Unit 7: Corrosion in Nuclear Environments

ME 5203 – Nuclear Materials

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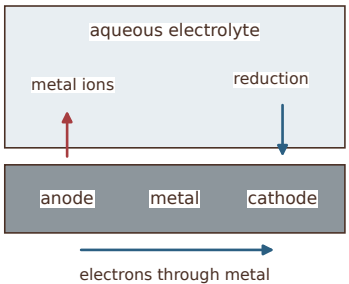
Corrosion links the material to its environment

- Reactions can remove load-bearing metal.
- Localized attack can penetrate deeply with little average mass loss.
- Stress and irradiation alter how damage develops.

Unit 7 question

Which reaction, transport path or local mechanical condition controls degradation?

Coupled reactions and two current paths



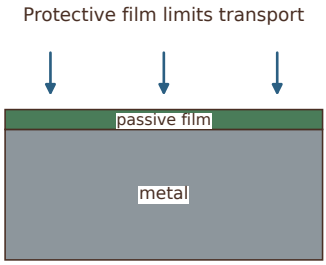
Unit 7: Outline

Part	Main question
Electrochemistry	What sets reaction direction and rate?
Reactor water	How do radiation and chemistry change the environment?
Cracking	How do stress, boundaries and irradiation interact?
Zirconium alloys	How do oxidation and hydrogen affect cladding?
Advanced coolants	Why does compatibility depend on the complete system?

Thermodynamic driving force and reaction rate differ

- A reaction may lower Gibbs free energy under the specified conditions.
- The rate also depends on interfaces, transport and activation barriers.
- A stable oxide may slow further reaction if it forms an effective barrier.

Environment and alloy composition must both be specified.

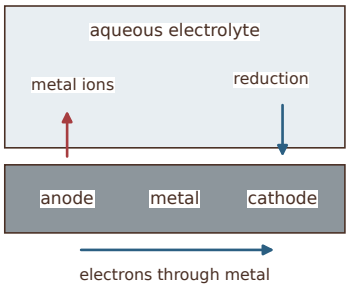


The corrosion cell has two current paths

- The anode supplies electrons through oxidation.
- The cathode consumes electrons through reduction.
- Electrons move through the metal.
- Ions carry current through the electrolyte.

Anodic and cathodic sites can lie on the same component.

Coupled reactions and two current paths

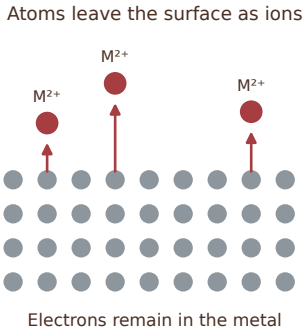


Metal dissolution is an anodic reaction

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e^{-}$$

- An iron atom leaves as a dissolved ion.
- Two electrons remain available in the metal.
- The surrounding solution and film determine the actual dissolved species.

The equation gives electron bookkeeping for this chosen reaction.



The environment supplies the cathodic reaction

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

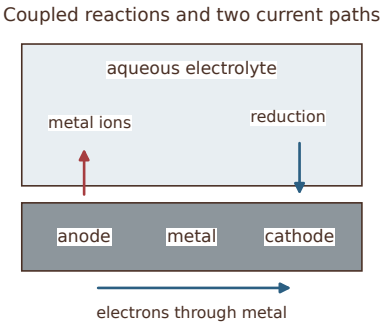
$$2H^+ + 2e^- \rightarrow H_2$$

- Oxygen reduction can support corrosion in aerated water.
- Hydrogen evolution can support corrosion in acidic conditions.
- Several cathodic reactions may operate together.

Electron bookkeeping couples the half-reactions

Question

How many Fe atoms dissolve as Fe^{2+} for each O_2 molecule reduced by the four-electron reaction?

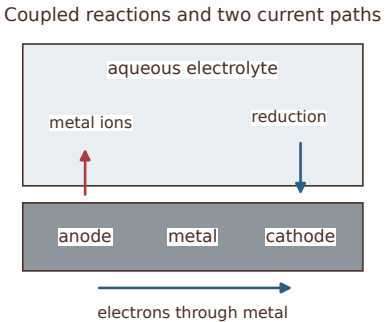


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$$2Fe \rightarrow 2Fe^{2+} + 4e^-$$



Electron bookkeeping couples the half-reactions

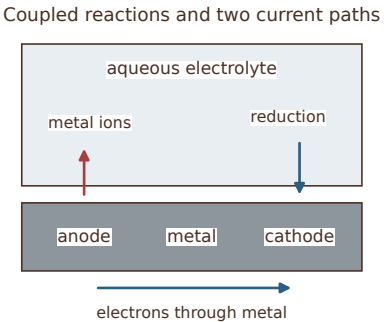
Question

How many Fe atoms dissolve as Fe^{2+} for each O_2 molecule reduced by the four-electron reaction?

$$2Fe \rightarrow 2Fe^{2+} + 4e^-$$

Answer

Two Fe atoms supply four electrons. Thus two anodic events balance one O_2 reduction event.



Equilibrium electrode potentials need a reference

- An electrode potential compares an electrode with a reference.
- Standard reduction potentials refer to specified standard states.
- The standard hydrogen electrode defines the conventional zero.
- Actual surface films and solution chemistry can change the observed behavior.

A useful distinction

A standard potential table and a galvanic series measured in service water answer different questions.

The Nernst equation adjusts an equilibrium potential

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

- E°: standard potential for the written reduction reaction.
- R: gas constant; T: absolute temperature.
- n: electrons transferred; F: Faraday constant.
- Q: reaction quotient written using activities.

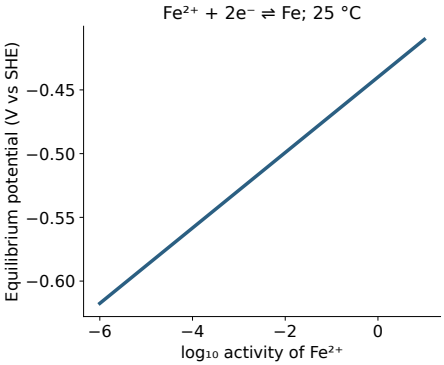
Iron ion activity shifts the Fe equilibrium potential

$$\mathrm{Fe}^{2+} + 2e^- \rightleftharpoons \mathrm{Fe}$$

$$E = E^\circ + \frac{RT}{2F} \ln a_{\mathrm{Fe}^{2+}}$$

- Pure solid Fe has unit activity.
- Lower Fe-ion activity shifts this equilibrium potential downward.

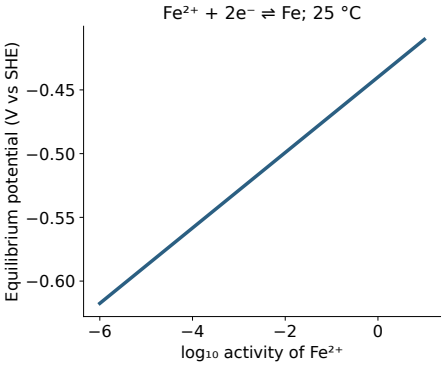
The plotted example assumes 25 °C and $E^\circ = -0.44$ V vs SHE.



A decade change in activity

Question

At 25 °C, Fe^{2+} activity decreases by a factor of ten. What is the potential shift?

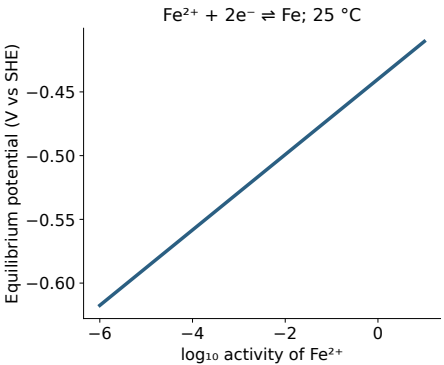


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$$\Delta E = \frac{0.05916}{2} \log_{10}\left(\frac{a_2}{a_1}\right)$$



A decade change in activity

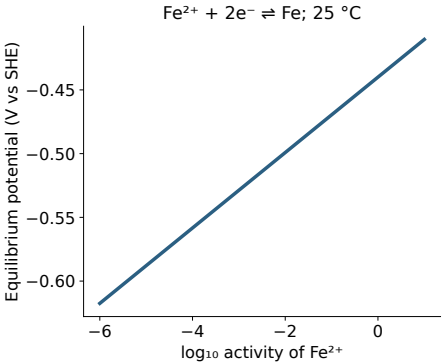
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$$\Delta E = \frac{0.05916}{2} \log_{10}\left(\frac{a_2}{a_1}\right)$$

Answer

$\Delta E = -0.05916/2 = -0.0296$ V, or about -29.6 mV.



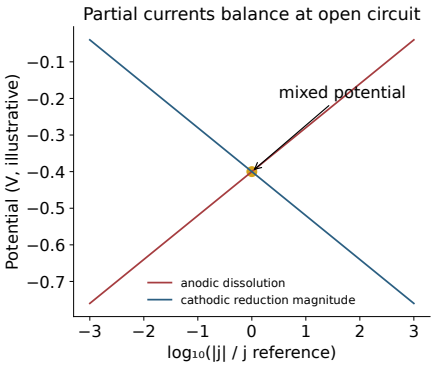
Open-circuit corrosion can have zero net current

$$\sum j_{\text{anodic}} + \sum j_{\text{cathodic}} = 0$$

- Anodic current is positive in this sign convention.
- Cathodic current is negative.
- The partial reaction rates can remain nonzero when their sum is zero.

Meaning

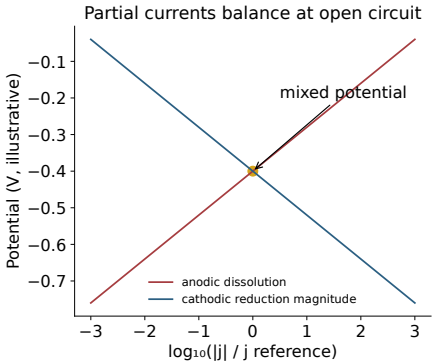
Zero external current does not imply zero metal dissolution.



Mixed potential comes from coupled reaction kinetics

- The intersection balances anodic and cathodic partial currents.
- Its potential is the corrosion potential.
- Its current magnitude estimates dissolution only with the appropriate reaction model.

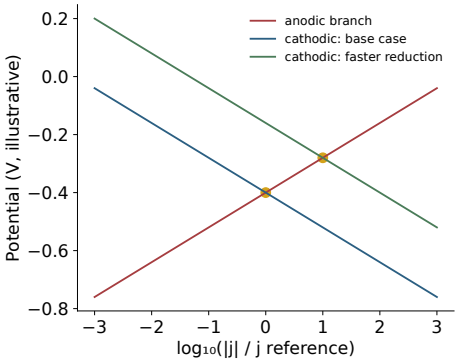
The horizontal axis uses the magnitude of each partial current.



Faster cathodic kinetics can increase metal loss

- The blue and green curves represent two cathodic conditions.
- With the same active anodic branch, faster reduction shifts the intersection.
- Both corrosion potential and current change in this example.

A passive anodic response can produce a different result.

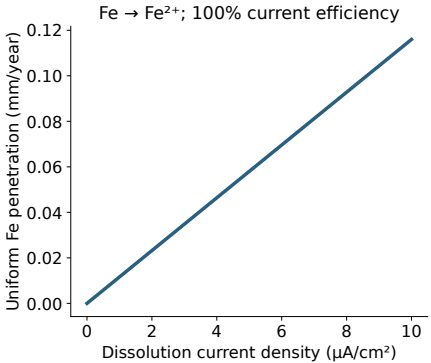


Faraday charge balance converts current into metal loss

$$m = \frac{MIt}{nF}$$

- m: dissolved mass; M: molar mass.
- I: dissolution current; t: elapsed time.
- n: electrons per dissolved atom; $F = 96485$ C/mol.

Use the metal-dissolution current and state the current efficiency.

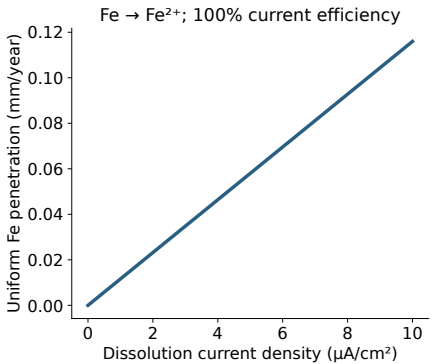


Uniform penetration follows from mass and density

$$\dot{x} = \frac{Mj}{nF\rho}$$

- $j = I/A$: current per exposed area.
- ρ: metal density; $\dot{x}$: uniform penetration rate.
- Consistent units are essential.
- A uniform-loss estimate cannot locate a deep pit.

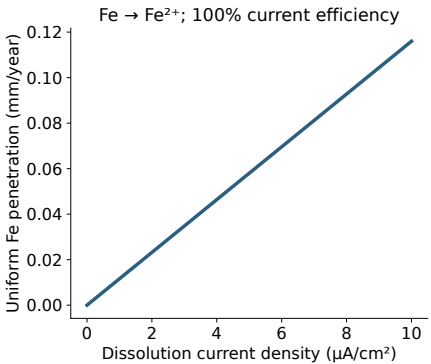
The figure assumes Fe^{2+} dissolution and 100% current efficiency.



Worked example: current to iron penetration

Question

Assume $j = 1\ \mu\text{A/cm}^2$, $M = 55.85\ \text{g/mol}$, $n = 2$ and $\rho = 7.87\ \text{g/cm}^3$. Find the uniform rate.

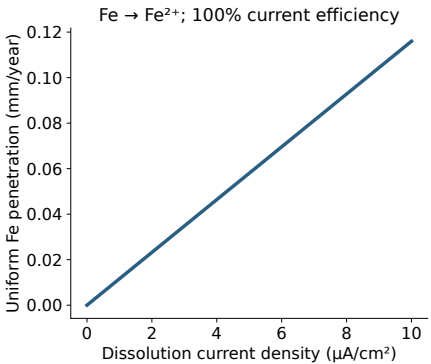


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$$\dot{x} = \frac{55.85(10^{-6})}{2(96485)(7.87)}\ \text{cm/s}$$



Worked example: current to iron penetration

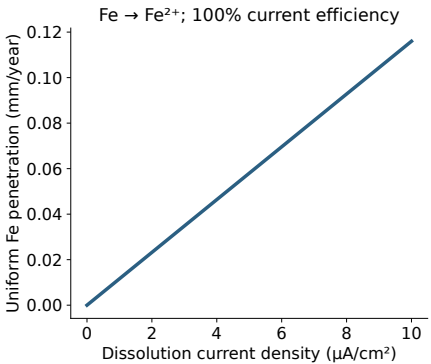
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$$\dot{x} = \frac{55.85(10^{-6})}{2(96485)(7.87)}\ \text{cm/s}$$

Answer

$\dot{x} \approx 0.0116$ mm/year. A tenfold current gives a tenfold rate under these assumptions.

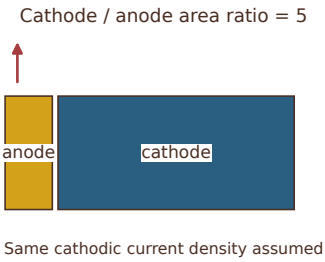


Galvanic coupling also depends on exposed area

$$j_a A_a = |j_c| A_c$$

- A_a, A_c: anodic and cathodic areas.
- j_a, j_c: average partial current densities.
- A small anode can carry a large local current density when coupled to a large cathode.

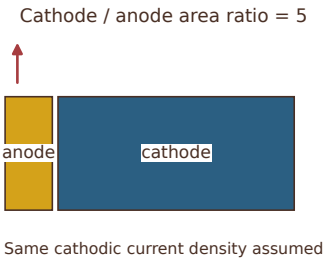
Polarization and transport still determine the actual currents.



A small anode coupled to a large cathode

Question

Assume $A_c/A_a = 5$ and $|j_c| = 2\ \mu\text{A/cm}^2$. What average anodic current density balances it?

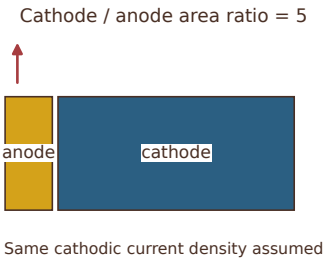


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$$j_a = |j_c|\frac{A_c}{A_a}$$



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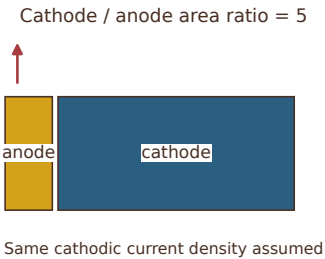
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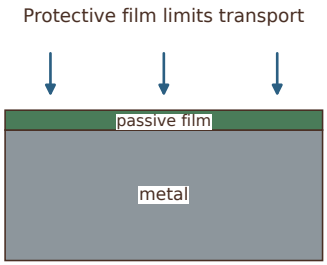
$j_a = 2(5) = 10\ \mu\text{A/cm}^2$. This uses a specified cathodic current, not a complete galvanic prediction.



Passivity requires a functioning surface barrier

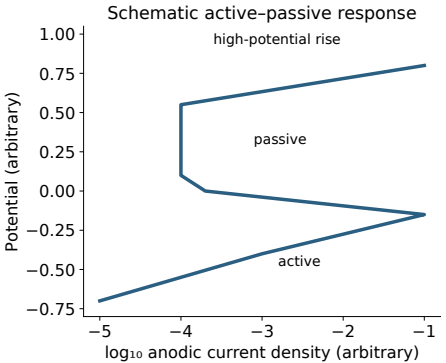
- A thin surface film can greatly reduce reaction and transport rates.
- Continuity, adhesion and local chemistry affect protection.
- Repassivation repairs damage when conditions permit.
- Real passive films can contain several oxides and hydroxides.

Bulk oxide stability alone does not establish film performance.



The active–passive curve shows a changing surface state

- Current initially rises on the active branch.
- Film formation can lower the anodic current.
- A passive range sustains a relatively low current.
- Higher potentials can introduce new dissolution or gas-evolution reactions.



Localized breakdown and transpassivity are different

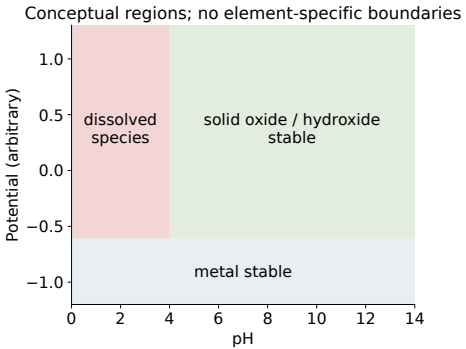
Process	Physical meaning
Localized breakdown	A pit or other local active site forms in a passive surface.
Transpassive behavior	Higher potential changes film chemistry and dissolution reactions.
Oxygen evolution	Gas production can contribute to measured current.

A high current by itself does not identify which process occurred.

Pourbaix maps show stable chemical states

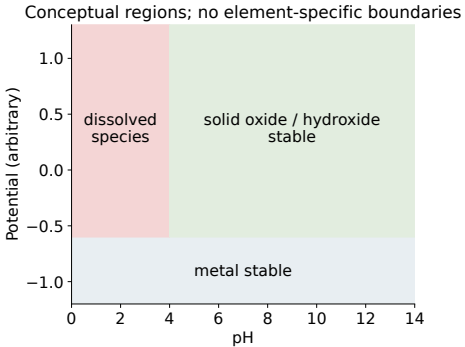
- The axes are potential and pH.
- A metal-stability region indicates thermodynamic immunity.
- Dissolved-species stability permits dissolution.
- A stable solid compound may support passivity.

This diagram shows the idea only. Its boundaries do not represent Fe or another element.



A Pourbaix map does not supply a corrosion rate

- Activities, temperature and the selected species define its boundaries.
- Film porosity and adhesion require additional evidence.
- Local pit chemistry may differ from bulk pH.
- Reaction kinetics determine how quickly a state is approached.

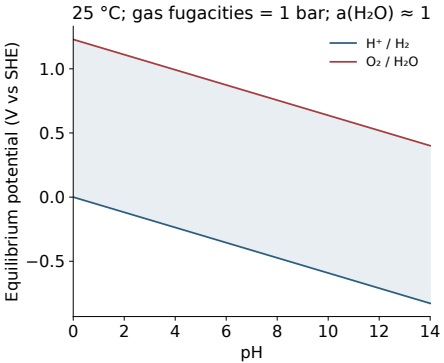


Water stability lines shift with pH

$$E_{\mathrm{H^+/H_2}} = -0.05916\,\mathrm{pH}$$

$$E_{\mathrm{O_2/H_2O}} = 1.229 - 0.05916\,\mathrm{pH}$$

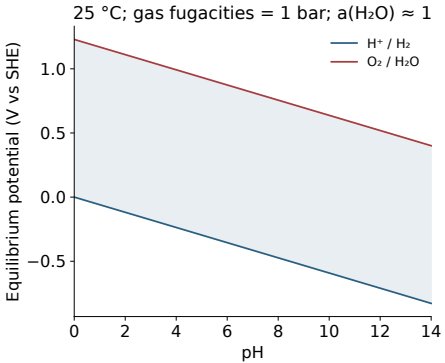
Potentials are in V vs SHE at 25 °C, with unit gas fugacity relative to 1 bar and water activity near one.



A pH change moves both water equilibrium lines

Question

At 25 °C, pH changes from 7 to 9. How much does each water line shift?

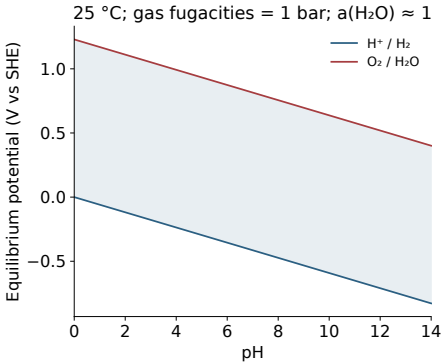


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$$\Delta E = -0.05916(9 - 7)$$



A pH change moves both water equilibrium lines

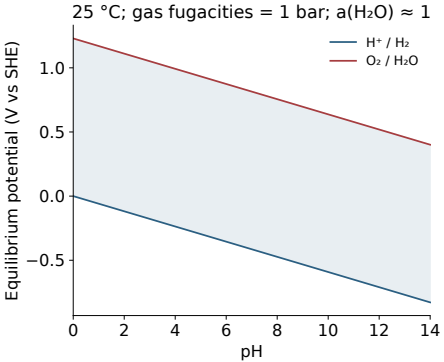
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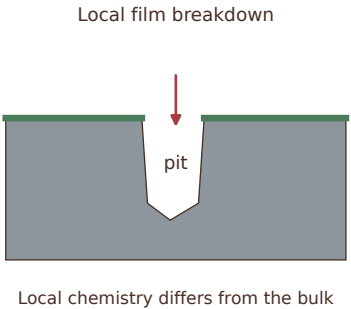
Answer

Both shift by -0.118 V. This is an equilibrium shift, not a predicted corrosion-potential change.



A pit develops its own chemical environment

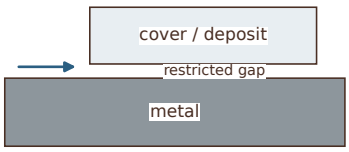
- Local film breakdown exposes metal.
- Dissolved metal ions can hydrolyze and acidify the pit.
- Ion migration maintains charge balance.
- Restricted exchange can sustain conditions unlike the bulk solution.



Crevices restrict exchange with the bulk water

- A narrow gap limits transport.
- Local oxygen consumption can alter cathodic support.
- Hydrolysis and ion migration can change the trapped solution.
- Deposits and joints can create such gaps.

Restricted exchange changes local chemistry



Oxygen depletion, hydrolysis and ion migration

Average mass loss can hide localized penetration

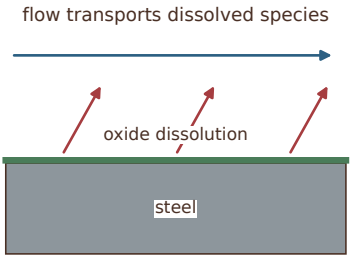
Observation	What it establishes
Small mass loss	Limited total dissolved mass
Deep pit	Large penetration at one location
Crack network	A fracture process requiring further diagnosis
Thin wall	Loss of section that needs a spatial thickness map

Inspection must match the expected damage geometry.

Flow-accelerated corrosion couples dissolution and transport

- The surface oxide can dissolve into the water.
- Flow transports dissolved species away.
- Underlying metal continues to react as the barrier is lost.
- Chemistry, temperature, alloy content and flow geometry affect thinning.

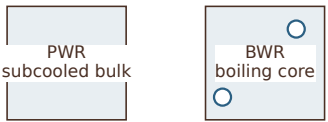
FAC differs from purely mechanical erosion by particles or cavitation.



FAC couples chemistry and mass transfer

PWR and BWR cores create different water histories

- PWR bulk coolant stays subcooled; local nucleate boiling can occur at the cladding.
- BWR water boils in the core.
- Radiation and dissolved gases influence both systems.
- Boiling and phase separation change species transport in a BWR.



Radiation, dissolved gases and flow affect both

PWR chemistry control coordinates several functions

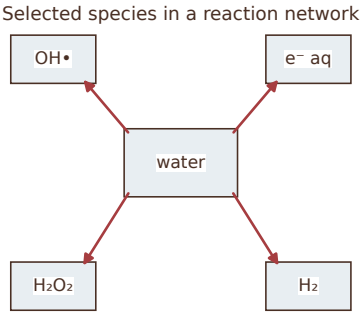
Control	Purpose
Dissolved hydrogen	Influence oxidizing radiolysis products and electrochemical conditions
Boron and alkalinity	Coordinate reactivity control with pH and material compatibility
High purity	Limit aggressive impurities and unwanted deposits

The appropriate concentrations depend on the plant and operating state.

Water radiolysis forms a reaction network

- Energy deposition produces species such as e^-_{aq}, $H^\bullet$ and $OH^\bullet$.
- Reactions also produce molecular H_2 and H_2O_2.
- Subsequent reactions compete with transport and surface reactions.

The drawing lists selected products; it is not a balanced overall reaction.



Both reducing and oxidizing species matter

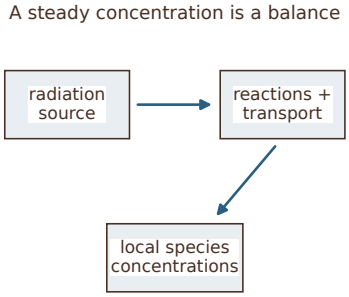
Species or process	**Possible role**
$OH^{\bullet}$, H_2O_2	Strong oxidizing chemistry in relevant reactions
e^-_{aq}, $H^{\bullet}$	Reducing pathways and rapid radical reactions
H_2 addition	Changes the network and surface reaction balance
Flow and boiling	Redistribute species and change residence times

Local concentration follows production, reaction and flow

$$\frac{dc}{dt} = G - kc - \frac{c - c_{\text{in}}}{\tau}$$

- c: species concentration; G: volumetric production rate.
- k: first-order loss coefficient; τ: residence time.
- c_{in}: inlet concentration.

This one-species balance illustrates the idea.
Real radiolysis requires coupled reactions.

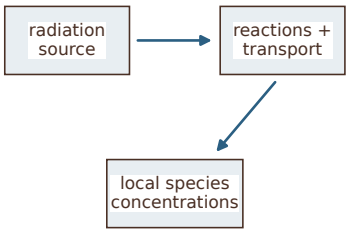


A simple chemistry balance at steady state

Question

Let $c_{\text{in}} = 0$, $G = 10$ concentration-units/s, $k = 2\ \text{s}^{-1}$ and $\tau = 0.5$ s. Find c_{ss}.

A steady concentration is a balance



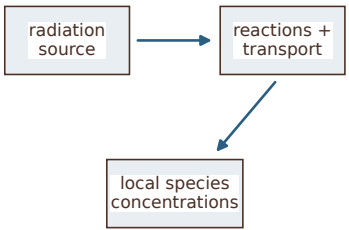
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$$c_{\text{ss}} = \frac{G}{k + 1/\tau}$$

A steady concentration is a balance



A simple chemistry balance at steady state

Question

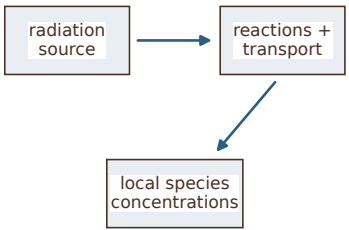
Let $c_{\text{in}} = 0$, $G = 10$ concentration-units/s, $k = 2\ \text{s}^{-1}$ and $\tau = 0.5$ s. Find c_{ss}.

$$c_{\text{ss}} = \frac{G}{k + 1/\tau}$$

Answer

$c_{\text{ss}} = 10/(2+2) = 2.5$ concentration units. Shorter residence time lowers it in this model.

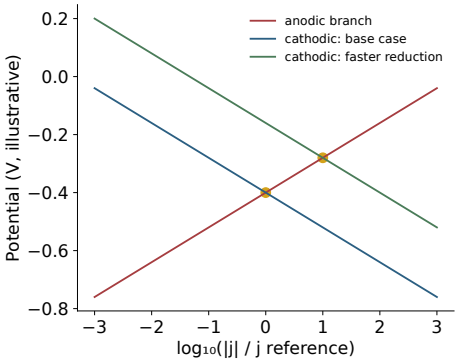
A steady concentration is a balance



Corrosion potential reflects all coupled surface reactions

- An ECP measurement describes a local surface condition.
- Oxidants, hydrogen and surface catalysis affect the partial currents.
- Temperature and transport affect the same balance.

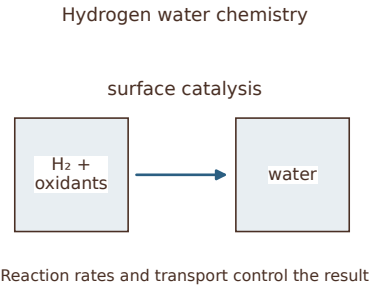
A dissolved-oxygen concentration alone cannot determine ECP in irradiated water.



Hydrogen water chemistry changes the reaction balance

- Hydrogen addition can reduce oxidizing species and lower ECP in relevant BWR regions.
- Surface catalysts can promote recombination reactions.
- Flow, boiling and surface condition affect effectiveness.

Control decisions consider plant-wide consequences as well as local cracking.



Low potential does not eliminate every cracking mechanism

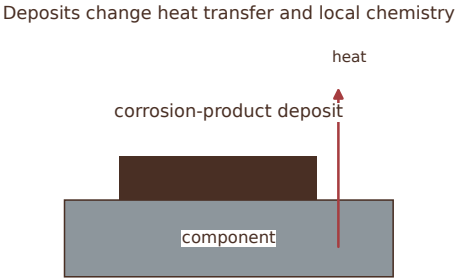
- Reducing chemistry can mitigate some oxidizing-water SCC conditions.
- Susceptible Ni-base alloys can still suffer primary-water SCC.
- Material state, temperature and local stress remain important.

An ECP criterion must belong to a defined material and environment.

Corrosion products can move and deposit elsewhere

- Products generated on one surface can enter the coolant.
- Transport and precipitation can form deposits on another surface.
- Deposits can alter heat transfer and concentrate local chemistry.

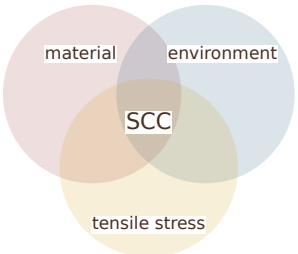
The source location and the damage location may differ.



SCC combines material state, tension and environment

- The material must be susceptible under the exposure conditions.
- Applied or residual tensile stress supplies crack-opening loading.
- The environment assists initiation or growth.

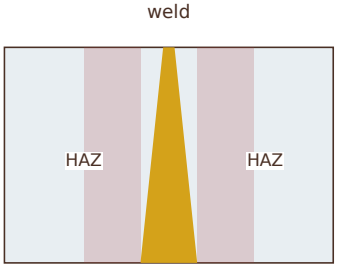
Changing one factor can reduce susceptibility, but its effectiveness needs evidence.



Residual stress can supply the crack-opening load

- Welding creates nonuniform heating and cooling.
- Mechanical constraint can leave tensile residual stresses.
- Machining and cold work can also alter surface stress and microstructure.

A component can contain local tensile stress without a large external load.



Thermal history and residual stress vary with position

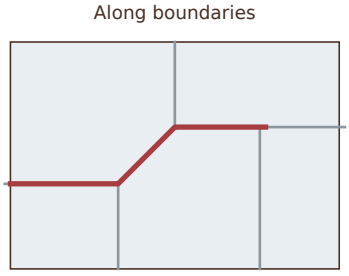
Initiation and propagation need different evidence

Stage	Useful observations
Initiation	Surface condition, local strain, incubation time and small cracks
Propagation	Crack length, growth rate, crack-tip loading and environment
Final fracture	Remaining ligament, toughness and applied loading

A final fracture surface does not reveal the complete initiation history.

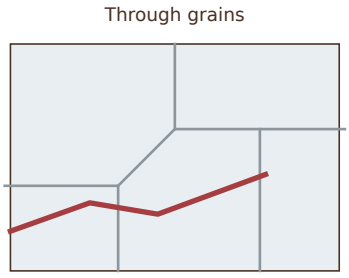
Intergranular cracks follow the boundary network

- Boundary chemistry or local deformation can create susceptible paths.
- The fracture path provides evidence about where damage occurred.
- Different mechanisms can produce a similar intergranular appearance.



Transgranular cracks pass through grains

- Slip and crystallographic orientation can influence the path.
- Environment-assisted and purely mechanical processes can both cross grains.
- Diagnosis needs loading, chemistry and microstructure together.

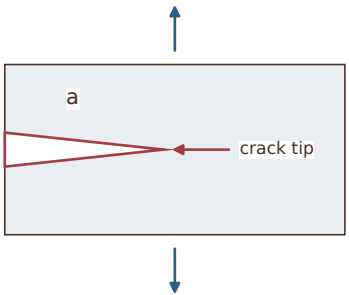


Stress intensity describes mode-I crack-tip loading

$$K_I = Y\sigma\sqrt{\pi a}$$

- Y: geometry factor; σ: nominal tensile stress.
- a: crack dimension appropriate to the chosen geometry.
- K_I: units of MPa$\sqrt{\text{m}}$ when σ is in MPa and a in m.

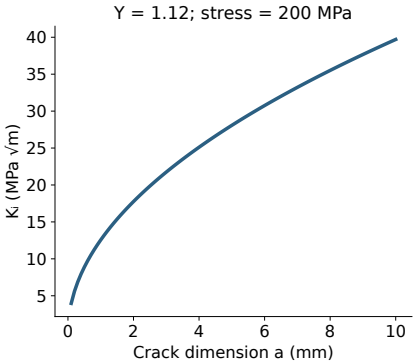
Linear-elastic fracture mechanics requires a suitable geometry and limited crack-tip plasticity.



Worked example: crack size and loading

Question

Use $Y = 1.12$, $\sigma = 200$ MPa and $a = 1$ mm. Estimate K_I.

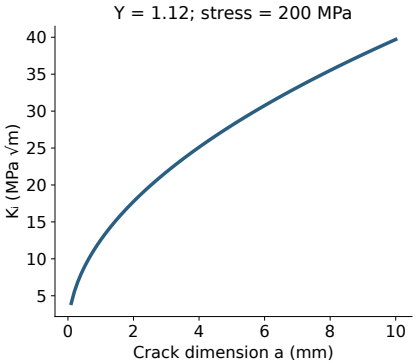


Worked example: crack size and loading

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Use $Y = 1.12$, $\sigma = 200$ MPa and $a = 1$ mm. Estimate K_I.

$$K_I = 1.12(200)\sqrt{\pi(0.001)}$$



Worked example: crack size and loading

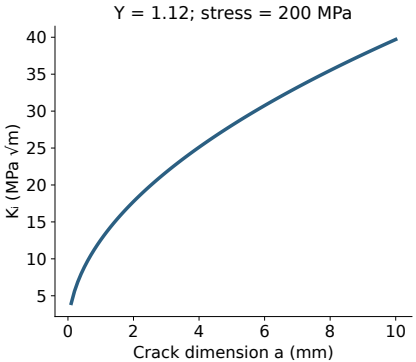
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$$K_I = 1.12(200)\sqrt{\pi(0.001)}$$

Answer

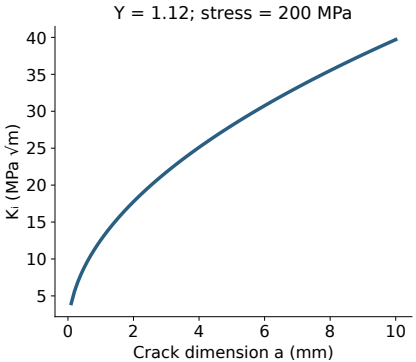
$K_I \approx 12.6$ MPa$\sqrt{\text{m}}$. Convert millimetres to metres before taking the square root.



A crack grows four times longer

Question

At fixed stress and geometry factor, a grows from 1 to 4 mm. What happens to K_I?

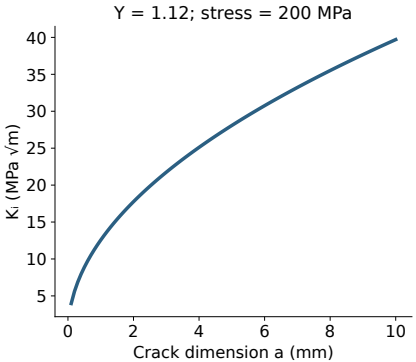


A crack grows four times longer

Question

At fixed stress and geometry factor, a grows from 1 to 4 mm. What happens to K_I?

$$K_I \propto \sqrt{a}$$



A crack grows four times longer

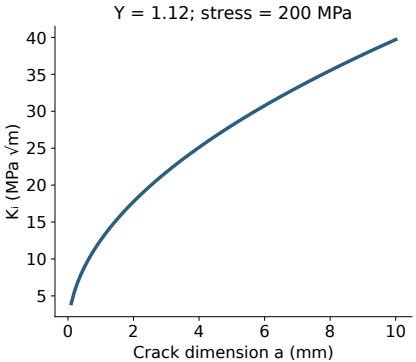
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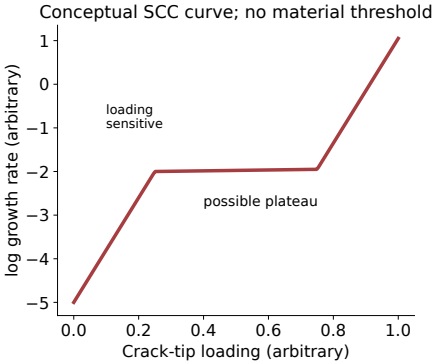
K_I doubles. In the preceding example it rises from about 12.6 to 25.1 MPa$\sqrt{\text{m}}$.



SCC growth curves depend on material and environment

- Growth can increase strongly with crack-tip loading.
- Some conditions show an intermediate rate plateau.
- Higher loading can lead toward rapid mechanical fracture.

The sketch shows possible regimes, not a universal SCC law.



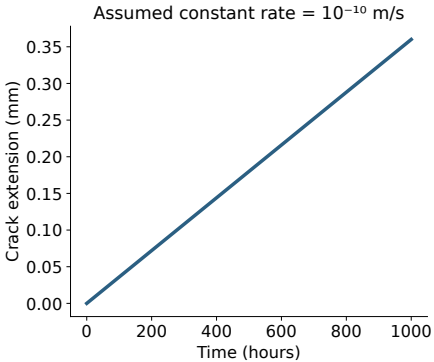
An SCC threshold is conditional

- A reported threshold belongs to a test method and exposure history.
- Detection limits and test duration affect the observation.
- Small cracks and changing local chemistry complicate extrapolation.
- A single threshold is not a universal guarantee of no cracking.

Worked example: crack extension at a stated rate

Question

Assume a constant $da/dt = 10^{-10}$ m/s for 1000 hours. Find the extension.

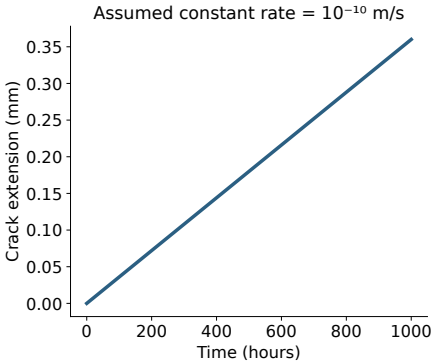


Worked example: crack extension at a stated rate

Question

Assume a constant $da/dt = 10^{-10}$ m/s for 1000 hours. Find the extension.

$$\Delta a = \frac{da}{dt}\, t = (10^{-10})(1000 \times 3600)$$



Worked example: crack extension at a stated rate

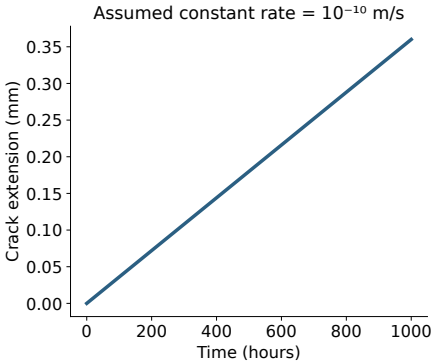
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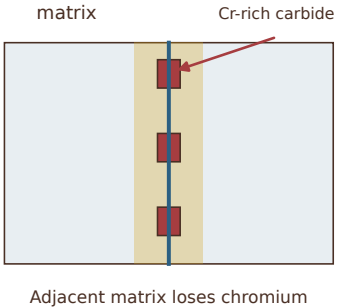
$\Delta a = 3.6 \times 10^{-4}$ m $= 0.36$ mm. This assumes the rate remains constant.



Sensitization changes grain-boundary-adjacent chemistry

- Cr-rich carbides can form during suitable thermal exposure.
- Their growth draws chromium from nearby matrix regions.
- Local depletion can weaken corrosion resistance.

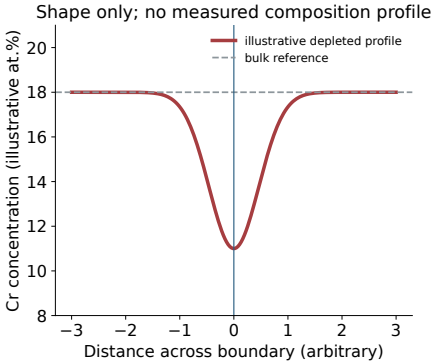
Thermal sensitization can occur without irradiation.



Bulk chromium content can hide local depletion

- A bulk composition measurement averages over a large volume.
- A narrow depleted zone can control local attack.
- The carbide itself is chromium rich while adjacent matrix is depleted.

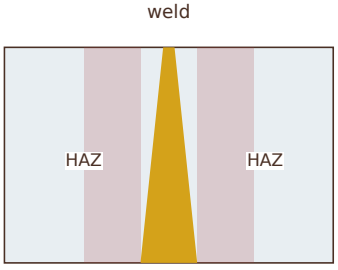
The curve illustrates the depleted matrix profile; it omits the carbide composition.



Weld heat-affected zones can become susceptible

- Time and temperature vary across the joint.
- Carbide precipitation depends on that thermal history.
- Residual stress can act on the same locally altered region.

Composition and processing determine whether sensitization actually develops.



Thermal history and residual stress vary with position

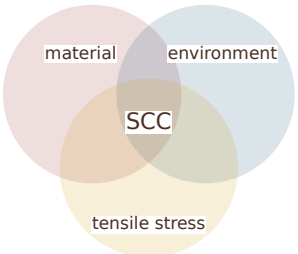
Mitigation must address the relevant SCC contribution

Change	Contribution addressed
Lower carbon or suitable stabilization	Reduce sensitization under relevant processing conditions
Controlled welding and heat treatment	Change local microstructure and stress
Stress management	Reduce crack-opening loading
Water chemistry control	Change environment-assisted reactions

BWR IGSCC connects sensitization, stress and chemistry

- Susceptible stainless-steel piping has shown intergranular cracking.
- Sensitization and weld residual stress can act together.
- Oxidizing water chemistry can promote attack in susceptible material.

Intergranular morphology alone does not prove thermal sensitization.



Primary-water SCC affects susceptible Ni-base alloys

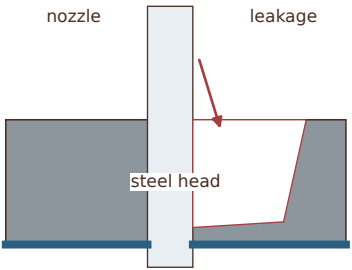
- Alloy 600 and related weld metals have a service history of PWSCC.
- Temperature, processing and tensile stress affect susceptibility.
- Higher-Cr Alloy 690 and suitable weld metals generally improve resistance.

Qualification still includes the actual material condition and service exposure.

Davis-Besse shows how one defect can drive another

- In 2002, inspection found severe reactor-vessel-head degradation.
- Leakage through a nozzle region exposed head steel to borated coolant.
- Corrosion removed steel above the stainless cladding.

The drawing explains the sequence; its dimensions are not those of the actual cavity.

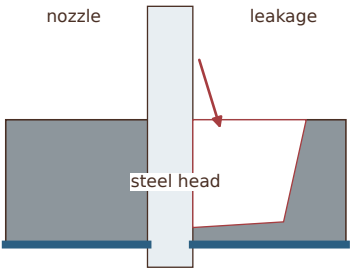


Corrosion cavity above stainless cladding

The Davis-Besse lesson extends beyond alloy selection

Question

Would improving nozzle cracking resistance alone address every part of this degradation sequence?



Corrosion cavity above stainless cladding

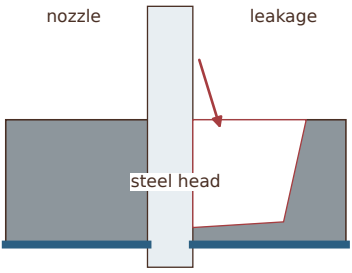
The Davis-Besse lesson extends beyond alloy selection

Question

Would improving nozzle cracking resistance alone address every part of this degradation sequence?

Answer

It addresses one cause. Leakage detection, inspection access, corrosion evaluation and response to deposits also matter.

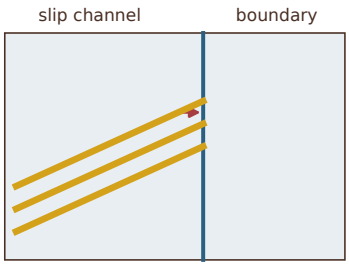


Corrosion cavity above stainless cladding

Irradiation changes several SCC-relevant material features

- Defect evolution can increase strength and localize slip.
- Defect-solute coupling can change boundary chemistry.
- Boundary oxidation and local loading can interact.

These changes act together in irradiated water-exposed components.



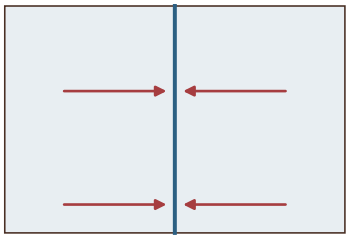
Localized deformation loads the boundary

Radiation-induced segregation comes from coupled fluxes

- Vacancies and interstitials move toward sinks.
- Their transport couples differently to alloying elements.
- Boundary composition can shift from the bulk value.

Element trends depend on alloy and irradiation conditions.

Defect fluxes couple to solute transport



Boundary composition can differ from the bulk

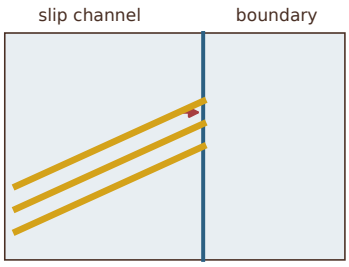
Sensitization and RIS can produce different depletion histories

Thermal sensitization	**Radiation-induced segregation**
Carbide precipitation draws Cr from nearby matrix.	Defect-solute transport changes sink composition.
Controlled by thermal exposure and composition.	Controlled by irradiation, temperature and transport coupling.
Can occur without radiation.	Requires the irradiation-driven defect population.

Dislocation channels concentrate boundary loading

- Localized slip carries strain through a narrow region.
- A channel meeting a boundary can create high local stress.
- Boundary orientation and slip transmission affect that loading.

The average applied stress does not fully describe the local boundary condition.



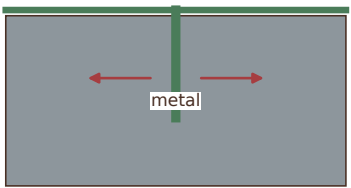
Localized deformation loads the boundary

Boundary oxidation can combine with local stress

- Water exposure can oxidize susceptible boundaries.
- Oxidation changes their local resistance to separation.
- Amplified boundary stress can then promote initiation.

These coupled effects have been observed in irradiated stainless steels.

Boundary oxidation and local loading

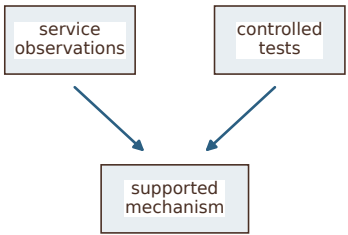


Dose alone cannot identify the IASCC mechanism

- Dose changes several aspects of the microstructure at once.
- Temperature and irradiation history alter those changes.
- Water chemistry and mechanical state also vary.

Evidence needed

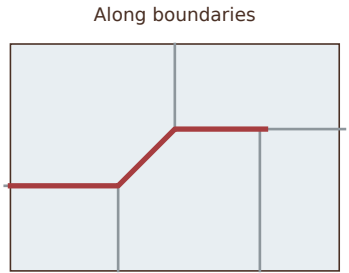
Compare boundary chemistry, deformation and oxidation under controlled conditions.



A low-carbon stainless steel cracks after irradiation

Question

Does low carbon prove that the intergranular crack cannot be environmentally assisted?



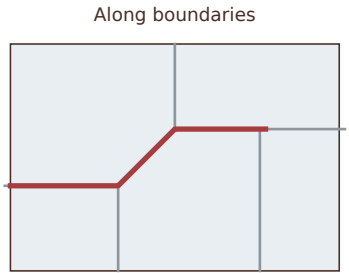
A low-carbon stainless steel cracks after irradiation

Question

Does low carbon prove that the intergranular crack cannot be environmentally assisted?

Answer

No. Low carbon addresses thermal sensitization, but irradiation can change deformation and boundary chemistry through other routes.



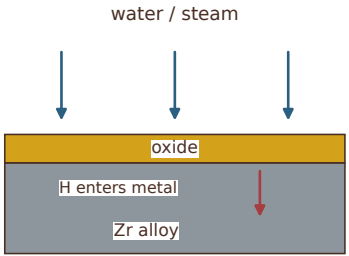
IASCC assessment combines complementary observations

Observation	What it helps test
Boundary chemical profiles	Segregation and local depletion
Slip and strain maps	Localized deformation and boundary loading
Oxide characterization	Environmental penetration and reaction products
Matched crack tests	Effects of material state and exposure

Zirconium oxidation also produces hydrogen

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$$

- The oxide grows while metal is consumed.
- Some corrosion-generated hydrogen can enter the alloy.
- The oxide-growth rate and pickup fraction are separate quantities.

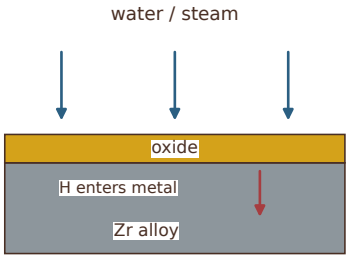


Oxidation and hydrogen pickup are distinct measures

Oxide protection depends on transport and integrity

- A compact barrier can slow further oxidation.
- Phase constitution, stress and connected defects affect transport.
- Cracking and porosity can weaken protection.

Protective Zr oxide contains monoclinic and tetragonal phases.



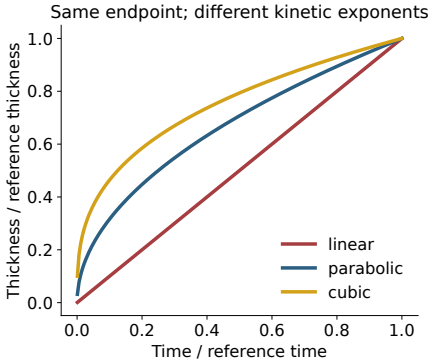
Oxidation and hydrogen pickup are distinct measures

Power-law kinetics describe distinct time dependences

$$x^m = kt$$

Exponent	Thickness dependence
$m = 1$	$x \propto t$ (linear)
$m = 2$	$x \propto t^{1/2}$ (parabolic)
$m = 3$	$x \propto t^{1/3}$ (cubic)

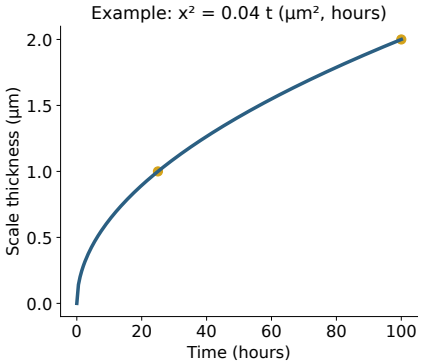
x: scale thickness; k: rate constant with units that depend on m.



Parabolic growth reflects an increasing transport distance

- A thicker scale can create greater transport resistance.
- If flux scales as $1/x$, integrating the growth rate gives $x^2 \propto t$.
- The growth rate decreases as the scale thickens.

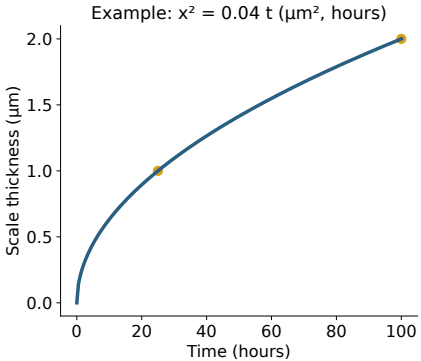
The exponent is evidence to interpret with the film structure.



Worked example: parabolic scale growth

Question

An initially bare surface reaches $x = 1$ μm at 25 hours. Assume $x^2 = k_p t$. Find k_p and x at 100 hours.

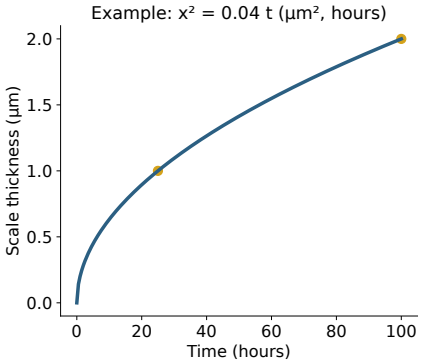


Worked example: parabolic scale growth

Question

An initially bare surface reaches $x = 1\ \mu$m at 25 hours. Assume $x^2 = k_p t$. Find k_p and x at 100 hours.

$$k_p = \frac{1^2}{25}, \qquad x = \sqrt{k_p t}$$



Worked example: parabolic scale growth

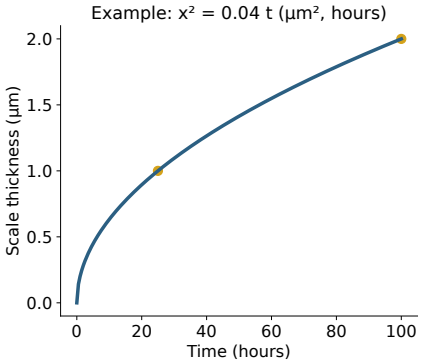
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Answer

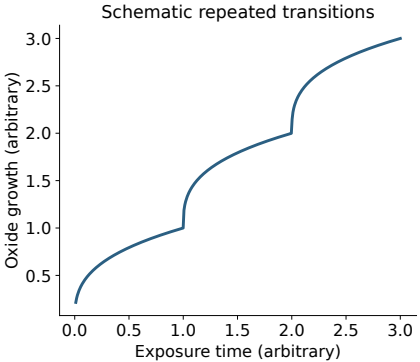
$k_p = 0.04\ \mu\text{m}^2/\text{h}$ and $x(100\,\text{h}) = 2\ \mu\text{m}$. Four times the time doubles thickness.



Zirconium oxide can pass through repeated transitions

- An initially slowing growth regime can change as the oxide evolves.
- Cracking, stress and transport paths contribute to transition behavior.
- Repeated transitions can yield an approximately linear long-time trend.

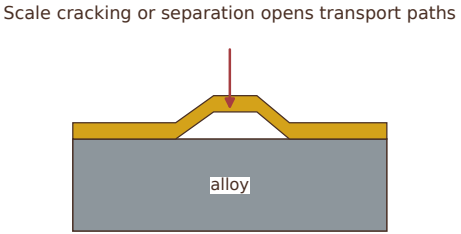
The sketch does not assign a universal transition thickness or time.



Mass gain and metal consumption use different bookkeeping

- A retained oxide adds oxygen mass to the specimen.
- Metal converted into oxide is no longer part of the load-bearing metal.
- Spallation and dissolution can separate measured mass gain from total reaction.

Converting mass gain to thickness requires composition, density and retention assumptions.

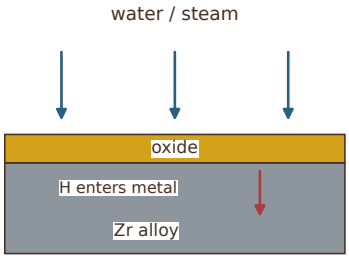


Hydrogen pickup fraction describes retained hydrogen

$$f_H = \frac{N_{H,\text{absorbed}}}{N_{H,\text{generated}}}$$

- Use a consistent hydrogen-atom basis.
- The fraction depends on alloy, oxide and exposure history.
- Hydrogen can dissolve in the matrix or precipitate in hydrides.

A fixed pickup percentage is not universal.

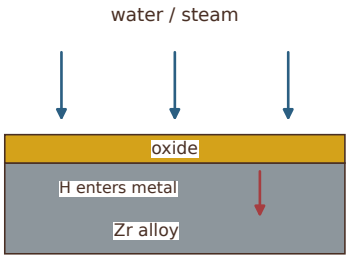


Oxidation and hydrogen pickup are distinct measures

Hydrogen bookkeeping for a stated oxidation amount

Question

One millimole of Zr oxidizes through the water reaction. If 15% of generated H atoms enter the metal, how many are absorbed?



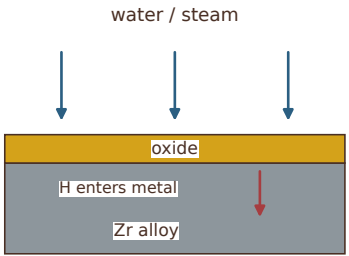
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$$n_{H,\text{generated}} = 4n_{\text{Zr,oxidized}}$$



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Hydrogen bookkeeping for a stated oxidation amount

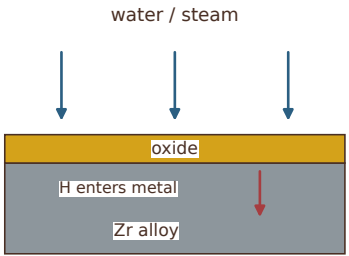
Question

One millimole of Zr oxidizes through the water reaction. If 15% of generated H atoms enter the metal, how many are absorbed?

$$n_{H,\text{generated}} = 4n_{\text{Zr,oxidized}}$$

Answer

Four mmol of H atoms are generated. Absorbed H is $0.15(4) = 0.60$ mmol of H atoms.

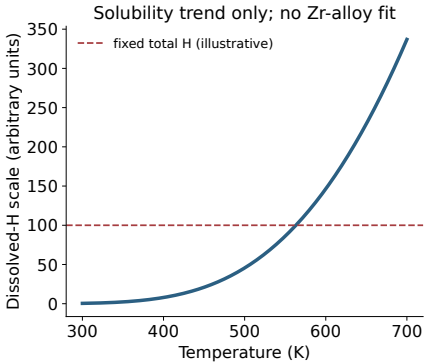


Oxidation and hydrogen pickup are distinct measures

Cooling changes the dissolved-hydrogen capacity

- Hydrogen solubility generally decreases as temperature falls.
- Hydrides can precipitate when the dissolved inventory exceeds the accessible solubility.
- Precipitation and dissolution can show hysteresis.

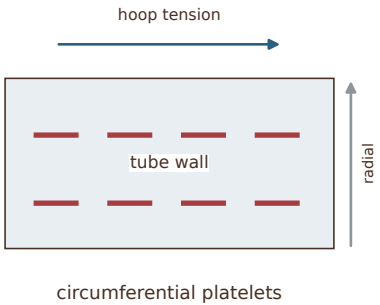
The curve illustrates the trend only; it is not a cladding-alloy correlation.



Hydride morphology matters alongside total hydrogen

- Platelet distribution and connectivity affect crack paths.
- Texture and precipitation history influence orientation.
- Stress during cooling can favor damaging arrangements.

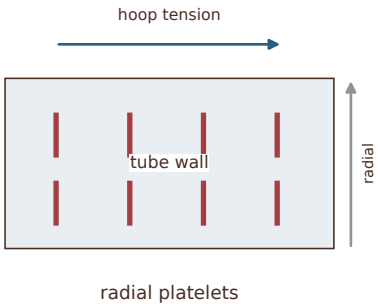
Total hydrogen content alone does not determine ductility.



Radial hydrides can open under hoop tension

- The sketch unwraps a small part of the tube wall.
- Hoop tension acts horizontally.
- Radial platelets can form paths across the wall and open under that loading.

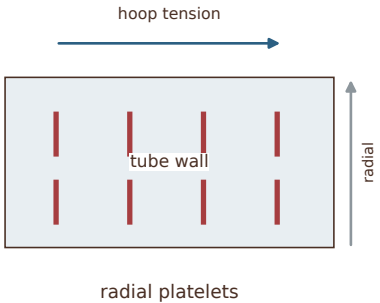
Connectivity and the surrounding metal still affect fracture.



Why cooling history matters for stored cladding

Question

Two tubes have the same total hydrogen. Must they have the same resistance to hoop-loading fracture?



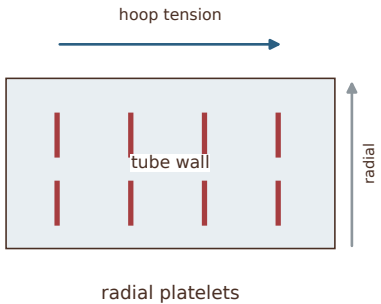
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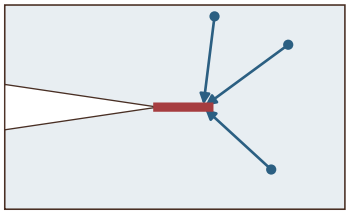
No. Hydride orientation, distribution, thermal history and metal condition can differ.



Delayed hydride cracking advances through repeated local events

- Hydrogen redistributes near a stressed crack tip.
- A hydride can precipitate under suitable local conditions.
- Hydride fracture permits incremental crack advance.
- Transport and precipitation take time.

H redistribution, hydride formation, fracture



Incremental advance under suitable conditions

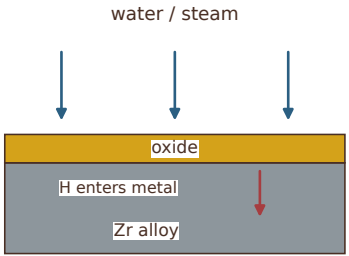
Hydrides in an image do not establish active DHC

Need to establish	Relevant evidence
Hydrogen availability	Inventory and spatial distribution
Mechanical loading	Crack-tip stress and geometry
Thermal conditions	Temperature and prior heating/cooling
Time-dependent advance	Crack growth under the stated exposure

High-temperature steam adds a rapid oxidation challenge

- Reaction rates can rise sharply at elevated temperature.
- Zr oxidation releases heat and produces hydrogen.
- Oxygen uptake changes metal condition as well as oxide thickness.

Normal-operation corrosion trends cannot simply be extrapolated through an accident transient.



Oxidation and hydrogen pickup are distinct measures

Advanced coolants create different compatibility problems

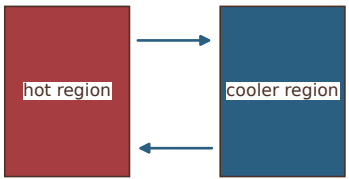
Environment	Key material questions
Sodium	Dissolution, mass transfer and carbon/oxygen impurities
Lead or lead–bismuth	Alloy dissolution and protective-oxide control
Molten salts	Redox-dependent selective dissolution and impurity effects
High-temperature helium	Trace-gas oxidation and carbon transfer
Supercritical water	Oxidation, cracking and changing transport properties

A loop can dissolve material in one region and deposit it elsewhere

- Temperature changes solubility and reaction equilibria.
- Circulation carries dissolved species between regions.
- Deposition can alter flow passages and surface chemistry.

An isothermal coupon cannot reproduce every effect in a nonisothermal loop.

Temperature gradients drive mass transfer



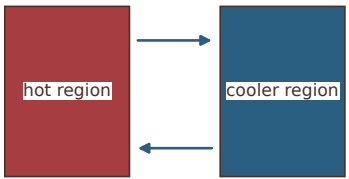
Dissolution and deposition depend on chemistry

Sodium compatibility depends on impurity and mass transfer

- Structural alloys can have useful compatibility under controlled conditions.
- Oxygen and carbon affect reactions and element transfer.
- Temperature gradients can drive redistribution through the loop.

Alloy condition and coolant chemistry must accompany a compatibility claim.

Temperature gradients drive mass transfer

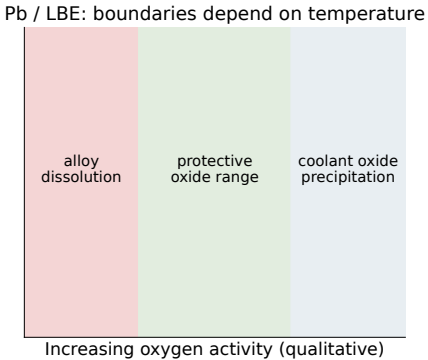


Dissolution and deposition depend on chemistry

Lead and LBE require a controlled oxygen range

- Too little oxygen can leave the alloy vulnerable to dissolution.
- A suitable range can support an oxide on the structural alloy.
- Too much oxygen can cause coolant-oxide precipitation.

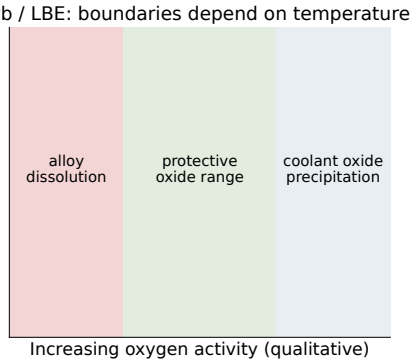
The boundaries depend on temperature and material chemistry.



Oxygen control does not settle every liquid-metal concern

- Film stability, adhesion and erosion resistance remain relevant.
- Wetting and local stress can affect liquid-metal embrittlement susceptibility.
- Flow and temperature determine whether a protective condition persists.

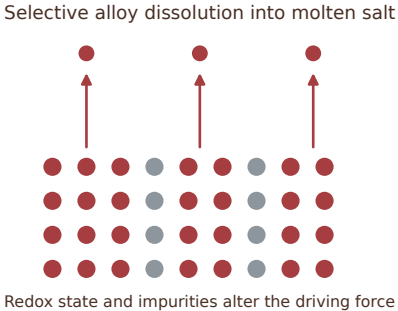
Tests must represent the selected alloy–coolant pair.



Molten salts can selectively dissolve alloying elements

- Halide-salt corrosion can remove less noble alloy components.
- Chromium can be selectively depleted from structural alloys.
- Salt redox state and impurities alter the reaction driving force.

An oxide that protects in water may not provide the same protection in a salt.

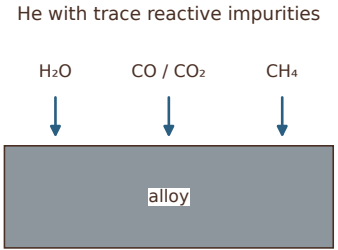


Salt corrosion control includes the entire chemical system

Variable	Why it matters
Salt composition and redox	Set chemical driving forces
Moisture and other impurities	Introduce additional reactive species
Alloy and container materials	Permit selective dissolution or dissimilar-material effects
Thermal gradients and flow	Transport dissolved products around the system

Trace impurities control reactions in hot helium

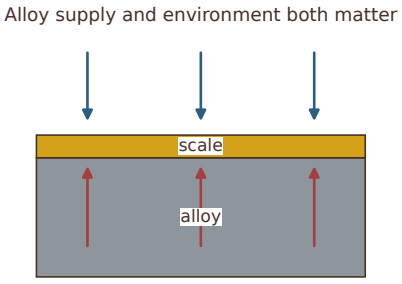
- Helium itself is chemically inert.
- Water and carbon-containing impurities can react with the alloy.
- Gas ratios determine oxygen and carbon chemical potentials.
- The same alloy can oxidize, carburize or decarburize under different conditions.



Protective scales need an alloy supply of the scale-forming element

- Growth consumes elements from the underlying alloy.
- Depletion can limit continued scale formation.
- Thermal cycling creates mismatch stresses and can promote spallation.

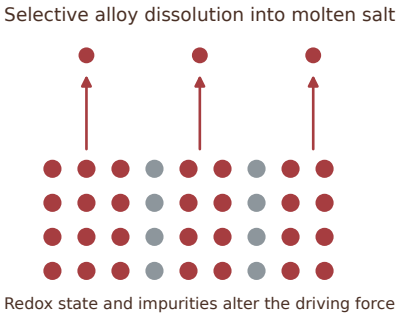
Chemical stability and mechanical integrity must persist together.



A protective oxide in water is proposed for a molten salt

Question

Is good aqueous passivity sufficient evidence of compatibility in the salt?



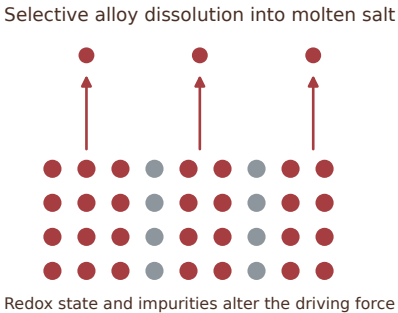
A protective oxide in water is proposed for a molten salt

Question

Is good aqueous passivity sufficient evidence of compatibility in the salt?

Answer

No. Evaluate oxide stability, selective dissolution, redox state, impurities and transport in the actual salt.



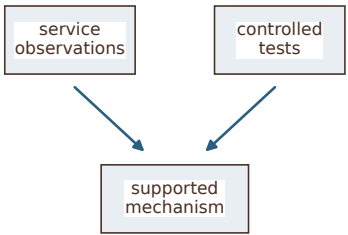
Corrosion testing must reproduce the mechanism-driving conditions

Test choice	**What to control**
Mass-loss or thickness test	Surface state, temperature, chemistry and product removal
SCC initiation test	Stress/strain history and detection of early cracks
Precracked growth test	Crack geometry, loading and environmental history
Flowing-loop test	Velocity, gradients and chemistry transport

An isolated measurement rarely establishes the full mechanism

- Combine morphology with chemical and structural characterization.
- Compare exposed and unexposed material states.
- Separate observations from the interpretation they support.

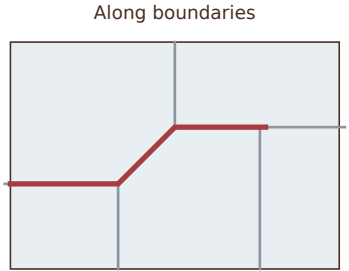
A successful mitigation should address the demonstrated cause.



Diagnosis exercise: cracking with little general metal loss

Question

A water-exposed welded component develops intergranular cracks but little average thinning. Which records and measurements are most useful?



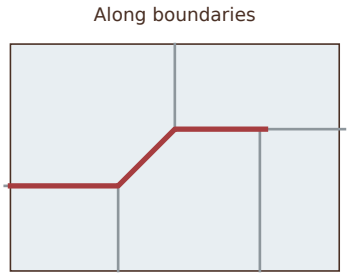
Diagnosis exercise: cracking with little general metal loss

Question

A water-exposed welded component develops intergranular cracks but little average thinning. Which records and measurements are most useful?

Answer

Weld and thermal history, local stress, water chemistry, irradiation exposure, boundary chemistry and oxide/fracture observations.



The course connects structure to component performance

Earlier unit	Connection to corrosion
2: Structure and defects	Boundaries, phases and local atomic environments
3: Radiation damage	Defect production and energy deposition
4: Defect evolution	Transport, segregation and sink behavior
5: Mechanical response	Hardening, localized deformation and crack loading
6: Fuel systems	Cladding barriers, oxidation and hydrogen

Corrosion Assessment

Question	Evidence
What reacts?	Alloy, film, fluid and reaction products
What sets the rate?	Kinetics, transport and surface condition
Where does damage concentrate?	Gaps, pits, boundaries, welds and crack tips
What drives loss of integrity?	Section loss, local loading and evolving toughness

Optional backup: deriving uniform penetration

$$Q = It, \qquad n_{\text{metal}} = \frac{Q}{nF}, \qquad m = \frac{MIt}{nF}$$

$$x = \frac{m}{\rho A} = \frac{Mjt}{nF\rho}$$

This derivation assumes a defined dissolution valence, uniform loss, constant density and 100% current efficiency. Multiply by the appropriate efficiency when only part of the current dissolves the metal.

Optional backup: temperature dependence of a rate constant

$$k = A \exp\left(-\frac{Q_a}{RT}\right)$$

$$\ln \frac{k_2}{k_1} = \frac{Q_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- A: prefactor; Q_a: activation energy; T: absolute temperature.
- Use one mechanism and a defensible temperature range.
- Changes in films or phases can invalidate a single Arrhenius extrapolation.

Optional backup: converting oxygen gain to consumed zirconium

$$\frac{m_{\mathrm{Zr,consumed}}}{m_{\mathrm{O,gained}}} = \frac{M_{\mathrm{Zr}}}{2M_{\mathrm{O}}} \approx \frac{91.22}{32.00} = 2.85$$

- Assume stoichiometric ZrO_2 and complete product retention.
- Measured gain must represent oxygen uptake alone.
- Oxide density converts retained oxide mass to thickness.
- Spallation, dissolution and hydrogen uptake require additional bookkeeping.