EC-009 SUPPLEMENTAL READING

Electrochemical Basics, Part 2: The Corrosion Cell and Its Reactions

The four parts of a corrosion cell, the paired reactions that drive it, and why corrosion concentrates at the anode. Companion reading for EC-009 - The Electrochemical Cell, in the Electrochemistry & the Galvanic Series set.

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Introduction

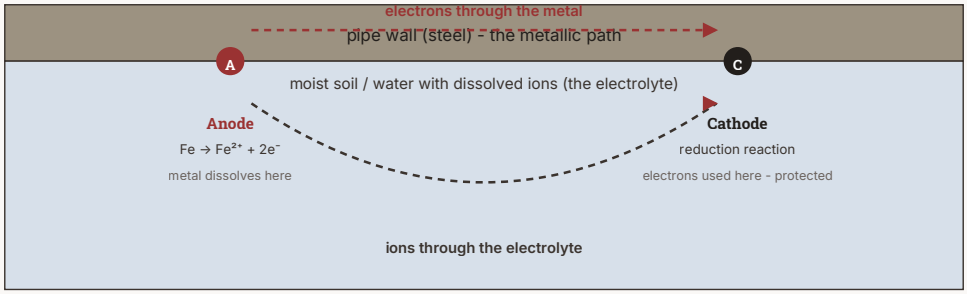
Metallic structures like pipelines, storage tanks, and bridges face constant threats from environmental exposure. These threats often manifest as corrosion, a process that can lead to structural weakening, leaks, or failures if not addressed. At its heart, corrosion isn't just a chemical reaction; it's an electrochemical one, powered by the formation of corrosion cells that drive metal degradation in predictable ways.

For corrosion field technicians and integrity professionals, grasping the basics of an electrochemical cell is more than theoretical knowledge; it's a practical foundation for assessing risks, implementing protective measures, and troubleshooting issues in the field. This understanding helps explain why corrosion tends to concentrate at specific sites, allowing for targeted interventions like cathodic protection systems.

The Fundamentals of a Corrosion Cell

Before diving into the reactions, it's essential to define what makes up a corrosion cell. Often referred to as an electrochemical cell in this context, it represents the smallest unit where corrosion occurs. Unlike a controlled lab setup, these cells form naturally on metal surfaces due to environmental or material variations. A basic electrochemical cell requires four key components to function:

1. **Anode:** the electrode where oxidation takes place. Metal atoms lose electrons, transforming into positively charged ions that dissolve into the surrounding medium. On a steel pipeline, the anode is where iron atoms oxidize, leading to visible pitting or material loss.
2. **Cathode:** the site of reduction. Electrons flow to this area and are consumed by reactions involving species like oxygen or hydrogen ions from the environment. Importantly, no metal dissolution happens at the cathode; it's effectively protected.
3. **Electrolyte:** the conductive medium that connects the anode and cathode ionically. Common electrolytes in field settings include soil with moisture, seawater, or even the pore water in concrete. The electrolyte allows ions to migrate, maintaining electrical neutrality.
4. **Metallic Path:** also known as the electronic conductor, typically the metal structure itself - a pipeline segment or tank wall. It provides a low-resistance path for electrons to travel from the anode to the cathode, closing the circuit.



The four parts of a corrosion cell at the pipe wall. Remove any one and the cell stops.

> **Without all four elements, the cell cannot operate.** In practice, these components are often microscopic or localized on the same metal surface, making detection challenging without tools like potential surveys.

To illustrate, consider a buried steel pipeline: a small coating holiday exposes the metal to soil (the electrolyte). Microstructural differences in the steel create anodic and cathodic zones, with the pipe body serving as the metallic path. This setup initiates corrosion, often undetected until advanced stages.

Electrochemical Reactions Driving the Process

The corrosion cell operates through paired half-reactions: oxidation at the anode and reduction at the cathode. These reactions occur simultaneously, with electron and ion flows sustaining the cycle.

Anodic Reaction: Oxidation and Metal Loss

The anodic reaction is where the damage begins. Metal atoms at the anode release electrons, ionizing and entering the electrolyte. For iron-based alloys, common in pipelines and tanks, the primary reaction is:

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

This represents iron losing two electrons to form ferrous ions, which then react further to form corrosion products like rust ($Fe_2O_3 \cdot H_2O$). The rate of this reaction depends on factors like the

metal's nobility and environmental aggressiveness. In field terms, this translates to measurable metal loss - technicians might observe it as uniform thinning or localized pitting, where anodic sites deepen over time.

Electron Flow Through the Metallic Path

Electrons liberated at the anode don't stay put; they migrate through the metallic path to the cathode. This flow is driven by the potential difference between the anode (more negative) and cathode (more positive). In a pipeline, this could span microscopically or several feet, depending on the cell's scale. Measuring this current indirectly via techniques like close interval surveys helps identify active cells, as per standards like NACE SP0169 (Control of External Corrosion on Underground or Submerged Metallic Piping Systems).

Cathodic Reaction: Reduction and Electron Consumption

At the cathode, electrons are consumed in reduction reactions, balancing the system. The dominant reaction varies by environment:

Aerobic conditions (oxygen present) - typical in well-aerated soils or surface waters, oxygen reduction prevails:

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

This produces hydroxide ions, which can lead to alkaline conditions near the cathode, sometimes forming protective scales.

Anaerobic or acidic conditions - in low-oxygen or acidic electrolytes, hydrogen evolution takes over:

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

This is common in sour environments or under deposits, where hydrogen gas bubbles might be visible during inspections. Other reactions, like metal-ion reduction (e.g., $Fe^{3+} + e^- \rightarrow Fe^{2+}$), can occur but are less common in natural corrosion.

Ion Migration in the Electrolyte

To prevent charge buildup, ions must move through the electrolyte. Positive ions (cations like Fe^{2+}) head toward the cathode, while negative ions (anions like Cl^- or OH^-) move to the anode. This ionic current completes the circuit, much like in a battery. In soil electrolytes, resistivity plays a role; low-resistivity soils (e.g., clay with high moisture) accelerate ion flow

and thus corrosion rates, as outlined in ASTM G57 (Standard Test Method for Measurement of Soil Resistivity).

Why Corrosion Prefers the Anode

Preferential corrosion at the anode stems from the cell's thermodynamics. The anode is the least noble (most active) site, with a lower electrode potential, making oxidation energetically favorable there. Several factors establish anodic sites:

- **Heterogeneities in the metal** - inclusions, grain boundaries, or weld zones can create micro-anodes. In carbon steel, ferrite phases might act as anodes relative to pearlite.
- **Environmental gradients** - differential aeration cells form when oxygen levels vary. Oxygen-rich areas (e.g., near the surface) become cathodic, while oxygen-deprived zones (e.g., under coatings) turn anodic, as per NACE SP0285 (External Corrosion Control of Underground Storage Tank Systems by Cathodic Protection).
- **Galvanic coupling** - connecting dissimilar metals, like steel to copper, makes the less noble metal (steel) the anode. A classic issue in mixed-metal systems.

The anode-cathode area ratio amplifies this: a small anode paired with a large cathode concentrates current density, accelerating corrosion.

Analogy to a Battery

Thinking of a corrosion cell as a battery demystifies it. In a battery, the anode (negative terminal) oxidizes, releasing electrons; electrons flow through an external circuit (wire) to the cathode (positive terminal), where reduction occurs; and the electrolyte enables ion flow internally. In corrosion, the "battery" is unwanted - the current it generates erodes the structure. Cathodic protection counters this by connecting an external anode (sacrificial or impressed) to supply electrons, overriding natural cells.

Practical Examples in Corrosion Control

- **Buried pipelines** - coating holidays create anodic sites. Electrons flow along the pipe to cathodic areas, with soil ions migrating to balance.
- **Offshore structures** - in seawater, steel platforms form cells where aerated upper zones are cathodic and submerged anaerobic areas anodic. Hydrogen evolution dominates below, accelerating cracking.

- **Reinforced concrete** - steel rebar in concrete can corrode if chloride ingress depolarizes the passive layer, turning rebar sections anodic.

Implications for Effective Corrosion Control

Knowledge of corrosion cells directly informs strategies like cathodic protection. By applying a negative potential (e.g., −850 mV vs. CSE), the entire structure becomes cathodic, suppressing anodic reactions. Design considerations include electrolyte resistivity (affecting current distribution) and anode-cathode ratios (influencing protection efficiency). Monitoring via periodic surveys ensures ongoing effectiveness. Integrating this with coatings and inhibitors provides a multi-layered defense.

Key Takeaways

The basic electrochemical cell - anode, cathode, electrolyte, and metallic path - drives corrosion through oxidation at the anode and reduction at the cathode. Preferential anodic corrosion arises from potential differences and environmental factors, leading to targeted metal loss. By understanding these reactions and mechanisms, technicians can better identify cells, apply standards like NACE SP0169, and implement controls to mitigate risks. This foundational insight empowers more accurate risk assessments, efficient surveys, and durable asset protection in challenging environments.