as related of electrochemical factors such as potential, has been demonstrated many times.

The specific action of the environments included in Table 9-18 in promoting SCC of alloys employed in thermal power plants will be discussed in the following subsections. However, it is convenient to discuss here some basic concepts.

One of the most important conditions that should be satisfied in order to induce environmentally-assisted subcritical crack growth, in particular when anodic dissolution is the dominant process responsible for crack advance (as seems to be the case for the alloy / environment systems listed in the center and the left of Table 9-18), can be expressed as follows. The rate of anodic dissolution at the crack tip should overcome by several orders of magnitude the anodic dissolution rate on the exposed metal surface, otherwise general dissolution will occur. This explains why SCC occurs in alloy / environment systems in which the alloy is essentially passive due to the presence of a protective oxide film. Moreover, if the dissolution rate of the incipient crack walls is close to that at the crack tip, pitting will tend to occur, instead of SCC. In general terms, it is clear that a critical balance must exist between anodic activity and passivity at the metal / solution interface in order for anodic dissolution to occur over a narrow front and hence to preserve the high aspect ratio of the crack. A completely passive condition, on the other hand, cannot lead to

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TABLE 9-19
LIST OF LIQUID ENVIRONMENTS KNOWN TO CAUSE STRESS CORROSION CRACKING IN CARBON STEELS AND AUSTENITIC STAINLESS STEEL

Up to	Carbon Steels	Austenitic Stainless Steels
1950	Hydroxides, OH ⁻ Nitrates, NO ₃ ⁻ Cyanides, CN ⁻	Acid Chlorides, MgCl ₂ , CaCl ₂ , ZnCl ₂ Neutral Chlorides, NaCl + O ₂ (or H ₂ O ₂)
1985	Carbonates, HCO ₃ ⁻ + CO ₃ ²⁻ Carbon Monoxide + Carbon Dioxide, CO + CO ₂ + H ₂ O Hydrogen Sulfide, H ₂ S Ferric Chloride, FeCl ₃ Ammonia, NH ₃ + O ₂ Phosphates, H ₂ PO ₄ ⁻ + HPO ₄ ²⁻ Sulfates, SO ₄ ²⁻ Nitrites, NO ₂ ⁻ Water + O ₂	Hydroxides, OH ⁻ Acidified Chlorides, NaCl + H ₂ SO ₄ Fluorides, F ⁻ Bromides, Br ⁻ Water + O ₂ Thiocyanates, SCN ⁻ Thiosulfates, S ₂ O ₃ ²⁻ Tetrathionates, S ₄ O ₆ ²⁻ Polythionic Acids, H ₂ S ₂ O ₆ Sulfurous acid, SO ₂ + HSO ₃ ⁻ Hydrogen Sulfide, H ₂ S + O ₂

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SCC, because any incipient crack nucleus would be readily rendered inactive by rapid repassivation.

In addition to these concepts, some generalizations can be established regarding the role of anionic species. In the absence of microstructural features that determine the formation of a pre-existing active path (e.g., chromium depletion along grain boundaries in sensitized austenitic stainless steels), the anion involved (e.g., chloride) should be able to induce in a variety of alloys localized breakdown of passivity. Accordingly, for stainless steel in the mill-annealed condition, the potential above which transgranular SCC can occur in chloride solutions corresponds precisely to the critical potential for pitting corrosion. However, the range of potentials within which SCC generally occurs is relatively narrow, because at slightly higher potentials pitting corrosion extends over the whole exposed metal surface. In case of transgranular cracking, very localized pitting corrosion tends to occur preferentially over the slip steps produced by plastic deformation, defining a strain-generated active path.

For alloys that are not commonly regarded as being "passive," such as carbon and low alloy steels, the environments in which SCC occurs do lead to the formation of passive films as illustrated in Figure 9-103. The potential-pH conditions for severe cracking susceptibility of carbon steels are encountered when a protective film (phosphate, carbonate, magnetite, etc) is either thermodynamically stable or metastable but, if ruptured, soluble species such as $\text{Fe}(\text{OH})_b^{(2-b)+}$ (where $b = 0$ to 3) or HFeO_2^- can form. In this case, the main role of the anions is to retard the repassivation process on the exposed metal surface, following film rupture produced by the action of the applied stress or strain. At potentials higher than those corresponding to SCC susceptibility, the repassivation rate is so high that the passive film effectively inhibits dissolution at the crack tip. At potentials lower than the so-called Flade potential, active dissolution through a poorly protective surface film takes place and, therefore, the conditions are favorable for general corrosion rather than SCC.

For a variety of alloy/environment systems, in which anodic dissolution at the crack tip seems to be the predominant crack propagation mechanism, an extremely good correlation has been observed [23] between the crack growth rate and the average current density measured on fast straining or abrading surfaces, as shown in Fig. 9-104. The relationship between both quantities derives from the application of the Faraday's law, according to the following equation

$$V = \frac{M}{ZF\rho} i_a \quad (123)$$

where M is the atomic mass of the metal, Z is the charge of the metal cation, F is the Faraday constant, ρ is the density of the metal, and i_a is the anodic current density on a rapidly strained metal surface, with the assumption that it is equivalent to the current density at the active crack tip. Since the anodic current density, i_a , for charge-transfer reactions under activation control is dependent upon temperature (see Section 9-3), it is apparent that temperature has an important effect on crack propagation rates and therefore on SCC susceptibility. Similar considerations can be applied to the accelerating effect of increasing anodic potentials on crack velocity, as observed for a variety of alloy/environment systems. However, as discussed above, relatively large potential increases can alter the nature of the anodic process, leading to pitting corrosion if the potential is well above the pitting potential or to passivation if the formation of a passive film is favored (cf. Fig. 9-103).

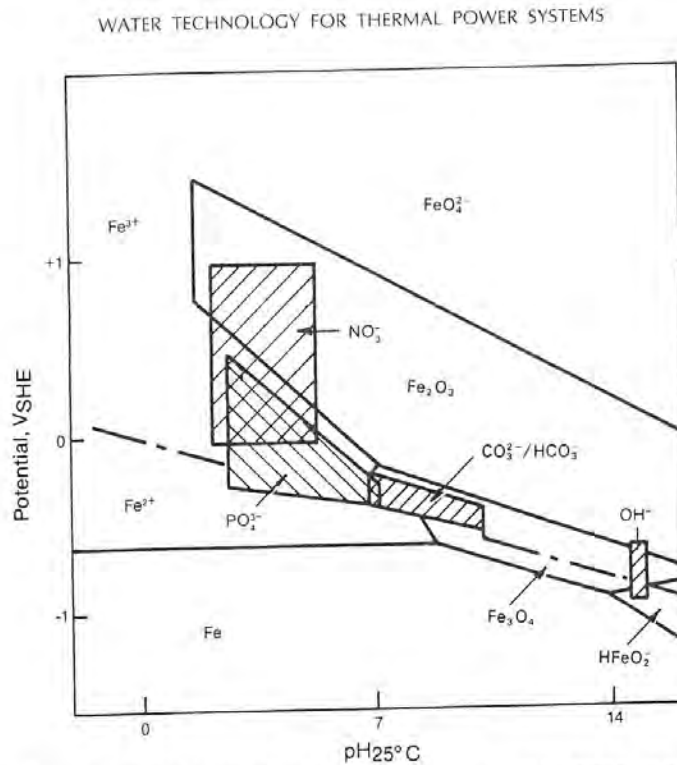


FIG. 9-103 RELATIONSHIP BETWEEN pH-POTENTIAL CONDITIONS FOR SEVERE CRACKING SUSCEPTIBILITY OF MILD STEEL IN VARIOUS ENVIRONMENTS AND THE STABILITY REGIONS FOR SOLID AND DISSOLVED SPECIES ON THE POURBAIX DIAGRAM. NOTE THAT SEVERE SUSCEPTIBILITY IS ENCOUNTERED WHERE A PROTECTIVE FILM (Phosphate, Carbonate, Magnetite, etc.) IS THERMODYNAMICALLY METASTABLE, BUT IF RUPTURED, STABLE SOLUBLE SPECIES (Fe^{2+} , HFeO_2^-) CAN FORM [30].

The influence of reducible species in the environment (such as O_2 , H_2O_2 , Fe^{3+} , etc.) has frequently been over-emphasized by claims that their presence is an essential requirement for the occurrence of SCC. However, as discussed in more detail in some of the following subsections, it has been demonstrated that their main role is to alter the corrosion potential of the exposed metal surface. The potential can also be displaced electronically (with a potentiostat) to a range within which the alloy is susceptible to SCC in a similar environment (pH, temperature, solution composition, etc.), but in the absence of reducible species. This suggests that the dominant electrochemical factor is the potential established at the metal/solution interface, rather than the nature and concentration of the reducible species per se. Under natural corrosion conditions, the corrosion potential (see Section 9-4.2) is undoubt-

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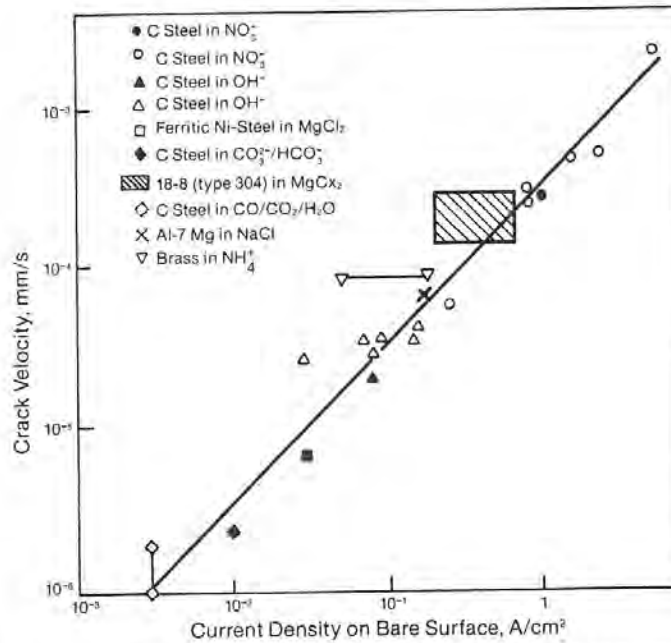


FIG. 9-104 OBSERVED CRACK VELOCITIES AND CURRENT DENSITIES ASSOCIATED WITH 'BARE' SURFACES FOR VARIOUS ALLOY/ENVIRONMENT SYSTEMS. THE LINE IS THAT CALCULATED FROM EQ. 9-123 [23]. SOURCES OF DATA POINTS ARE REPORTED IN THAT REFERENCE.

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edly the prime variable of interest, but slight changes in the composition of the environment arising from varying operational conditions may lead, in the cases of some alloys, to significant variations in the corrosion potential. This potential may lie within or fall outside the cracking range, leading in some circumstances to dramatic changes in cracking susceptibility. Wide variations in cracking response have been reported many times for laboratory experiments conducted under apparently equivalent conditions, principally because not enough attention was paid to the potential changes brought about by the presence of certain species in solution. Without doubt, many unexplained service failures in the thermal power industry could be understood from this viewpoint.

In order to further illustrate this point, let us consider the effect of non-reducible cations on SCC. Many of the cations encountered in the aqueous environments typical of the thermal power industry are readily hydrolyzed, according to the following equation,



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thereby altering the pH of the environment. However, it is commonly accepted that cations have practically no influence on the kinetics of anodic or cathodic processes on metal surfaces. Therefore, we do not expect that they will directly affect the susceptibility of an alloy to SCC. However, it is known that the time to failure of AISI 304SS in boiling aqueous chloride solutions decreases, following the sequence $\text{Li}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ [31]. The apparent explanation is that the pH decreases along the same sequence and, therefore, the increased susceptibility is not due to the effect of the cation per se, but to the change in the pH of the solution.

It has been found, however, that some cations have a specific influence on SCC susceptibility [32], and this is an area that deserves closer scrutiny. Other cations, such as NH_4^+ , are extremely important in the SCC of α -brasses in ammoniacal solutions (see Section 9-5.5.5). Also, in this case, the effect is indirect, because, according to the following equilibrium,



both the concentration of NH_4^+ and the pH control the concentration of NH_3 , which is a strong ligand of both copper and zinc (the main alloying elements of α -brasses).

These basic mechanistic concepts of SCC have been extensively discussed and reviewed by many authors [24-30]. It is beyond the scope of this chapter to deal in more detail with the arguments developed in such reviews. Before passing to a descriptive discussion of the alloy-environment systems of interest in the power generating industry, it is convenient, however, to discuss briefly the mechanisms suggested for those systems located on the right side of the spectrum depicted in Table 9-18. At the far right end, mechanical fracture in the absence of corrosion processes is exemplified by the brittle failure of high-strength steels. Moving to the left in the spectrum, the role of the environment becomes more and more pronounced, but it should be noted that high-strength steels are known to be susceptible to SCC in pure water or humid air, even in the absence of reducible species (a very mild environment). On the other hand, the presence of specific reduced species, such as H_2S , significantly enhances the cracking propensity [32]. For these materials, there is now enough evidence to support the concept that hydrogen-embrittlement (HE) is the dominant failure process. A more detailed discussion of this phenomenon, as well as the prevailing mechanistic interpretations, is presented in Section 9-5.7.

For more ductile alloys, in which HE has also been postulated [33] as a possible mechanism for SCC, Ford [30] has emphasized that the sequence of the rate-controlling steps at a given crack-tip electrode potential and pH may be the same for anodic oxidation processes and for hydrogen discharge, as described by the elementary steps presented in Section 9-4.1.4. In the case of HE, the final electrochemical step of interest is not the chemical or electrochemical desorption of the H_2 molecule, but the entry of atomic hydrogen into the metal lattice. However, the previous steps of mass transport in the solution and charge transfer at the metal/solution interface, as well as the mass transfer to the bulk of the solution of the solvated cations produced by the charge-transfer reaction, may be the same for anodic dissolution-induced cracking and for HE. Both the hydrogen adatom coverage, which is critical to HE models, and the overall anodic oxidation rate that is critical to strain-induced anodic dissolution models, may be affected by the same rate-determining steps [30].

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In the case of SCC, since the metal surface is usually covered by a surface film, there are two important rate-controlling events for the charge transfer reaction (metal oxidation and/or hydrogen reduction) to occur at the appropriate rate within the crack enclave. One of them is the film (oxide, oxyhydroxide, salt, etc.) rupture rate at the crack tip, which is controlled by variables such as local stress, strain rate, film thickness and film rupture strain, substructure of moving dislocations, microstructure, etc. These parameters are dependent in a more general sense on the stress and the material (c.f., Fig. 9-96). The second is the repassivation rate of the crack walls in the vicinity of the crack apex, which is principally affected by the material and the environment (potential, pH, solution composition, etc.).

Both processes of subcritical crack growth, hydrogen-induced and anodic dissolution, may coexist or occur alternately depending upon minor variations in some of the parameters affecting the three major influential factors indicated in Fig. 9-96. This seems to be the case for some of the alloy-environments systems presented on the right side of Table 9-18 (i.e., low alloy steel in turbine environments).

To complete this introductory discussion, it should be noted that most of the mechanistic interpretations of SCC deal with the propagation stage. However, in many of the cases of SCC failure, there is indirect evidence that the initiation stage is the dominant term in the lifetime of the component, and we are of the opinion that not enough attention has been given to this aspect of SCC studies. In this regard, the process of film formation, and the alteration of the film properties by environmental changes, should be properly addressed. In the case of transgranular cracking of annealed stainless steels in concentrated chloride solutions, the subject has been more extensively studied. It is now established [34] that, under conditions leading to transgranular SCC, the original, air-formed oxide film is substantially modified, leading to a less protective state. The film is frequently contaminated with chloride ion. This seems to be the initial process that leads to the nucleation of cracks at specific sites on the metal surface, where the film, ruptured under stress, cannot be easily repaired. However, an alternative explanation has been proposed. It has been claimed [35], that selective dissolution of an alloy component induces the formation of a thin (10–20 nm) dealloyed layer with specific properties as the initial step in the nucleation of a transgranular crack. Detailed arguments have been put forward to explain the cleavage-like features of transgranular cracks, suggesting that the dealloyed layer is reformed at the crack tip following a fast short-range cleavage event. The discontinuous nature of crack growth during transgranular SCC was discussed by these authors [35], with particular reference to α -brasses (see Table 9-18), but the validity of this "dealloying" mechanism is far from unequivocal acceptance by the SCC fraternity.

9-5.5.1 Ferritic Steels. The first documented cases of SCC in the thermal-power industry are the catastrophic failures of steam boilers made of carbon steels in England at the end of the last century. Between 1865 and 1870, 288 cases of explosive failures were reported, which were later attributed to so-called "caustic embrittlement." At the time, the metallurgical nature of the phenomenon was established by determining that the fractures were intergranular. Around 1914, it was recognized that the failures were related to the quality of the feedwater. In order to control the general corrosion of carbon steels, the feedwater was kept slightly alkaline by the addition of small concentrations of NaOH. Since riveted boilers were employed, steam leaked past badly fitted rivets, so that concentrated NaOH was formed in the

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crevice. This led to SCC. A similar situation occurred where tubes had been rolled into tube sheets. SCC of plain carbon steels in steam locomotives and stationary steam plants became a widespread cause of costly failures.

As reviewed by Logan [36], it was concluded in the 1930s that SCC does not occur unless the concentration of the alkaline solution is very high. The range of temperatures and NaOH concentration above which cracking of carbon steels has been observed in service is illustrated in Fig. 9-105. It was also established that residual stresses, arising from the forming of the boiler, from distortion during riveting, or from rolling of the boiler tubes in the tubesheet, were a necessary and concurrent factor, even though the effect of additional service stresses could not be disregarded. The displacement of steam by diesel power on the railroads and the fabrication of pressure vessels by welding rather than riveting by no means solved the problem. It was, however, to a large extent controlled and mitigated by the use of inhibitors in locomotives and by proper conditioning of the feedwater in stationary boilers. This last aspect is covered elsewhere in this handbook. However, some of the environmental factors involved in the mechanism of caustic cracking of mild steels deserves consideration.

For many years, controversy surrounded the mechanistic interpretation of the role of additives and impurities. This was, to a large extent, due to contradictory experimental results. The whole picture became clear in the 1960s with the use of the potentiostat to control the potential applied to stressed specimens of carbon steels. Three independent studies, [37-39], identified a narrow range of potential (from approximately -1150 to -840 mV_{SCC}) within which intergranular SCC occurred on carbon steel exposed to deaerated, concentrated (20-35 w/o) NaOH solutions at temperatures around 100°C. Figure 9-106 illustrates the results of one of these studies, in which slow strain-rate tests were employed. Similar results were obtained in the other two studies [37, 38], using constant load testing at stress values close to 70% of the yield strength. An important aspect to be emphasized is that the open-circuit potential (corrosion potential) of the mild steel in the same environment usually lies about 50 mV below the lower limit of the cracking range. Therefore, under natural corrosion conditions, SCC is not expected, unless the presence of impurities or additives displaces the potential into the cracking range. It should be noted that cracking is promoted by a small amount of dissolved oxygen, whereas it is inhibited by higher oxygen levels. The role of oxygen at high concentrations or oxidizing inhibitors such as NO_3^- is now clearly understandable, because the corrosion potential is displaced well above the upper limit of the cracking range. A detailed discussion on the role of oxidizing inorganic inhibitors, as well as organic and non-oxidizing inorganic inhibitors, can be found in [40] and [41].

The effect of steel composition on the cracking of mild steel in concentrated caustic solutions has been reviewed by several authors [41, 42]. The majority of the data currently available concern the effect of carbon and indicate that the resistance to caustic cracking increases with increasing carbon content. Contents of about 0.15% carbon have a beneficial effect. On the other hand, if the carbon content is reduced to very low levels ($<0.004\%$), the susceptibility to SCC also decreases significantly and it seems that pure iron is not susceptible to this form of cracking. However, the mechanistic role of carbon is still controversial. At low carbon contents ($<0.1\%C$), carbon undergoes equilibrium segregation to ferrite grain boundaries, either as soluble carbon or as carbide particles or films, if the solubility limit of carbon in ferrite is

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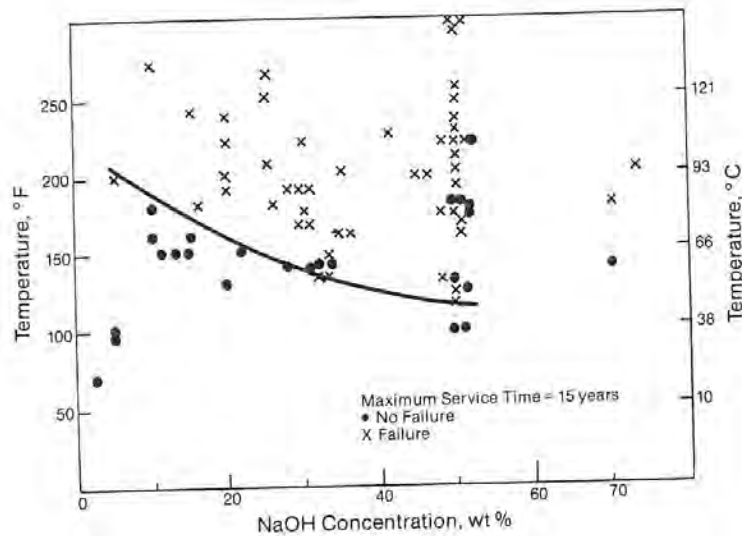


FIG. 9-105 EFFECT OF TEMPERATURE AND NaOH CONCENTRATION ON THE SCC SUSCEPTIBILITY OF CARBON STEELS IN SERVICE [42]

exceeded. As the carbon content is increased, the proportion of pearlite in the steel increases and the number of carbide particles in the grain boundaries also increases, thereby altering the distribution of the phases in a manner that could change the location of the selective dissolution processes that are involved in promoting intergranular stress corrosion cracking [41]. It is known that the anodic dissolution rate for iron carbide is higher than that for iron in sodium hydroxide solutions, although it is still not clear if this is the reason for the preferential dissolution along grain boundaries involved in the intergranular propagation of cracks. Nitrogen, phosphorus and sulfur may also segregate to ferrite grain boundaries and would also influence intergranular cracking, but these elements are present in very small quantities in normal mild steels. There are no systematic studies of their influence, but it is now recognized that segregation of phosphorus to grain boundaries in pure iron induces intergranular cracking in caustic solutions. It can be claimed, however, that this mechanism is not relevant to the caustic cracking of mild steels.

The effect of alloying additions has also been reviewed during the last decade [41, 42]. In moving from the plain carbon steels to low-alloy steels, the alloying additions may influence the SCC propensity by affecting the microstructure or by altering the segregation of impurities or carbon to grain boundaries. They may affect the passivation characteristics of the steel and also its mechanical properties.

Recently, Parkins et al. [43] assessed the influence of various alloying elements

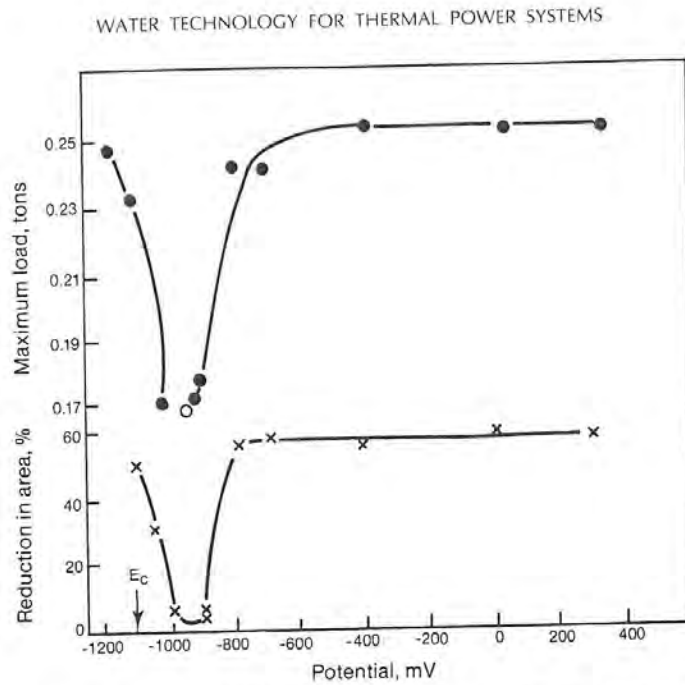


FIG. 9-106 MAXIMUM LOAD AND REDUCTION IN AREA OF MILD STEEL SUBJECTED TO CONSTANT STRAIN RATE TEST ($4.2 \times 10^{-6} \text{s}^{-1}$) AT VARIOUS POTENTIALS IN 35% NaOH AT 110°C [39]

in terms of a stress corrosion cracking index (SCCI), which, for caustic solutions, can be expressed by the following relationship:

$$SCCI_{OH} = 105 - 45\%C - 40\%Mn - 13.7\%Ni - 12.3\%Cr - 11\%Ti + 2.5\%Al + 87\%Si + 413\%Mo \quad (126)$$

The SCCI reflects both the width of the potential range for cracking and the cracking severity in terms of a time-to-failure ratio (the time-to-failure in caustic solution over the time-to-failure in an inert environment). From Eq. (126), it is apparent that elements like carbon, manganese, nickel, chromium, and titanium have a beneficial effect, while aluminum, silicon, and particularly molybdenum have a pronounced detrimental effect. However, it should be emphasized that Eq. (126) reflects the effect of alloying additions on the SCC behavior only in general terms, since accompanying changes in mechanical properties and microstructure, including grain boundary segregation and in particular carbide distribution, are also extremely important factors in determining the susceptibility to SCC. Nevertheless, the dominant factors

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seem to be electrochemical in nature, as reflected in the effect of the various alloying elements on the repassivation rate. The effect of heat treatment, as related to quenching and tempering operations, is very influential upon mechanical properties, microstructure and /or composition of grain boundaries, as well as the effect of grain size, mainly due to its influence on the yield strength. Therefore the relation of all these material variables to the SCC susceptibility should be considered carefully.

Even though the caustic cracking of boilers is not a recurrent problem in the thermal-power industry, due to improved control of the feedwater, it is interesting to note that in the pulp and paper industry widespread incidents of caustic cracking on non stress-relieved welds of carbon steel digesters have been reported recently [44].

In order to complete this discussion on stress corrosion cracking of carbon steels in environments of interest to the thermal power industry, it should be noted that in two separate investigations [45, 46] transgranular cracking of carbon steels has been observed in high-temperature, high-purity water in the presence of dissolved oxygen concentrations of 0.15 ppm. Transgranular cracking occurred at temperatures ranging between 150°C and 250°C and at a dissolved oxygen concentration of 0.16 ppm oxygen. At higher oxygen concentrations (1 and 8 ppm), the temperature range within which cracking was observed extends up to 300°C. At ~0.16 ppm oxygen, the transgranular cracks nucleate from pits formed under the straining conditions of the slow strain-rate tests employed in both investigations (cf. Section 9-5.2), whereas at high oxygen concentrations cracks were not initiated from pits. The authors of both investigations emphasized, however, that the crack propagates at very high stress levels, close to the ultimate tensile strength attained during slow strain-rate testing, and therefore may not pose a serious problem in the various environments encountered in BWR plants. It should be noted that plain carbon steel piping is extensively used in both BWR and PWR nuclear steam supply systems for the feedwater heater train. During the 1970s, BWR designs increasingly specified carbon steels for other systems that were previously constructed from stainless steel. Now, virtually the entire primary pressure boundary piping, the emergency core cooling systems, and the balance-of-plant piping is made of carbon steel. However, no incidents of stress corrosion cracking have been observed in BWRs, whereas a large number of environmentally-assisted cracking failures in secondary feedwater lines of PWRs have been reported. The catastrophic failure of a deaerator vessel in the pulp and paper industry [44] prompted an inspection program that extended to several industries. It was found that 30-40% of those vessels inspected exhibit cracks in welds and heat-affected zones. Analysis of various cases indicated a transgranular mode of crack propagation [47]. Cracking in both PWRs and in pulp and paper deaerator vessels has been attributed to corrosion fatigue, a subject that is discussed in Section 9-5.6. However, the possibility of environmentally-assisted cracking under monotonic loading cannot be neglected for carbon steels with moderately high tensile strength.

From the previous discussion, it is apparent that ferritic steels are susceptible to intergranular cracking in highly concentrated NaOH solutions due to enhanced anodic dissolution along pre-existing active paths. This explains the location of this alloy/environment system at the left of the spectrum depicted in Table 9-18. However, for the same type of material exposed to a mild environment (oxygenated pure water) under severe stress conditions, the crack path changes to transgranular.

STEEL
CORROSION

Corrosion

(126)

Stress
corrosion
cracking
is a
phenomenon
that
occurs
in
aqueous
environments
under
tensile
stress.
It
is
characterized
by
the
formation
of
cracks
that
propagate
through
the
metal
under
stress.
The
rate
of
crack
growth
is
dependent
on
the
environment,
the
stress,
and
the
material.
Stress
corrosion
cracking
can
be
prevented
by
reducing
the
stress,
changing
the
environment,
or
using
more
resistant
materials.

WATER TECHNOLOGY FOR THERMAL POWER SYSTEMS

Therefore, the location of this alloy / environment system is displaced to the right of the spectrum, as for those characterized by the existence of a strain-generated fracture path. For the environments of interest in the thermal power industry (water at temperatures ranging from 100°C to 288°C and oxygen concentrations up to a maximum of 1 ppm O₂ at about 100°C) transgranular cracks are not initiated at strain-generated slip steps on the metal surface, but rather from pits produced by the action of the environment in the presence of an applied stress or straining. As noted in Section 9-5.2.4, pits form at manganese sulfide inclusions present in the steel.

9-5.5.2 Stress Corrosion Cracking of Low-Alloy Steels. Low-alloy steel is a broad category of steels characterized by the presence of up to 5% of alloying elements. The differentiation between carbon steels and low-alloy steels is arbitrary to a certain degree. Both contain carbon, manganese and usually silicon, and sometimes copper or boron as specific additions. Steels containing more than 1.65% manganese, 0.60% silicon, and 0.60% copper are designated as alloy steels. However, from the compositional point of view, what characterizes a low-alloy steel is a specified and definite range of alloying elements. In thermal power systems, two types of low-alloy, high-strength steels are widely used. One class is represented by those steels employed for piping or pressure vessels, such as A533 Grade B Class 1, A508 Class 2, and A542 and A543, Class 1 and 2, each containing approximately 0.25C, 0.40–1.50 Mn, 0.2 Si, 0.5–1.0 Mo, 1.5–1.5 Cr, and /or 0.4–4.0 Ni. They are currently used in the quenched and tempered condition, in order to attain yield strengths of about 550–690 MPa (80–100 ksi). A critical discussion of the requirements for nuclear pressure vessel materials is presented in [48].

The other group consists of the low-alloy steels for turbine rotors and discs. Typical examples are A470 Class 8 and A 471 Class 8, that are mainly used for rotor and discs, respectively. They are Ni–Cr–Mo–V steels containing approximately 0.75–2.00 Cr, 2.00–4.00 Ni, 0.2–0.7 Mo, and 0.05V for A471 and 0.9–1.5 Cr, 0.75 Ni, 1.0–1.50 Mo, and 0.20–0.30 V for A470, with a C content of about 0.25%. They are also employed in the quenched and tempered conditions to attain yield strength ranging from 635 to over 1300 MPa (92–190 ksi).

The metallurgical structure of these steels is termed bainite, which is a mixture of very fine particles of carbides embedded in a ferrite matrix. The strength and toughness of the bainite structure is controlled mainly by the fine distribution of carbides. Alloying elements such as nickel, manganese, chromium, molybdenum and vanadium help achieve this condition. The risk and consequences of temper embrittlement in these steels have been briefly discussed at the beginning of Section 9-5.5. Pressure vessel steels are not found to be susceptible to stress corrosion cracking under the conditions prevailing in thermal power plants, but the risk of corrosion fatigue failures has prompted extensive research (see Section 9-5.6). On the other hand, numerous incidents attributed to SCC have been reported for turbine steels.

The first major reported instance of SCC in a low-pressure turbine disc was the catastrophic rupture in 1969 of a shrunk-on disc in the Hinkley Point A plant in England [49, 50]. Cracking was intergranular and originated at highly-stressed-keyways in the disc. The primary causes of SCC, besides stress, were believed to be a combination of low fracture toughness, resulting from temper embrittlement during slow furnace cooling after the tempering heat treatment, and a supposedly high concentration of NaOH within the keyways [50]. It was assumed that caustic con-

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concentrated to high levels in the keyway crevices of discs that were located just upstream of the Wilson line (the position at which supersaturated steam condenses to form water droplets). For a nuclear low-pressure turbine at a temperature of about 200°C and a pressure of 690 kPa (100 psia), it is predicted that an NaOH concentration of about 50 w/o can be attained in the water droplets if the caustic concentration in the steam exceeds 1 ppb [51]. After the incident, inspection of the remaining discs revealed the presence of cracks in two additional discs. The steel used in these discs was Fe-3Cr-0.5Mo. Later on, 810 discs from different plants in England were inspected and about 15% were found to have cracks in the keyways [52]. These discs were fabricated with different low-alloy steels. An extensive survey was conducted in the U.S. [53, 54] and the main conclusion of this study, coupled with the results of extensive programs in the U.K. and elsewhere can be summarized as follows:

(a) Cr-Mo and Ni-Cr-Mo-V steels are susceptible to SCC, but 3.5 Ni steel apparently is not.

(b) Temper embrittlement, even though extremely important, is not a prerequisite for SCC.

(c) Cracking occurs only in wet steam, at crevices and areas of limited steam access (i.e., at the location of the so-called Wilson line).

(d) Cracking is usually intergranular, following prior austenite grain boundaries, but may be transgranular, depending apparently upon the contaminants present in the steam.

(e) Hydroxides and/or sulfides appear to have been responsible for many cracking incidents, but SCC may also occur in high-purity wet steam. The role of other steam impurities has not been extensively investigated.

(f) The period of operation before cracking occurs appears to be related to the level of contamination present in the system and, possibly, to the type of water chemistry control employed.

The majority of the stress corrosion cracks have been detected by inspection before the cracks grew to a critical size and, with the exception of a few cases, the catastrophic consequences of disc disintegration have been avoided.

Extensive laboratory work has been conducted [55-67] in an attempt to define the conditions for cracking to occur, and to understand the mechanism of SCC on rotor materials. Part of this work has been recently reviewed by Speidel [66, 67].

The major parameters that influence crack growth rate in turbine steels are stress intensity, yield strength, composition of the environment, potential, and temperature. Speidel [66, 67] has emphasized that alloy composition does not have an important effect on the crack growth rate. As illustrated in Fig. 9-107, the crack propagation rate is extremely dependent on stress intensity. At very low stress intensities, close to the threshold stress intensity value ($K_{ISCC} \sim 10 \text{ MPa} \cdot \text{m}^{1/2}$), crack growth rates are lower than 10^{-11} m/s . The crack growth rate then increases with increasing stress intensity (Region I), until a plateau is reached where crack growth is independent of stress intensity (Region II). At even higher stress intensity the crack growth rate increases again (Region III). The crack growth rate at the plateau, as well as K_{ISCC} , are dependent on many environmental variables.

It is seen from Fig. 9-107 that the yield strength of the material (in this case ASTM A471 steel) has a strong influence on the plateau crack growth rate, in that the rate increases by more than four orders of magnitude when the yield strength is increased

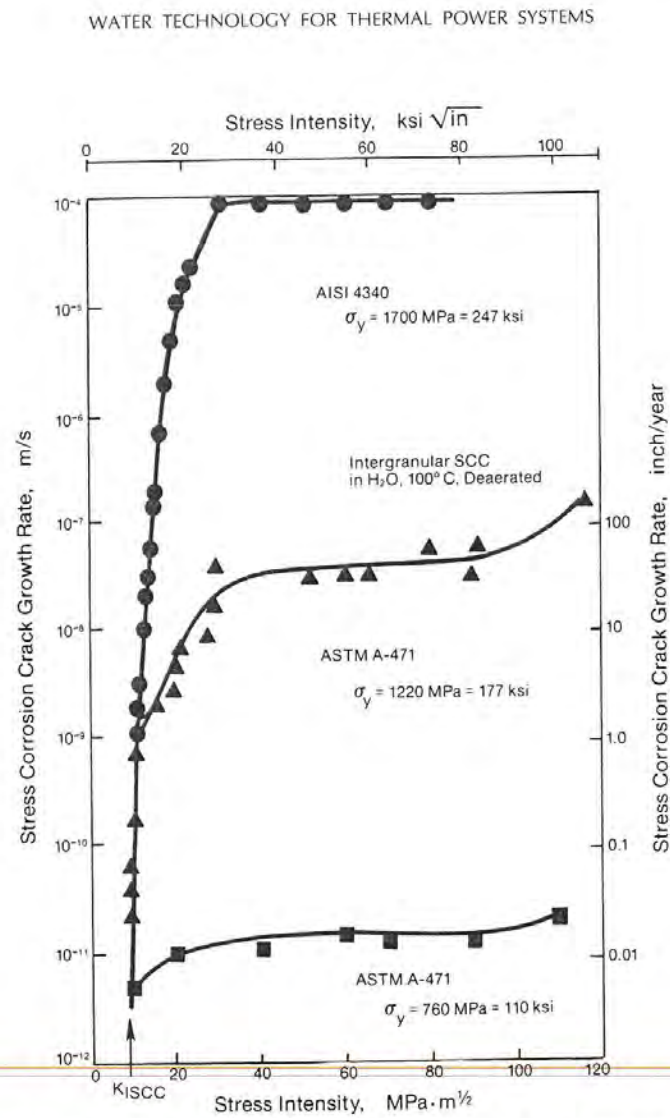


FIG. 9-107 EFFECT OF YIELD STRENGTH AND STRESS INTENSITY ON THE CRACK GROWTH RATE OF QUENCHED AND TEMPERED LOW-ALLOY STEELS EXPOSED TO HOT WATER. NOTE THAT $K_{I,SCC}$ IS NOT INFLUENCED BY THE STRENGTH LEVEL, IN CONTRAST TO THE CRACK GROWTH RATE AT INTERMEDIATE STRESS INTENSITY LEVELS [14].

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from 760 MPa to 1220 MPa by decreasing the tempering temperature. On the other hand, K_{ISCC} is practically not affected by the variation in the yield strength.

As summarized in Fig. 9-108, for a variety of steam-turbine rotor steels, the crack growth rate in Region II (K , from 30 to 60 $\text{Mpa}\cdot\text{m}^{1/2}$) is increased one million times by increasing the yield strength from 640 MPa to 1440 MPa. It is clear that the yield strength is a prime variable to be considered in developing strategies to control the SCC of turbine rotor steels. It should be noted that in both Figs. 9-108 and 9-107 the environment is very mild, deaerated water at 100°C. Fig. 9-108 also includes data for aerated 28% NaOH solution at 110°C, which indicate that the composition of the environment also has an important effect on the crack propagation rate. An increase of about 15 times is observed in the presence of a concentrated caustic solution compared with the crack growth rates measured in water. Speidel [67] has also discussed the relation of these laboratory data to apparent crack growth rates, as calculated from failure analysis of steam-turbine discs.

Similar conclusions regarding the influence of yield strength on crack growth rate have been reached by other investigators [54, 62], but there are differences in emphasis on the significance of the yield strength regarding service failures. The problem revolves around the initiation time for crack propagation. As pointed out by Roberts and Greenfield [62], on the basis of laboratory work, cracks are initiated in plain specimens exposed to steam at relatively high stress levels (110% of the yield strength), after prolonged periods (varying from 5000 up to almost 24,000 hr). They indicate that initiation times are highly variable, and that under service conditions they could be significantly affected by impurities present in the steam, flow conditions, etc. They claim, however, that initiation times are reduced by increasing the yield strength of the steel. Even more important, initiation times can be significantly increased by reducing the applied tensile stress or stress concentration effects, as is done by many turbine manufacturers through modifications in the design of the rotor [68]. The process of crack initiation seems to be related to the condition of the oxide film, as affected by temperature, flow rate, potential, and other properties of the environment, but it is obviously the more difficult parameter to account for when analyzing service failures and even laboratory tests.

The influence of metallurgical factors has been discussed at length in Vol. 3 of [54], mainly on the basis of investigations done on plain carbon steels in caustic solutions. Within this context, it is convenient to discuss the influence of molybdenum as an alloying element. Results of investigations conducted in the U.K., in conjunction with the conclusions derived from a survey of operating turbines [52], led to the conclusion that molybdenum is detrimental to SCC resistance, since 3Ni steels (no molybdenum) were found to be non-susceptible to cracking, both in laboratory experiments and service applications. However, with few exceptions, most of the experimental work has been conducted in concentrated NaOH solutions, an environment in which molybdenum is obviously extremely detrimental, as discussed in Section 9-5.5.1. On the other hand, the results of Speidel for deaerated water at 100°C [66], indicate that the absence of molybdenum in a variety of low-alloy steels does not affect the crack growth rate within Region II of the crack velocity vs. stress intensity curve. However, this observation does not imply that the addition of molybdenum to the steels may not be extremely important in the initiation stage. It is interesting to note that no crack initiation was detected in 3Ni steel at the same stress levels and exposure times at which molybdenum-containing steels showed the

THE
ALLOY
CONTAINED
RATE

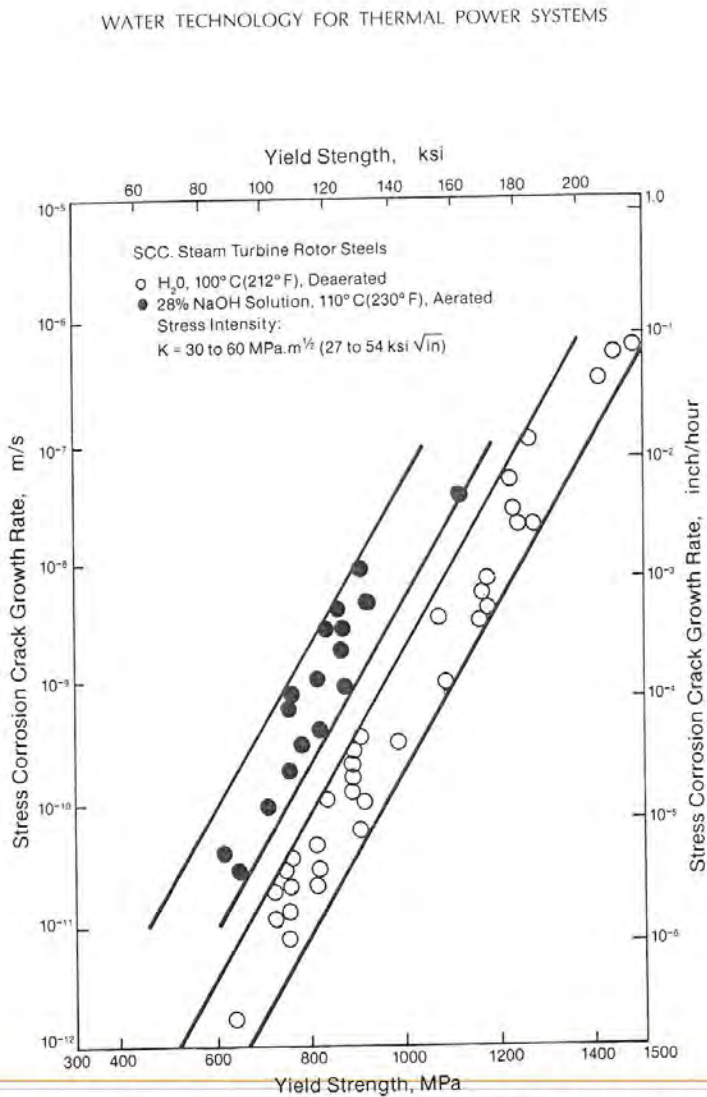


FIG. 9-108 EFFECT OF YIELD STRENGTH AND ENVIRONMENT COMPOSITION ON THE CRACK GROWTH RATE OF STEAM TURBINE ROTOR STEELS. NOTE THAT BOTH YIELD STRENGTH AND ENVIRONMENT ARE FIRST ORDER INFLUENTIAL PARAMETERS [67].

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Stress Corrosion Crack Growth Rate, inch/hour

1.0
10⁻¹
10⁻²
10⁻³
10⁻⁴
0.0

COMPOSITE
STEELS.
ORDER

initiation of cracks [62]. It has been demonstrated [69] that molybdic acid can be leached from 3CrMo steels in boiling water, and it is possible that this is the detrimental species although the mechanism by which it would act is not at all clear.

It is apparent from the extensive research conducted over the last decade that the presence of specific chemical species in aqueous solutions is not a requirement for the development of cracks in typical steam-turbine rotor steels. Pure condensed steam is enough. However, as already indicated, impurities can accelerate the process of crack initiation and can significantly increase the crack growth rate. It is beyond the scope of this section to discuss different processes of transport and concentration of impurities in steam turbines. The implications of these processes in relation to SCC of turbine materials, as influenced by the particular design of the steam-water cycle in BWR, PWR, and fossil-powered plants, and the operating conditions, has been reviewed in [54] (Vol. 4), [70] and [71]. See also Chapters 7, 18 and 16.

Species that seem to affect the SCC susceptibility of steam-turbine steels are OH⁻, Cl⁻, CO₃²⁻ and S²⁻. The effect of NaOH has been briefly discussed above. Although the effect of chloride has not been extensively investigated, it was found in two consecutive studies [61, 65] that 3.5% NaCl solution at temperatures ranging from 121°C to 157°C promotes transgranular cracking of A470 and A471 steels when the potential is above a critical value. In NaOH solutions which contain various concentrations of NaCl, a mixed mode of propagation, consisting of intergranular and transgranular cracks, was observed [61, 65]. Recently, the crack growth rate of NiCrMoV steels has been measured in a variety of simulated steam environments at 157°C [72]. It was found that cracking was intergranular in all solutions investigated, with the exception of aerated pure water, in which transgranular propagation was observed. Intergranular stress corrosion cracking of 3CrMo and NiCrMoV has also been observed at potentials close to the active-passive transition in sodium or ammonium acetate and sodium propionate solutions at 90°C [55, 73, 74]. Another factor that influences the crack growth rate is temperature. Apparent crack growth rates (calculated from field failure analyses done for U.K. plants) plotted as a function of reciprocal temperature show an Arrhenius dependence [52]. An apparent activation energy of 46 kJ (11kcal)/mole is calculated from such plots, whereas a similar analysis using data from U.S. plants gave 25 kJ (6 kcal)/mole [53, 54].

Many authors have studied the effect of potential on SCC susceptibility of low-alloy turbine steels in concentrated NaOH solutions [55, 56, 58, 59, 63, 64]. As for other alloy/environment systems it was found that the susceptibility is a strong function of potential. Typical results are shown in Fig. 9-109, in which the behavior of a 3Cr-0.5Mo steel is compared with that of plain carbon steels in deaerated 8m NaOH solution at 100°C, after 24 hr exposure at stresses corresponding to the yield strength. It is seen in this figure that the low-alloy steel shows two cracking ranges. One corresponds to the range of potentials within which mild steels are also susceptible to intergranular cracking, whereas the second appears at higher anodic potentials. Similar results were observed in temperature-embrittled specimens, and in specimens that were subsequently deembrittled, but the latter specimens showed reduced susceptibility and slower crack growth rates in the potential range of -500 to -300 mV_{H₂/H₂O} compared with the embrittled material. The authors also report that the open-circuit potential of the low alloy steel invariably attained stationary values in the more anodic cracking zone. Other low-alloy steels (3.5NiCr-MoV, 4.5NiCrMo, 3NiCrMoV), were also found to be susceptible to cracking in this zone.

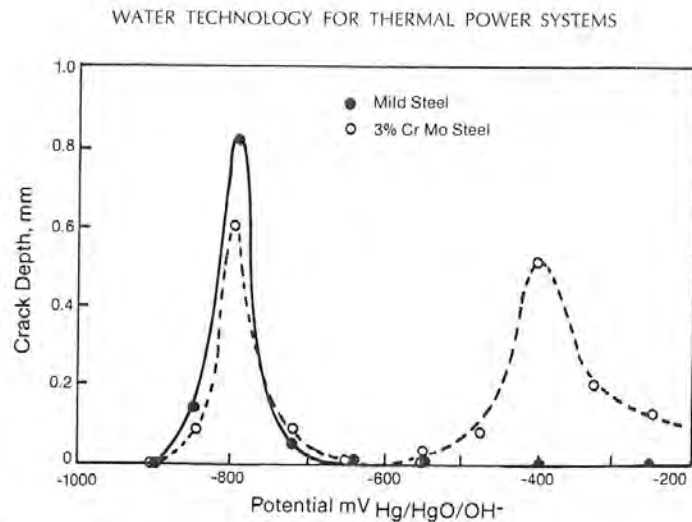


FIG. 9-109 CRACK DEPTH VERSUS POTENTIAL FOR MILD STEEL AND 3% CrMo STEEL EXPOSED FOR 24 hr TO 8 M NaOH AT 100°C, UNDER AN APPLIED STRESS EQUAL TO THE YIELD STRENGTH [56]

As shown in Fig. 9-109, plain carbon steels were immune to SCC in the more anodic cracking region. In the low-alloy steel the crack path was also intergranular, but instead of following the ferritic grain boundaries, cracks run along the prior austenite grain boundaries. These results have been essentially confirmed in other studies carried out using different low alloy steels, even though the cracking ranges are not as precisely delineated [60, 61, 63, 64] as those shown in Fig. 9-109.

An important aspect that should be emphasized, however, is that low-alloy steels are also subject to intergranular SCC at cathodic potentials [75]. In this case, the dominant phenomenon is obviously hydrogen embrittlement. Since there are no measurements of corrosion potentials of low-alloy steels under operating conditions in turbine environments, it is not possible to establish if the mechanism of SCC in service is film rupture coupled with anodic dissolution or hydrogen-induced cracking. While in concentrated caustic solutions, anodic dissolution seems to prevail, suggesting that turbine steels in these environments should be located at the left of the spectrum depicted in Table 9-18, the observation that cracking occurs also in high-purity, wet steam led to a different conclusion. It is well known [76] that high strength steels, such as AISI 4340 are susceptible to HE in high-purity water or steam. Therefore, it is expected that, for turbine rotor alloys, a HE mechanism is operative suggesting that the appropriate location for the turbine rotor steel/steam system is at the far right of the spectrum shown in Table 9-18. However, previous findings [54] indicate that the presence of small concentrations of dissolved oxygen in the water-steam environment (> 15 ppb) induced cracking of turbine discs in several plants. The most severe case of cracking was found in a BWR, in which the oxygen

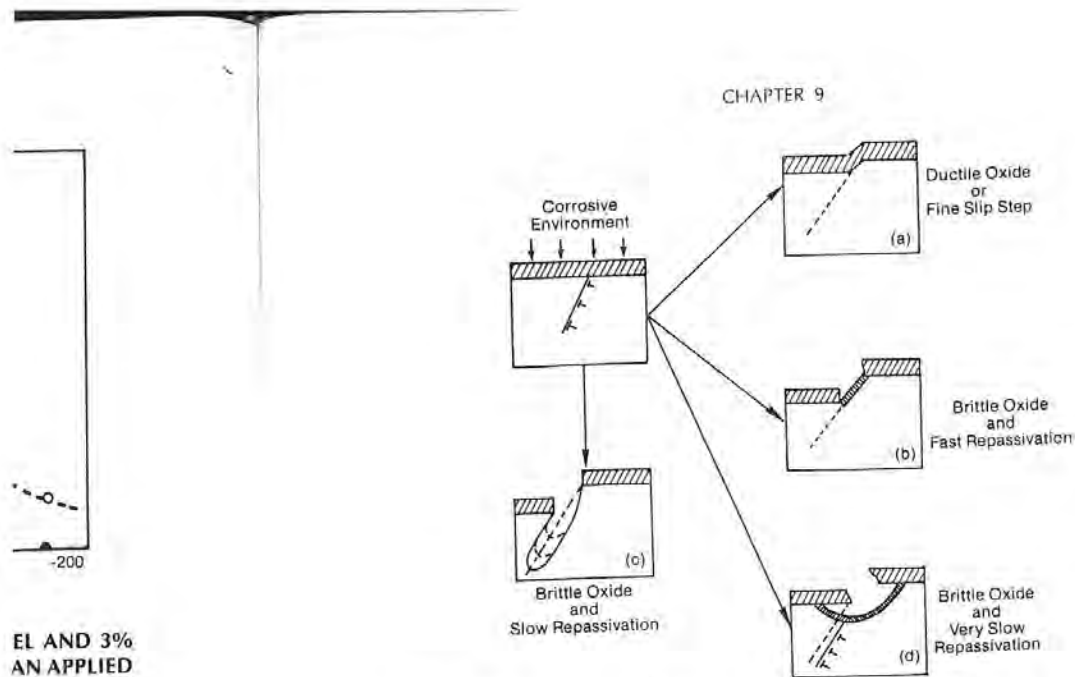


FIG. 9-110 SCHEMATICS DIAGRAMS OF FILM RUPTURE AND REPASSIVATION PROCESSES AS RELATED TO STRESS CORROSION AND CRACKING

more anodic
granular, but
prior austenite
other studies
angles are not
3.

low-alloy steels
this case, the
there are no
ing conditions
ism of SCC in
uced cracking.
prevail, sug-
the left of the
rs also in high-
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ater or steam.
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evious findings
oxygen in the
fiscs in several
ich the oxygen

content in the steam was between 20 and 30 ppm. It is known that the presence of oxygen inhibits HE of high-strength steels [76], which makes less plausible the suggestion that rotor steels failed by this mechanism in operating steam turbines. It should be emphasized that an understanding of the prevailing mechanism has practical implications in terms of the approach that has to be adopted to mitigate cracking by controlling the environment. In the case of turbine steam environments, there is a host of potentially detrimental impurities that could be reduced to very low levels by appropriate monitoring and control of the feedwater chemistry. In particular, CO₂ seems to be an aggressive contaminant [77, 78]; its main effect is the acceleration of the crack growth rate [72]. In addition, it is well known that solutions containing HCO₃⁻ / CO₃²⁻ are potent cracking agents for mild steels.

9-5.5.3 Stress Corrosion Cracking of Austenitic Stainless Steels. Austenitic stainless steels are extensively used in nuclear reactors. They are used in the cast and welded forms, as well as in the wrought condition. Typical stainless steel components include pressure vessel cladding, vessel internals, pumps, valves, heat exchanger tubes, etc. In particular, they are commonly employed for the piping systems of PWRs and BWRs. The alloy chosen for this application world-wide is AISI 304 SS, but in German PWRs the stabilized version AISI 347 SS has been selected.

The performance of AISI 304 SS, has been extremely good in terms of general corrosion resistance, but numerous cracking incidents have been reported. Initially, most of the cases involved the presence of chloride ions, leading to transgranular

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 Public Document – Not Public Data Has Been Excised
 Public Document

Supplement

Xcel Energy Information Request No. S51
Docket No.: E002/GR-12-961, E002/GR-13-868; E999/AA-13-599;
E999/AA-14-579; E999/AA-16-523; E999/AA-17-492;
E999/AA-18-373
Response To: Department of Commerce
Requestor: Michael Zajicek
Date Received: July 7, 2023

Question:

Topic: Sherco 3 operation and maintenance
Reference(s): Daniels Direct Testimony

In his direct testimony at page 13, Mr. Daniels states that “While it has been shown time and again that elevated concentrations of sodium hydroxide in steam have contributed to turbine rotor failures by SCC, the literature also states that, in the presence of sufficiently high stresses, SCC can occur in ‘pure water’” With respect to this testimony:

- a. Please produce all documents on which Mr. Daniels relies to support the statement that “it has been shown time and again that elevated concentrations of sodium hydroxide in steam have contributed to turbine rotor failures by SCC.”
- b. Please produce all documents on which Mr. Daniels relies to support the statement that “in the presence of high stresses, SCC can occur in ‘pure water.’”
- c. Please explain the mechanism that would cause corrosion of the finger-pinned dovetail joints in pure water and result in SCC and the amount of time in a pure water environment that it would take to result in the type of cracking found in the Sherco 3 L-1 LP finer (sic)-pinned joints.
- d. Is it Mr. Daniels opinion that corrosion in the L-1 finger-pinned joints is not accelerated by the presence of sodium hydroxide in steam? If so, please produce all documents that support that opinion.

Response:

- a. Xcel Energy objects to this information request as overly broad. However, see ASME Handbook on Water Technologies for Thermal Power Systems, Paul Cohen, Editor-in-Chief, Chapter 9 Corrosion of Steam Cycle Materials, by Digby D. Macdonald and Gustavo A. Cragolino, Section 9-5.5 Stress Corrosion Cracking. More particularly section 9-5.5.2 Stress Corrosion Cracking of Low-Alloy Steels, pg. 850-856. A copy of Chapter 9 is produced contemporaneous with this request, as Attachment A to this response.
- b. See response to subpart a. (The ability of SCC to form in pure water, pure steam, or pure condensate is mentioned in this section of the referenced handbook.) However, the statement taken from Mr. Daniels' testimony cited at the beginning of this document is misrepresented. The sentence quoted continues ... "where the concentration of sodium hydroxide is so small that it could not be measured." Thus, the theoretical concept of "pure water or pure steam" is here defined as water or steam in which the sodium hydroxide concentration is too low to be analytically determined. Intergranular stress corrosion cracking in low alloy steel has always been associated with the presence of some concentration of caustic. This is well documented in the above referenced material. The question here is whether this particular GE turbine design, (specifically the finger dovetails) can operate with prudent chemistry control without developing SCC. Furthermore, Mr. Daniels' statement is consistent with GEK-25407c, wherein GE states that the state of knowledge regarding SCC in turbine rotor material does not allow GE to establish a safe level caustic in the steam for their turbines.
- c. Experts, such as Mr. Macdonald, cited above, agree that the mechanism for stress corrosion cracking is not fully understood. However, Mr. Daniels has no reason to expect that the mechanism in this failure would be any different than for any other caustic SCC corrosion. Namely, it is a combination of a susceptible material, environmental conditions, stresses (design and operating stresses), and time.
- d. No, the presence of caustic in the steam would find its way into the high-stress areas of the finger dovetails, and would accelerate caustic stress corrosion cracking in this area.

Supplement:

- b. Xcel Energy further cites to Deposition Exhibit 688, at page 22, in which GE states as follows: "While extensive work done investigating SCC has shown that it is very often associated with 'corrosive' contamination by chemicals such as sulfides, hydroxides and chlorides, it can also occur in pure water."

Witness: David Daniels
Preparer: David Daniels
Title: Senior Principal Scientist
Department: Acuren Inspection, Inc.
Telephone: 512-407-8598
Date: July 19, 2023
Supplemented: July 28, 2023

- Not-Public Document – Not For Public Disclosure**
- Public Document – Not-Public Data Has Been Excised**
- Public Document**

Xcel Energy Information Request No. S97
 Docket No.: E002/GR-12-961, E002/GR-13-868; E999/AA-13-599;
 E999/AA-14-579; E999/AA-16-523; E999/AA-17-492;
 E999/AA-18-373
 Response To: Department of Commerce
 Requestor: Michael Zajicek
 Date Received: August 21, 2023

Question:

Topic: Cycle Chemistry Performance
 Reference(s): Multiple, see below

This request incorporates by reference the instructions provided in Department Information Request No. S95.

Request: Concerning risk management associated with mechanical carryover from the steam drum to the steam path:

- a. Provide evidence of mechanical carryover risk management program and mechanical carryover performance at Sherco 3 prior to November 2011.
- b. Provide all available chloride and sulfate analysis results for drum water and steam samples at Sherco 3 prior to November 2011.
- c. Provide drum level control and drum pressure performance data for Sherco 3 prior to November 2011.

Amended Request: In response to Xcel’s request for clarification of Request Nos. 97a and 97c, the Department amends its request as follows:

- a. Provide evidence that, prior to November 2011, Xcel had in place a process, system, mechanism, or method for managing the mechanical carryover of liquid water from the Sherco 3 drum boiler into the steam path to the turbines. Provide all data evidencing or relating to any measurement or monitoring of mechanical carryover of liquid water from the Sherco 3 drum boiler along with the corresponding MW output of Sherco 3 for each pressure measurement.

- b. Provide all available chloride and sulfate analysis results for drum water and steam samples at Sherco 3 prior to November 2011.
- c. Provide all data produced as a result of Xcel's monitoring and/or measurement, prior to November 2011, of the liquid water level in the Sherco 3 drum boiler along with the corresponding MW output of Sherco 3 for each level measurement. Provide all data evidencing or relating to any measurement or monitoring, prior to November 2011, of the internal steam drum pressure of the Sherco 3 boiler along with the corresponding MW output of Sherco 3 for each pressure measurement.

Response:

- a. The design of the steam drum by the boiler manufacturer establishes the mechanical carryover of the drum. Xcel Energy's process for managing mechanical carryover from the Sherco 3 drum boiler into the steam path relied on routine physical inspection of the drum internals, as described below.

At Sherco, since 1987, the steam drum has been opened for inspection and repaired every three years. The primary purpose is to assess the inner liner and steam separation equipment. The drum liner is inspected for any signs of wear or damage along the total length of the drum. Any damage to the liner is repaired in place. Hardware is checked for tightness and any looseness is corrected. There are inspection ports built into the liner to access the shell. These ports are opened to inspect the shell and to remove any settled oxide at the bottom of the drum. Initial steam separation occurs at the cyclone separators. These are assessed in place to determine if a portion or all of the cyclone separators need to be removed for further inspection and repair. The inlet ducts are the entrance point of the steam/water mix into the cyclone separator. These are inspected prior to and after the removal of the cyclone separators. Repairs are made to these in the drum. Further steam separation occurs above the cyclone separators at the secondary steam separators. The secondary steam separators are inspected and any damaged separators are replaced. The purpose of the drum inspection and subsequent repairs is to restore design functionality to the drum every overhaul (every three years).

Because Xcel Energy's maintenance process relied on physical inspection, there are no records of measuring or monitoring the amount of mechanical carryover from the Sherco 3 drum boiler. From 2000 to 2011, routine inspections performed on the Unit 3 turbine showed no indication of problems with mechanical carryover that would have triggered additional testing.

- b. The laboratory at the plant did not have the ability to analyze for ppb levels of chloride and sulfate, nor was such testing typically performed on a routine basis. For fossil-fired steam cycles, cation conductivity is the continuous measurement that determines the risk of ppb levels of chloride and sulfate in the steam. Indeed, from at least 2000 to November 2011, routine chloride and sulfate analysis was not required by EPRI or GE; rather, it was expected that plants would only use cation conductivity to infer these parameters. Nevertheless, there were times when Sherco sent samples from various points in the steam cycle on all three units to the Chestnut Street Laboratory for analysis of chloride and sulfate by ion chromatography. Results from this testing can be found in Attachment 1 to this response and in previously produced documents marked as XCEL_Sherco_09_0000697, XCEL_Sherco_09_0000749 - XCEL_Sherco_09_0000752, XCEL_Sherco_05_0101523, XCEL_Sherco_09_0008613. The capability to analyze for low ppb concentrations of chloride and sulfate by ion chromatography, including during the period between 2000 and 2011, was exceptional for the industry and points to the emphasis that Sherco and NSP placed on steam cycle chemistry. Very few fossil-fired power plants of similar size had the capacity to perform these analyses, even by a corporate laboratory.
- c. The steam drum level and MW generation of Unit 3 were stored in the PI system and is provided in Attachment 2 to this response. Drum pressure and corresponding MW generation was included in the PI data previously produced at XCEL_Sherco_09_0001231.

To the extent additional documents or information responsive to this information request are identified, Xcel Energy will supplement this response.

Witness:	David Daniels	
Preparer:	Adam Henderson	Darin Schottler
Title:	Manager, Operations	Director, Regional Capital Projects
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Telephone:	763-261-3394	612-630-4403
Date:	August 30, 2023	

**Northern States Power Company, doing business as Xcel Energy
Information Request**

Docket No.: E002/GR-12-961, E002/GR-13-868; E999/AA-13-599;
E999/AA-14-579; E999/AA-16-523; E999/AA-17-492;
E999/AA-18-373; OAH 65-2500-38476
Sherco 3

Requestor: Xcel Energy – Lauren Steinhäuser, Assistant General Counsel
Requestor email: lauren.steinhäuser@xcelenergy.com
Requested from: Minnesota Department of Commerce
Date of Request: October 6, 2023 Information Request No. 34
Response Due: October 18, 2023

Question:

Reference: Rebuttal Testimony of Stephen E. Klotz, p. 4, lines 2-3

- a. Specify and fully describe the “cycle chemistry specifications and related programs” developed by Mr. Klotz for Consumers Energy, including the year(s) in which each such specification and related program was developed and implemented and identification of any plant(s) to which it applied.
- b. For each such “cycle chemistry specification[] and related program[]” identified in subpart (a) provide all documents describing that specification and related program.
- c. For each “cycle chemistry specification[] and related program[]” identified in subpart (a), indicate whether the specification and related program developed by Mr. Klotz replaced an already existing specification and related program. If so, please describe the specification and related program it replaced and indicate how long that prior specification and related program had been in place.
- e. Specify and fully describe any differences in each “cycle chemistry specification[] and related program[]” identified in subpart (a), including the basis for such differences.
- d. Confirm that each “cycle chemistry specification[] and related program[]” identified in subpart (a) included all EPRI cycle chemistry guidelines (as that term is used on page 9, line 1 of Mr. Klotz’s Direct Testimony), including but not limited to all recommended contaminant

limits, sampling points, shutdown timing limits, testing processes and intervals, monitoring processes, and steam purity.

Response: The Department objects to the Request on the ground that it is untimely. Under the ALJ's Second Prehearing Order, all discovery requests were to be served so that answers would be received by October 6. Contrary to that requirement, Xcel served this request on October 6.

Notwithstanding its objection, the Department responds as follows: Mr. Klotz retired in 2021 and no longer has access to Consumers Energy (CE) cycle chemistry related documentation. As such, it's not possible to provide all the requested information in detail.

- a. Mr. Klotz developed cycle chemistry specifications for each of CE's 14 coal-fired generating units and both of CE's combined cycle units that were operational during his 12 plus years with the company. Specifications included startup, normal operation and shutdown limits for cycle chemistry parameters at sample locations around the water and steam cycle.

Mr. Klotz also developed cycle chemistry related programs for CE's fleet of generating units. Examples include but are not limited to cycle chemistry alarm response procedures, mechanical carryover testing protocols, boiler tube sampling protocols, chemical cleaning protocols and procedures, online pH analyzer calibration procedures, and fleet cycle chemistry performance tracking protocols.

- b. Mr. Klotz retired in 2021 and no longer has access to Consumers Energy (CE) cycle chemistry related documentation.
- c. All the cycle chemistry specifications developed by Mr. Klotz replaced existing specifications. When EPRI issued new cycle chemistry guidelines, the specifications for all applicable units were revised to align with the new guidelines. Generally, these were minor revisions to the specifications. In some cases, specification revisions were extensive. An example of an extensive revision included eliminating the injection of reducing agent from a newly purchased combined cycle plant and aligning the existing specification with EPRI's guidelines for neutralizing amine treatment. Other examples of specification changes include converting from AVT-R to AVT-O feedwater chemistry and converting from AVT boiler treatment to a low-level phosphate boiler treatment.

Most of the cycle chemistry program development work conducted by Mr. Klotz involved replacing or revising existing programs. Examples of new program development include mechanical carryover testing protocols for combined cycle units, online pH analyzer calibration procedures, a reheater flushing procedure, and protocols for managing cycle chemistry compliance on units scheduled for near-term retirement.

- d. Cycle chemistry specification changes were made to align with new EPRI guidelines or to change feedwater or boiler chemistry treatment programs. Internal CE procedures, guidelines, and protocols were developed or revised to improve the overall performance of CE's cycle chemistry program.
- e. CE's cycle chemistry specifications did not align 100% with all EPRI recommendations. CE's approach was to align with EPRI recommendations whenever practical and to address gaps based on an evaluation of risk and cost. The basis for any exceptions to EPRI recommendations were well documented and were reviewed and approved by plant management before implementation.

Preparer:

Title:

Department:

Telephone:

Date: