

Caustic Stress Corrosion Cracking in Carbon Steels: Mechanisms, Operating Windows, and Control Strategies in Boilers and Refineries

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Abstract

Caustic stress corrosion cracking (caustic SCC, historically termed caustic embrittlement) remains a high-consequence degradation mode for carbon steel pressure components in boilers and refineries when three conditions align: a locally concentrated alkaline electrolyte, a sustained tensile stress field, and a susceptible microstructure or surface state created by fabrication, welding, aging, or service exposure. This review adopts a mechanism-first framework that links electrochemical and mass-transport conditions produced by caustic concentration (under deposits, in crevices, and in boiling or heat-flux hotspots) to crack-tip processes that govern initiation and propagation. Anodic dissolution bursts driven by protective film instability and localized chemistry are treated as the baseline pathway, while hydrogen uptake is addressed as a conditional contributor that becomes important under sufficiently cathodic potentials and appropriate transport conditions. Recent peer-reviewed studies (2021-2025) are integrated to strengthen the mechanism-first claim, and quantitative anchors for pH and temperature are provided to support an operating-window approach. Finally, a hierarchy of controls and specific non-destructive examination techniques (WFMT, PAUT, TOFD) is mapped to practical integrity management.

Keywords

Caustic Embrittlement, Alkaline SCC, Carbon Steel, Boilers, Refineries, Under-Deposit, Crevice Chemistry, PAUT, TOFD, WFMT

1. Introduction

Alkaline stress corrosion cracking in steels has been recognized for more than a century, yet it remains operationally relevant because modern plants still create

local conditions that drove classical caustic embrittlement: concentration of NaOH in restricted geometries, elevated temperature, and tensile stress. In boilers, local concentration develops under deposits and within hideout regions on the water-side, especially where heat flux promotes boiling and evaporative concentration. In refineries, alkaline environments arise from caustic service, neutralization chemistry, or localized enrichment in crevices and stagnant zones. The consequence space ranges from pinhole leaks to through-wall cracking in pressure boundaries.

A persistent challenge is that failures are governed by local chemistry, not captured by bulk sampling. Therefore, this review connects plant-level concentrating features to the micro-scale electrochemical environment at crack tips. The baseline mechanism is dissolution-driven cracking that emerges when protective films become unstable and localized anodic dissolution couples with plasticity at stressed interfaces. Hydrogen uptake can become significant when electrochemical potentials are sufficiently cathodic relative to the hydrogen equilibrium and when transport allows atomic hydrogen to enter the steel. **Figure 2** illustrates this coupling between local chemistry, potential, and crack processes.

2. Literature Review

Recent open-access reviews of refinery corrosion emphasize that mitigation is most effective when mechanistic understanding is tied to unit-specific environments [1]. Peer-reviewed alkaline SCC studies in hot NaOH solutions demonstrate strong concentration and temperature dependencies and show that electrochemical conditions can shift the balance between dissolution and hydrogen-related contributions [2] [3]. Recent crack inspection literature summarizes modern NDE capabilities and highlights how inspection reliability and sizing depend on technique selection and defect morphology [4] [5].

Although peer-reviewed work directly targeting carbon steel caustic SCC in boiler hideout conditions is comparatively scarce, boiler waterside failure analyses provide quantitative anchors for credible local pH excursions under deposits [6]. Microstructural studies isolating the influence of cementite morphology help explain aging-related changes in corrosion film evolution and near-surface transport [7]. Finally, crevice-driven cracking studies reinforce that geometry and mass transport restriction can be as important as bulk chemistry in setting local electrochemical conditions and crack kinetics [8].

3. Methodology (Review Protocol)

This is a narrative review with a mechanism-first selection protocol. Sources were prioritized if they were peer-reviewed journal articles or open-access reviews, provided experimental or quantitative information relevant to caustic SCC or alkaline electrochemistry, and contained sufficient methodological detail to support mechanistic inference. Industry practices and standards were used only as context where peer-reviewed evidence is limited. Studies from 2021-2025 were intentionally included to address recent progress.

4. Research Results and Mechanistic Synthesis

Figure 1 shows a mechanism-inspired, qualitative susceptibility map that links metal temperature and local NaOH enrichment to relative caustic SCC likelihood. It anchors the discussion by illustrating why localized concentration dominates risk even when bulk chemistry is controlled.

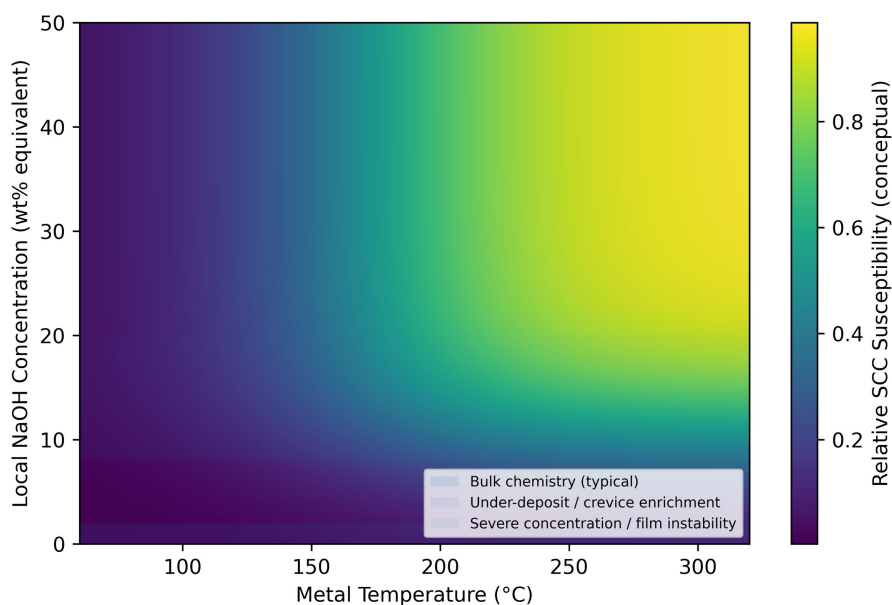


Figure 1. Conceptual risk map linking metal temperature and local NaOH enrichment to relative SCC susceptibility (copyright-safe, created for this work).

Local chemistry concentration is produced by under-deposit transport restriction, crevice confinement, hideout and return cycles, and boiling-film enrichment in boilers [6], and by poor mixing or stratification in refinery caustic handling [1]. These concentration mechanisms amplify hydroxide activity at the steel surface, altering passive film stability and setting the crack-tip electrolyte state.

Electrochemical potential determines when hydrogen evolution is thermodynamically possible and when hydrogen uptake may become kinetically significant. In alkaline solutions, the hydrogen equilibrium potential on the SHE scale shifts negatively with increasing pH and can be written as E_{H_2} (V vs SHE) = $0.000 - 0.059 \times \text{pH}$ at 25°C. Thus, at pH 14 the equilibrium is approximately -0.83 V vs SHE. Hydrogen evolution becomes practically significant when the local potential is at or more cathodic than the equilibrium by an overpotential governed by surface conditions, film coverage, and temperature. Hot-NaOH SCC experiments show that dissolution-film rupture can dominate in alkaline media, while hydrogen contributions increase under sufficiently cathodic potentials and appropriate transport [3]. Weldment studies further confirm that NaOH concentration materially changes SCC response [2].

Microstructure influences susceptibility through film evolution and near-surface transport. Cementite morphology is particularly relevant for aging equip-

ment. Lamellar cementite in pearlite forms continuous pathways that can influence galvanic coupling and preferential dissolution, whereas spheroidization during long-term high-temperature exposure changes interfacial area and alters local plasticity. Studies isolating cementite morphology effects show that cementite distribution can change corrosion layer formation and protection behavior [7].

Figure 2 shows the mechanism-first pathway linking local concentration, film instability, potential-dependent hydrogen effects, and crack initiation and propagation.

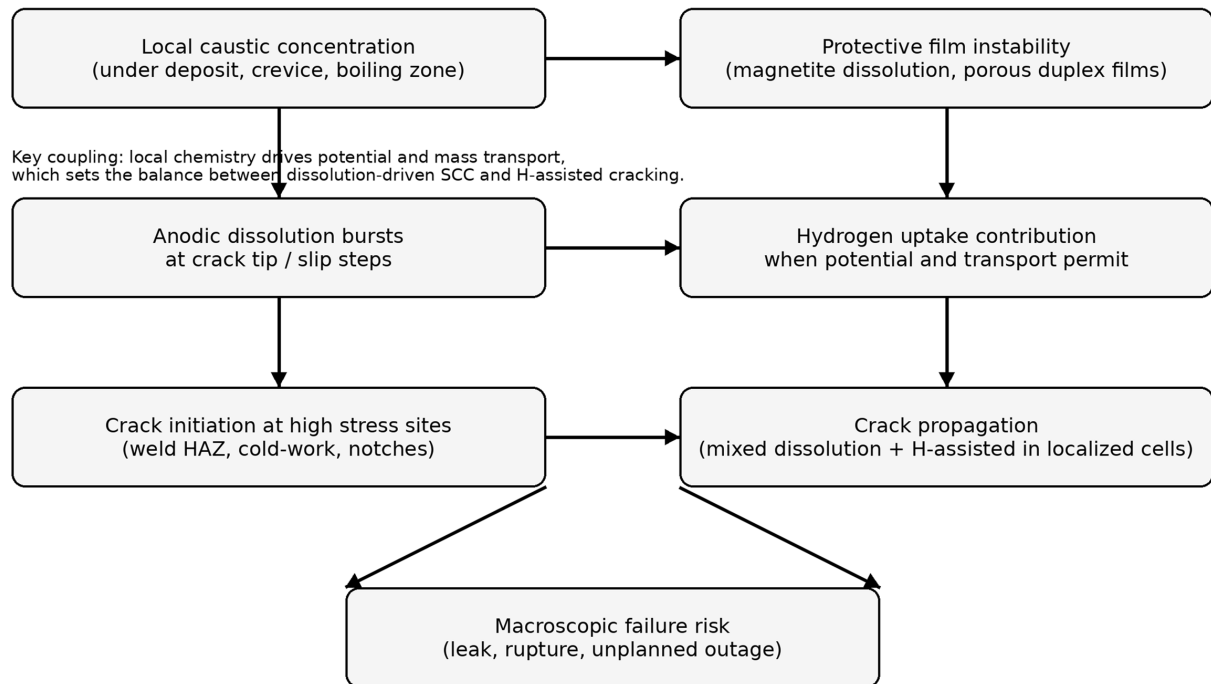


Figure 2. Mechanism-first pathway for caustic SCC in carbon steels (copyright-safe, created for this work).

Crevice is a unifying risk factor because they couple concentration, oxygen depletion, and potential shifts. Crevice-driven cracking studies reinforce that geometry and mass transport restriction can be as important as bulk chemistry in setting local electrochemical conditions and crack kinetics [8].

Table 1 summarizes quantitative anchors for bulk pH, credible localized excursions, temperature ranges, and hydrogen-equilibrium reference values that support the operating-window discussion.

5. Operating Windows: pH, Temperature, and Concentration

Operating windows should be expressed as bulk targets plus a conservative allowance for local enrichment. Boiler waterside analyses support bulk pH maintained around 9 - 11 with credible under-deposit effective pH exceeding 12.9 during concentration events [6]. Temperature amplifies electrochemical kinetics and concentration severity through boiling and thin-film evaporation. Consistent with alkaline SCC studies in hot NaOH [2] [3], risk ranking should pri-

oritize high heat-flux regions and hot spots above about 200°C, while components consistently below about 150°C are generally lower likelihood if local concentration is controlled.

Table 1. Quantitative anchors for operating windows and risk multipliers.

Context	Bulk condition (typical)	Localized condition (credible)	Primary implication
Boiler waterside	pH ~9 - 11 [6]	Effective pH > 12.9 under deposits [6]	Hideout enrichment can destabilize films and initiate SCC
Temperature	Moderate metal T < 150°C (lower likelihood)	Hot spots >200°C (higher likelihood)	Kinetics accelerate, films destabilize, crack growth increases
Caustic availability	Low free caustic in bulk water	Concentration within porous deposits and crevices	Local NaOH activity controls dissolution rates and potential
Potential relative to H ₂	H ₂ equilibrium about -0.53 to -0.65 V vs SHE at pH 9 - 11	H ₂ equilibrium near -0.77 V vs SHE or lower at pH > 13	Hydrogen uptake more likely if local potential is sufficiently cathodic

6. Control Strategies and Mitigation

Mitigation should follow a hierarchy of controls. The most robust actions eliminate concentrating geometries and reduce deposit formation. Chemistry control limits free caustic availability and reduces hideout-return amplification [6]. Stress management reduces crack-driving force. Materials strategies shift the operating window by stabilizing films under alkaline exposure. **Figure 3** summarizes this hierarchy in a form suitable for integrity program planning.

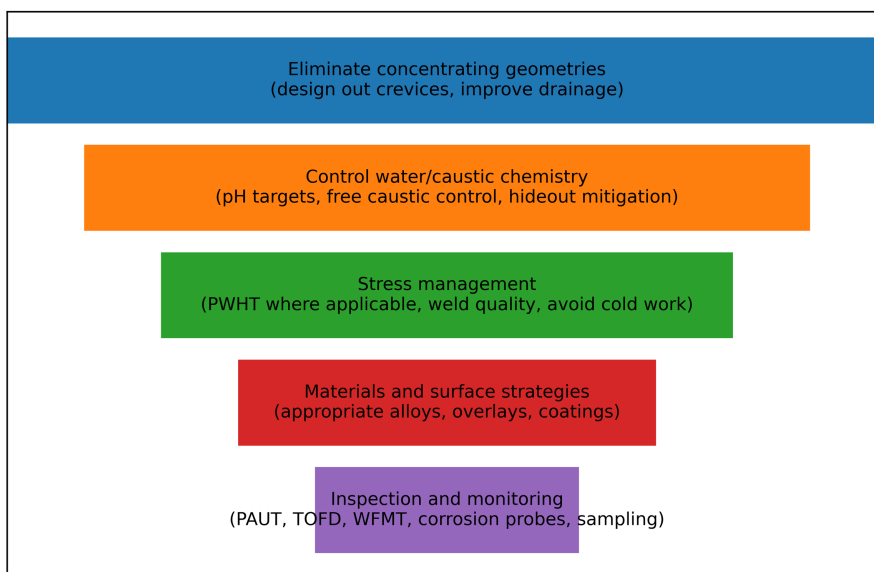


Figure 3. Hierarchy of controls for managing caustic SCC risk (copyright-safe, created for this work).

7. Inspection and Monitoring (NDE)

For surface-breaking cracking in ferromagnetic steels, wet fluorescent magnetic particle testing (WFMT) provides high sensitivity at weld toes and accessible attachments. For subsurface cracking, ultrasonic methods are required. Phased-array ultrasonic testing (PAUT) enables beam steering and focusing, improving coverage in complex geometries and supporting crack characterization. Time-of-flight diffraction (TOFD) is valuable for through-wall sizing because diffracted signals from crack tips can provide robust depth estimates. Modern reviews summarize capabilities and limitations and emphasize procedure qualification [4]. Inspection-plan design case studies demonstrate how TOFD sizing performance depends on component geometry and defect orientation [5].

8. Implications for Integrity Management

First, caustic SCC is primarily a local-environment problem, therefore integrity programs should manage deposits, crevices, drainage, and mixing limitations rather than relying on bulk sampling alone [1] [6]. Second, potential control matters because it determines whether hydrogen uptake is plausible, and hydrogen effects can accelerate cracking under sufficiently cathodic conditions [3]. Third, microstructure evolves with aging, and cementite morphology changes can alter film evolution and near-surface transport, motivating microstructure-informed risk ranking in older equipment [7].

9. Conclusions

- 1) Caustic SCC is governed by the alignment of local caustic concentration, tensile stress, and a susceptible steel state.
- 2) Bulk pH control around 9 - 11 does not preclude localized excursions above 12.9 under deposits, which can create aggressive crack-tip environments [6].
- 3) Dissolution-film rupture is a robust baseline in hot NaOH, while hydrogen uptake becomes significant only when potentials are sufficiently cathodic and transport allows [2] [3].
- 4) Cementite morphology (lamellar vs spheroidized) should be considered in aging equipment because it influences film evolution and near-surface transport [7].
- 5) Inspection should specify WFMT for surface cracks and PAUT or TOFD for volumetric characterization and sizing, supported by modern NDE literature [4] [5].

Graphical Abstract

The graphical abstract (**Figure GA**) summarizes the necessary-condition triad for caustic SCC and the operating-window concept.

Graphical Abstract: Caustic SCC in Carbon Steels (Boilers and Refineries)

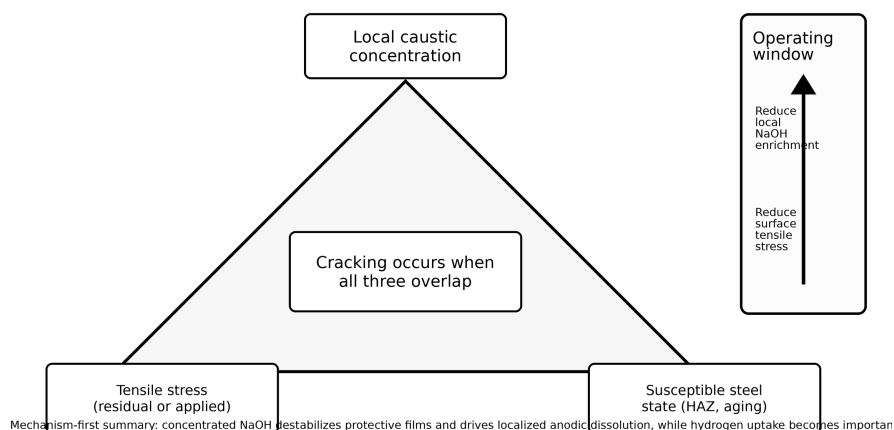


Figure GA. Author-generated graphical abstract (high-resolution) summarizing the caustic SCC triad and operating-window levers.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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