Corrosion Cells and Factors Causing Corrosion

Module Seven of CCE 281 Corrosion: Impact, Principles, and Practical Solutions

Lesson Objectives

- Compare the mechanisms that can initiate and propagate a corrosion process
- Identify the factors causing a corrosion situation
- Discuss the importance of the information associated with and surrounding a corrosion failure
- Predict the presence of corrosion cells
- Plan corrosion experiments to reveal corrosion cells
- Compare the impact of different factors on corrosion damage

Required Reading

This Module consists of fourteen Web pages of required reading. The pagination is visible at the bottom of each page with direct links to adjacent pages.

Additional information can be found in sections 7.1 to 7.6 of the reference textbook (Corrosion Engineering: Principles and Practice).

Introduction

As described in the previous Chapter, corrosion damage may take various forms which are themselves triggered by apparently different compounding factors. The initiation and progression of corrosion processes indeed depend on the complex interaction of a multitude of factors such as:

- Nature of the metal or alloy
- Presence of inclusions or other foreign matter at the surface
- Homogeneity of the metallic structure
- Nature of the corrosive environment
- Incidental environmental factors such as variations in the presence of dissolved oxygen, of temperature, and in the velocity of movement either of the environment or of the system itself
- Other factors such as stress (residual or applied, steady or cyclic)
- Oxide scales (continuous or broken)
- Presence of deposits on surfaces
- Fayed surfaces and the possibility of corrosion crevices
- Galvanic effects between dissimilar metals
- Occasional presence of stray electrical currents from external sources
The nature of the driving forces behind these factors has been the subject of scientific studies by many scientists in the early part of the twentieth century. In a landmark paper, Mears and Brown have summarized 18 mechanisms, listed in the following Table, by which differences in potential may develop on metal surfaces [1].

**Causes of corrosion currents**

<table>
<thead>
<tr>
<th>Causes of corrosion currents</th>
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<tbody>
<tr>
<td>1. Impurities in the metal</td>
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<td>2. Orientation of grains</td>
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<td>3. Grain boundaries</td>
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<td>4. Differential grain size</td>
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<tr>
<td>5. Differential thermal treatment</td>
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<td>6. Surface roughness</td>
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<td>7. Local scratches or abrasions</td>
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<td>8. Difference in shape</td>
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<td>9. Differential strain</td>
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<td>10. Differential pre-exposure to air or oxygen</td>
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<td>11. Differential concentration or composition of solution</td>
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<td>12. Differential aeration</td>
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<td>13. Differential heating</td>
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<td>14. Differential illumination</td>
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<td>15. Differential agitation</td>
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<tr>
<td>16. Contact with dissimilar metals</td>
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<tr>
<td>17. Externally applied potentials</td>
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<tr>
<td>18. Complex cells</td>
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</table>

There is a vast body of information relating practically all the previously listed factors to actual field observations and subsequent analysis of failed components. These failure investigations are typically carried out in a detailed mechanistic ‘bottom-up’ manner whereby a failed component would be sent to the laboratory where analytical techniques would then be used following well established protocols. Chemical analysis, hardness testing, metallography, optical and electron microscopy, fractography, X-ray diffraction and surface analysis are specialized tools used in such investigations.

However, this approach alone provides little or no insight into the real causes of failure. Underlying causes of serious corrosion damage that can often be cited include human factors such as lack of corrosion awareness, inadequate training and poor communication. Further underlying causes may include weak maintenance management systems, insufficient repairs due to short term profit motives, a poor organizational ‘safety culture’, defective supplier's products, or an incorrect material selection.

It is thus apparent that there can be multiple causes associated with a single corrosion mechanism. Clearly, a comprehensive failure investigation providing information on the root cause of failure is much more valuable than one merely establishing the corrosion mechanism(s). Establishing the real causes of corrosion failures (often related to human behavior) is a much harder task than merely identifying the failure mechanisms.

In contrast to the traditional scientific mechanistic approach, systems engineers prefer the ‘top-down’ approach that broadens the definition of the system and is more likely to include causes of corrosion failures such as human behavior. This is consistent with the lessons to be learned from the UK Hoar Report which stated that corrosion control of even small components could result in major cost savings because of the effect on systems rather than just the components [2].
Information Module

- Introduction
- Information to Look for
- Identifying the Corrosion Factors
- Examples of Corrosion Cells
  - Galvanic cells
  - Concentration cells
  - Differential aeration or oxygen concentration cells
  - Temperature cells
  - Stray current cells
  - Stress cells
  - Surface film cells
  - Microbial corrosion cells
- Experiments to Reveal Corrosion Cells
  - Corrosion in Action, the book
  - Classic experiments

See also CCE 513: Corrosion Engineering

References


Information to Look for

It is not always possible to anticipate the actual environment in which a metallic structure will operate. Even if initial conditions were known completely, there is often no assurance that operating temperatures, pressures, or even chemical compositions will remain constant over the expected equipment lifespan. The complexity of corrosion processes and their impact on equipment often buried or out-of-sight complicates many situations, rendering simple life prediction difficult.

Even corrosion tests carried out in controlled conditions often yield results with more scatter than many other types of materials test results because of a variety of factors, an important one being the effect on corrosion rates due to minor impurities in the materials themselves or in the testing environments [3]. The accuracy of data against testing time and number of factors presented in the 3-D plot shown in the following Figure illustrates the relative difficulties associated with reproducing industrially realistic corrosion problems. This intrinsic complexity has made the transformation of corrosion testing results into usable real life functions for service applications a difficult task [4].
Temperature Effects

In most chemical reactions, an increase in temperature is accompanied by an increase in reaction rate. A rough rule-of-thumb suggests that the reaction rate doubles for each ten degree Celsius rise in temperature. Although this rule has many exceptions, it is important to take into consideration the influence of temperature when analyzing why materials fail.

Changing the temperature of an environment can influence its corrosivity. Many household hot water heater tanks, for example, were historically made of galvanized steel. The zinc coating offered a certain amount of cathodic protection to the underlying steel, and the service life was considered adequate. Water tanks seldom were operated above 60°C. With the development of automatic dishwashers and automatic laundry equipment, the average water temperature was increased so that temperatures of about 80°C have now become common in household hot water tanks.

Coinciding with the widespread use of automatic dishwashers and laundry equipment was a sudden upsurge of complaints of short-life of galvanized steel water heater tanks. Electrochemical measurements showed that in many cases, iron was anodic to zinc above 75°C, whereas zinc was anodic to iron at temperatures below 60°C. This explained why zinc offered no cathodic protection above 75°C, and why red water and premature perforation of galvanized water tanks occurred so readily at higher temperatures. This particular problem was partly solved by using magnesium...
sacrificial anodes or protective coatings, and by the replacement with new alloys.

**Fluid Velocity Effects**

Unless otherwise protected, metals generally owe their corrosion resistance to a tightly adherent, protective film that builds up on the metal surface by corrosion processes. This film may consist of reaction products, adsorbed gases, or a combination of these. Any mechanical disturbance of this protective film can stimulate attack of the underlying metals until either the protective film is reestablished, or the metal has been corroded away. The mechanical disturbance itself can be caused by abrasion, impingement, turbulence, or cavitation.

Erosion-corrosion is encountered most frequently in pumps, valves, centrifuges, elbows, impellers, inlet ends of heat-exchanger tubes, and agitated tanks. Locations in flowing systems where there are sudden changes in direction or flow cross section, as in heat exchangers where water flows from the water boxes into the tubes, are likely places for erosion-corrosion. Under these conditions, which stimulate some corrosion of the metal surface, the effects of flow velocity may be to displace the corrosion products, thereby exposing fresh metal to the corrosion action of the solution. This action may lead to a much increased corrosion rate.

**Impurities**

Impurities present in minute amounts have often more influence on the corrosion behavior of materials than substances present in much greater quantities. Sometimes impurities in trace quantities may accelerate the corrosion attack while at other times they may act as inhibitors. The introduction of small amounts of ions of metals such as copper, lead, or mercury can cause severe corrosion of aluminum equipment, e.g. corrosion of upstream copper alloy equipment can result in contamination of cooling water. Under these circumstances, copper can plate out on downstream aluminum equipment and pipe, setting up local galvanic cells which can result in severe pitting and perhaps perforation.

**Presence of Microbes**

Microbes are present almost everywhere in soils, freshwater, seawater, and air. However, the mere detection of microorganisms in an environment does not necessarily indicate a corrosion problem. Nonetheless, it is well established that numerous buried steel pipes have suffered severe corrosion as the result of bacterial action.

In un aerated or anaerobic soils, this attack is attributed to the influence of the sulfate-reducing bacteria (SRB). The mechanism is believed to involve both direct attack of the steel by hydrogen sulfide and cathodic depolarization aided by the presence of bacteria. Even in aerated or aerobic soils, there are sufficiently large variations in aeration that the action of SRB cannot be neglected. For example, within active corrosion pits, the oxygen content becomes exceedingly low.

Bacteria, fungi and other microorganisms can play a major part in soil corrosion. Spectacularly rapid corrosion failures have been observed in soil due to microbial action and it is becoming increasingly apparent that most metallic alloys are susceptible to some form of microbiologically influenced corrosion (MIC).

The presence of aggressive microbes may also be quite severe in industrial water-handling systems, e.g. cooling water and injection water systems, heat exchangers, wastewater treatment facilities, storage tanks, piping systems, and all manner of power plants, including those based on fossil fuels, hydroelectric, and nuclear [5]. The following Table lists potential problem areas by industry [6].

Where MIC problems are most likely to occur [6]
### Presence of Stray Currents

The corrosion resulting from stray currents coming from external sources is similar to that from galvanic cells that generate their own current. However, stray current strengths can be much more damaging than ordinary galvanic cells and, as a consequence corrosion may be much more rapid. Stray currents causing corrosion may originate from direct-current distribution lines, substations, or street railway systems, and flow into an adjacent metallic structure. Alternating currents very rarely cause corrosion.

Another difference between galvanic-type currents and stray currents is that the latter are more likely to operate over long distances since the anode and cathode are more likely to be remotely separated from one another. Seeking the path of least resistance, stray currents from a foreign installation may travel along a pipeline or any other buried metallic structure causing severe corrosion where it leaves the line or current carrier.
Corrosion Factors

The factors listed earlier have been organized in a framework of six categories with a number of subfactors as shown in the following Table. According to Staehle's materials degradation model, all engineering materials are reactive and their strength is quantifiable, provided that all the variables involved in a given situation are properly diagnosed and their interactions understood [7]. The corrosion based design analysis (CBDA) approach was further developed from the initial framework as a series of knowledge elicitation steps to guide maintenance and inspection decisions on the basis on first principles [8].

Factors and contributing elements controlling the incidence of a corrosion situation [7]

<table>
<thead>
<tr>
<th>Factor</th>
<th>Sub-factors and contributing elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Chemical composition of alloy</td>
</tr>
<tr>
<td></td>
<td>Crystal structure</td>
</tr>
<tr>
<td></td>
<td>Grain boundary (GB) composition</td>
</tr>
<tr>
<td></td>
<td>Surface condition</td>
</tr>
<tr>
<td>Environment</td>
<td>Type, chemistry, concentration, phase, conductivity</td>
</tr>
<tr>
<td></td>
<td>Velocity, thin layer in equilibrium with relative humidity, wetting and</td>
</tr>
<tr>
<td></td>
<td>drying, heat transfer boiling, wear and fretting, deposits</td>
</tr>
<tr>
<td>Stress</td>
<td>Mean stress, maximum stress, minimum stress, constant load/constant</td>
</tr>
<tr>
<td></td>
<td>strain, strain rate, plane stress/plane strain, modes I, II, III, biaxial,</td>
</tr>
<tr>
<td></td>
<td>cyclic frequency, wave shape</td>
</tr>
<tr>
<td></td>
<td>Intentional, residual, produced by reacted products, thermal cycling</td>
</tr>
<tr>
<td>Geometry</td>
<td>Discontinuities as stress intensifiers</td>
</tr>
<tr>
<td></td>
<td>Creation of galvanic potentials</td>
</tr>
<tr>
<td></td>
<td>Chemical crevices</td>
</tr>
<tr>
<td></td>
<td>Gravitational settling of solids</td>
</tr>
<tr>
<td></td>
<td>Restricted geometry with heat transfer leading to concentration effects</td>
</tr>
<tr>
<td></td>
<td>Orientation vs. environment</td>
</tr>
<tr>
<td>Temperature</td>
<td>At metal surface exposed to environment</td>
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<tr>
<td></td>
<td>Change with time</td>
</tr>
<tr>
<td>Time</td>
<td>Change in GB chemistry</td>
</tr>
<tr>
<td></td>
<td>Change in structure</td>
</tr>
<tr>
<td></td>
<td>Change in surface deposits, chemistry, or heat transfer resistance</td>
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<tr>
<td></td>
<td>Development of surface defects, pitting, or erosion</td>
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<td></td>
<td>Development of occluded geometry</td>
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<tr>
<td></td>
<td>Relaxation of stress</td>
</tr>
</tbody>
</table>

The two most important of these steps are described in the following Figures for respectively the environment and the material definitions. Each of the numbers in brackets in these Figures identifies an explicit action that needs to be considered for each definition.
A brief explanation of the individual elements in the environment definition follows:

1. "Nominal Chemistry" refers to the bulk chemistry. For components exposed to ordinary air atmospheres, the "Major" elements mean humid air. The "Minor" elements refer to industrial contaminants such as SO$_2$ and NO$_2$.
2. "Prior Chemistry History" refers to exposures to environmental species that might still reside on the surfaces or inside crevices.
3. "System Sources" refers to those environments that do not come directly from a component but from an outside source.
4. "Physical Features" includes occluded geometries, flow, and long range electrochemical cells.
5. "Transformations" refers, for example, to microbial actions that can change relatively innocuous chemicals such as sulfates into very corrosive sulfide species that may accelerate hydrogen entry and increase corrosion rates.
6. "Concentration" refers to accumulations much greater than that in the bulk environment due to various actions of wetting and drying, evaporation, potential gradients, and crevices actions that prevent dilution.
7. "Inhibition" refers to actions taken to minimize corrosive actions. This usually involves additions of oxygen scavengers or other chemicals that interfere directly with the anodic or cathodic corrosion reactions.

The end point of the process is an input to a location for analysis (LA) matrix that is illustrated in the following Figure for the locations in a steam generator.
The LA template of the locations that correspond to most likely failure sites along tubes in a steam generator of a pressurized water nuclear power plant is detailed in the following Table for the main failure modes and sub-modes considered in such analysis. Maintenance and inspection actions can be decided upon by following developing trends monitored in each LA matrix thus produced.


<table>
<thead>
<tr>
<th>Locations for analysis</th>
<th>Submodes of SCC</th>
<th>Submodes of IGC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OD</td>
<td>LPSCC (j=1)</td>
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<tr>
<td>Tubular expansion</td>
<td>x</td>
<td></td>
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<tr>
<td>(i=1)</td>
<td></td>
<td></td>
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<tr>
<td>Tubular expansion</td>
<td>x</td>
<td></td>
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<tr>
<td>(i=2)</td>
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<td></td>
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<tr>
<td>Top of tube sheet</td>
<td>x</td>
<td></td>
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<tr>
<td>(i=3)</td>
<td></td>
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<tr>
<td>Top of tube sheet</td>
<td>x</td>
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<tr>
<td>(i=4)</td>
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<tr>
<td>Sludge</td>
<td>x</td>
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<td>(i=5)</td>
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<tr>
<td>Free span</td>
<td>x</td>
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<tr>
<td>(i=6)</td>
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<tr>
<td>Free span</td>
<td>x</td>
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<tr>
<td>(i=7)</td>
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<tr>
<td>Tube support</td>
<td>x</td>
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<tr>
<td>(hot leg) (i=8)</td>
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<tr>
<td>Tube support</td>
<td>x</td>
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<tr>
<td>(cold leg) (i=9)</td>
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<tr>
<td>U-Bend</td>
<td>x</td>
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<tr>
<td>(i=10)</td>
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<tr>
<td>U-Bend AVB</td>
<td>x</td>
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<td>(i=11)</td>
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</table>

The framework summarized above, which was initially developed to predict the occurrence of stress corrosion cracking (SCC), was
extended to other corrosion modes/forms. Additionally, an empirical correlation was established between the factors listed in Table of factors and the forms of corrosion described earlier in the previous Module. Recognized corrosion experts were invited to complete an opinion poll listing the main sub-factors and the common forms of corrosion as illustrated in the example shown in the following Figure. Background information on the factors and forms of corrosion was attached to the survey. A total of sixteen completed surveys were returned subsequently analyzed.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Uniform</th>
<th>Pitting</th>
<th>Crevice</th>
<th>Galvanic</th>
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<tbody>
<tr>
<td>Material</td>
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<td>Composition</td>
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<td>Crystal structure</td>
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<tr>
<td>GB composition</td>
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<tr>
<td>Surface condition</td>
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<tr>
<td>Environment</td>
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<tr>
<td>non-natal</td>
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<tr>
<td>circumstantial</td>
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<tr>
<td>Stress</td>
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<td>applied</td>
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<tr>
<td>residual</td>
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<td>product built-up</td>
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<td>cyclic</td>
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<tr>
<td>Geometry</td>
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<td>galvanic potentials</td>
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<tr>
<td>restricted geometries</td>
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<tr>
<td>settling of solids</td>
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<tr>
<td>Temperature</td>
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<td>changing T</td>
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<td>Time</td>
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<td>changes over time</td>
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</table>

Opinion poll sheet for the most recognizable forms of corrosion problems

The following Figure presents the Box-and Whisker plots of the results obtained with pitting corrosion. When presented in this fashion, such results can provide a useful spectrum of factor and sub-factor confidence levels.
Example problem 7.1

Propose some arguments to explain the high variance, visible in the previous Figure, between expert opinions on the factors causing pitting corrosion.

Linking the corrosion factors with possible forms of corrosion in this fashion may provide guidance to inexperienced corrosion failure investigators who have typically limited knowledge of corrosion processes. A listing of the most important factors should therefore help to increase the awareness of the complexity and interaction of the variables behind most corrosion failures and reveal how ‘experts’ have reduced such complexity to a reduced set of variables, as the compiled results of the survey indicate in the following Figure.
Results of compiled survey of corrosion experts highlighting the most important correlations between corrosion forms and factors

An application of the compiled framework could be to test one’s skills against the ‘experts’ as illustrated in the following Figure.
Comparison of the answers of one expert with the some of the compiled expert survey results

Another application of this practical correlation would be to use the framework of factors vs. forms for archiving data in an orderly manner. Analysis of numerous corrosion failure analysis reports has revealed that information on important variables is often lacking [9]. The omission of important information from corrosion reports is obviously not always an oversight by the professional author. In many cases, the desirable information will simply not be (readily) available and require a special investigation to be completed.
Examples of Corrosion Cells

A difference in potential will be observed if electrically connected specimens of the same metal are immersed in solutions having different concentrations of ions of the metals. This is one common type of concentration cell. Another type is the oxygen concentration or differential aeration cell. This type and the metal ion cell can oppose one another. For example, variations in oxygen concentration can establish oxygen concentration cells. In solutions containing metal ions, the solubility of oxygen may vary, depending on the concentration of metal ions.

Local cells can be produced by differences among small nearby areas on the metal surface. They may result from differences in the metal, or the environment, or from impressed currents. Metal variations may be the result of composition differences. A second phase constituent will have a different corrosion potential compared to that of an adjacent solid solution. The difference may be in the thickness of a surface film at adjacent sites which in turn may reflect metal differences in the substrate.

The corrosion of guyed tower anchors such as shown in the following two Figures and which is becoming an issue of critical importance will be used in the next sections to illustrate some of these corrosion cells. Soil type can vary even within a few centimeters or inches and this variability can cause multiple corrosion cells on the same structure.
Basic anchor support design (Courtesy of Anchor Guard)
Examples of Corrosion Cells

Typical anchor support with a copper rod ground connection (Courtesy of Anchor Guard)

In many cases, the loss of one anchor to corrosion has resulted in the catastrophic loss of the supported communication tower as exemplified in the following Figures.
Anchor assembly cut by corrosion at the concrete anchorage (Courtesy of Anchor Guard)
Mangled communication tower fallen due to loss of the anchor shown in the previous Figure (Courtesy of Anchor Guard)

- Galvanic cells
- Concentration cells
- Differential aeration or oxygen concentration cells
- Temperature cells
- Stray current cells
- Stress cells
- Surface film cells
- Microbial corrosion cells

**Example problem 7.2**
What is a corrosion cell and what are its main components?

**Example problem 7.3**
Can you imagine some corrosion cells that would be cancelling each other?

**Example problem 7.4**
Describe the effects of corrosion stress cells in terms of energy release.

**Example problem 7.5**
Provide some examples where microbes have been found to be the root cause of corrosion problems.

**Example problem 7.6**
Can crevice corrosion degenerate in other forms of corrosion? Provide some examples.

**Example problem 7.7**
Why is it important to consider the electrical conductivity between various components when suspecting the presence of a galvanic corrosion problem?
Galvanic Corrosion Cells

Any two metals can be used to make a galvanic cell. Whether a metal will behave as an anode or a cathode in combination with another metal in the same soil environment, can usually be determined by its relative position on the galvanic series. The metal which appears higher up on the list (more negative) will, in general, be the anode and will thus corrode. The metal lower down on the list (more positive on the potential scale) will be the cathode and thus will not corrode. Of course, this galvanic action will not take place under open-circuit conditions; there must be a connecting circuit.

Are these corrosion cells common? The answer is yes. Whenever a copper pipe service line is directly connected to a cast iron gas or water main, a galvanic cell such as shown in the following Figure is formed. The soil is the electrolyte, the copper service line is the cathode, the iron (or steel) main is the anode, and the connecting circuit is completed by attaching the line to the main. Normally, such cells do not do any great amount of damage, because the anode (corroding metal) is so much larger than the cathode that the attack is spread out over a large area.

Underground corrosion cell involving connection of dissimilar metals

However, the situation can lead to the corrosion of steel when the surface area of the cathode (copper) approaches that
of the anode (steel) such as shown in the following Figure.

Schematic of the corrosion cells acting on an anchor support with a ground connection. (Courtesy of Anchor Guard)

It can also be a problem when the surrounding soil is more conductive or corrosive in the region where the galvanic coupling exists as in the following Figure. In this example the anodic corrosion of the anchor is partly due to the galvanic corrosion cell formed by the connection of ground copper rods.


Corrosion of a water main ductile iron adjacent to a copper fitting. (Courtesy of Drinking Water Services, City of Ottawa)

One way to minimize the dissimilar metal interaction that causes the corrosion of the structural steel anchor is to break the electrical path between these two components by adding insulators as shown below. However, this measure alone has proven to be only a partial solution to this type of problem since another corrosion cell is still active as will be described in the next section.
The addition of insulators between the ground rod and the steel anchor to stop the galvanic action. (Courtesy of Anchor Guard)
Concentration Corrosion Cells

This type of corrosion cells may occur in soils when a metal is exposed to an environment containing varying levels of electrolytes either of different substances or of the same substance in different amounts. For example, if one electrolyte is a dilute salt solution and the other a concentrated salt solution, a concentration cell may be formed. This takes place because one of the factors that determine an electrode potential is the electrolyte concentration.

The dissolved salts can be quite complex mixtures. They usually include compounds of aluminum, calcium, magnesium, and other metals, and they may be sulfates, chlorides, hydroxides, or any one of quite a variety of other compounds. The role played by these salts can also vary greatly. Chloride ions, for example, can be quite aggressive towards steel and sulfate ions can serve as nutrients to sulfate reducing bacteria (SRB) which themselves can be extremely damaging to most buried metals.

In the example shown in the previous section, the main difference in the environment surrounding the steel anchor is due to the variation of pH between the soil, which can vary greatly depending on the type of soil but often acidic, and the pH in the concrete anchorage for which the pH is always basic and higher than 10. Because this higher pH is protective to steel it naturally follows that the steel in concrete becomes the cathode drawing an anodic current from the adjacent steel in the soil. A concentration cell common during the corrosion of reinforced concrete exposed to salts containing chloride ions, e.g. marine environments or road deicing salts, is illustrated in the following Figure.
In such cell the reinforcing steel in contact with the mobile chloride ions may become vulnerable to corrosion due to the depassivation of the steel. The process is further accelerated due to the presence of bars embedded deeper in the concrete. These protected bars can then serve as cathodes because of the attaching strings serving as electrical connection. The resulting stresses produced by an accumulation of corrosion products may cause cracks to initiate and grow causing the degradation of reinforced concrete below. An equivalent volume expansion ratio of 3.0 to 3.2 has been measured due to the formation of corrosion products on steel bars embedded in concrete [4].
Cracking of concrete cover in marine environment.
Differential Aeration Corrosion Cells

The oxygen content of any solution ranks high on the list of factors influencing the corrosion of iron and numerous other metals. Elimination of oxygen by deaeration is a practical means of reducing corrosion, as in the case of steam boilers which are operated with deaerated feed water. Differential aeration cells can be caused by crevices, lap joints, dirt and debris, and moist insulation. Under these conditions, the oxygen starved areas are anodic, while the areas with free access to oxygen are cathodic. Common terms for this type of corrosion include crevice corrosion, oxygen screening, and poultice action.

Oxygen not only enables a corrosion reaction by maintaining a cathodic reaction, but it can promote one. This occurs where there is a difference in the concentration of dissolved oxygen between two points of the same metal surface. Since the direction of the reaction is towards equilibrium, the only way that equilibrium can be approached by corrosion will be to reduce the concentration of oxygen where it is highest. Such reduction can be done by consuming the oxygen as shown in the following equation.

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

The result is that where there is a difference in the concentration of dissolved oxygen at two points on a metal surface, the surfaces in contact with the solution containing the higher concentration of dissolved oxygen will become cathodic to surfaces in contact with a lower concentration of dissolved oxygen that will in turn suffer accelerated corrosion as anodes in an oxygen concentration cell. It is easy to demonstrate an oxygen concentration cell with an experimental setup using two containers as shown in the following Figure.
Experiment to demonstrate generation of a corrosion current by an oxygen concentration cell

In this experiment, pieces of steel electrically connected are immersed in a sodium chloride solution in the two containers. The solution in one container is saturated with oxygen and the solution in the other container is saturated with nitrogen. This establishes a difference in the concentration of dissolved oxygen in contact with the two pieces of steel. The high concentration of dissolved oxygen in one container makes the steel surface strongly cathodic to the steel in the other container. Dissolved oxygen concentration differences can also be established by velocity gradients and by crevices, but the location of anodes and cathodes from these sources is the opposite of a metal ion concentration cells. In the presence of a velocity gradient, more oxygen is brought to the surface moving at the highest velocity so that this surface becomes cathodic to any surface moving at a lower velocity because of the difference in oxygen availability.

In the following example the concentration cell is caused by differences in the electrolyte and in oxygen content around a buried anchor rod. The following **Figure** illustrates how soil stratification can produce an oxygen concentration cell on a tower anchor shaft. In this illustration, the upper soil layer is a loose somewhat gravelly soil below which there is a dense clay type soil.
Differences in the porosity of the soil that can lead to an oxygen concentration corrosion cell. (Courtesy of Anchor Guard)

The portion of the shaft in contact with the clay type soil acts as an anode to the portion of the shaft in contact with the looser gravely soil, which is consequently the cathode. Again, we have a corrosion cell where the shaft deteriorates in the anodic areas. Such differential aeration cells are also very common on buried pipes. For example, a pipe usually rests on undisturbed soil at the bottom of a ditch. Around the sides and on top of the pipe is relatively loose backfill which has been replaced in the ditch.

Because the backfill is more permeable to oxygen (and the path is shorter) diffusing down from the surface, a cell is formed. In this case, the anode is the bottom surface of the pipe and the cathode is the rest of the surface. The electrolyte is the soil, and the connecting circuit is the metallic pipe itself. When a pipe or cable passes under paving, such as an airport runway, parking lot, or street such as illustrated in the following Figure, the portion under the paving has less access to oxygen than does the area lying under unpaved soil.
Oxygen differential cell resulting from burial under paving producing an oxygen concentration cell

In this particular example, although the entire length of pipe under the paving is anodic, most of the attack will take place close to the edge. Because the path through the electrolyte is shorter to this part, most of the current takes this low-resistance path. In this example the oxygen concentration cell components are:

- The anode is the pipe under the paving
- The cathode is the pipe outside the paving
- The electrolyte is the soil
- The connecting circuit is the pipe or cable
**Temperature Corrosion Cells**

While concentration and oxygen cells are responsible for perhaps 90% of the corrosion in soils and natural waters, other cells such as the temperature cell shown below may be still quite damaging when they get established. In such cells, the two electrodes are of the same metal, but one is maintained at a higher temperature than the other by some external means. In most cases, the electrode at the higher temperature becomes the anode to cause what has been called thermogalvanic corrosion.

![Concentration cell resulting from heat differential](image)

In the gas transmission line example shown above, the compressed gas coming out of the station is hot, and, as it travels down the line, it loses heat by transfer to the surrounding soil (as well as losing some by expansion). The result creates a cell:

- The hot pipe near the compressor is the anode
- The cooler pipe down the line is the cathode
- The soil is the electrolyte
- The pipe itself is the connecting circuit
This is a particularly unfortunate type of cell because the high temperature just outside the compressor tends to damage the coating, so that the part of the line which is the anode is also likely to have the poorest coating. External corrosion of underslab, copper, hot water tubing has resulted in a great deal of construction defect litigations due to this type of corrosion [10]. Oil and gas well casings also experience similar cell attack. The pipe at some depth below the surface is at a higher temperature (this is a natural phenomenon; temperature increases with depth) and thus becomes the anode, the cooler pipe near the surface and the surface piping make up the cathode, the soil is the electrolyte, and the pipe is the connection.
Stray Current Corrosion Cells

In all cells described so far, the source of the energy which makes a cell active has been within the cell. The source has been the solution potential of the anode (the amount by which it is greater than that of the cathode), some distribution of energy in the metal, or a concentration gradient in the electrolyte.

It is possible to have a cell in which the energy is supplied in the form of electrical current from an outside source. An electroplating cell is one example. In this case, energy comes from a generator supplying direct current. A car battery which is being charged is another example. The power in this instance comes from the car's generator that actually forces current through the cell in a direction opposite to the driving voltage of the cell itself (the battery is really a set of three or six cells).

Impressed current cells in which the soil is the electrolyte are of two kinds: accidental and deliberate. The deliberately impressed current system is the one which supplies cathodic protection to increase the life of a structure by reducing the corrosion current. Accidental systems, however, may exist under a variety of circumstances. Any direct current flowing in the soil from any source whatsoever can, if it finds a pipeline or other metal object in its path, collect on the pipe in one area and discharge from it in another. The area where it collects becomes a cathode while the area where it discharges is an anode, and thus corrosion occurs.

The source of energy for such cells may be a distant generator, a direct current transmission line, a cathodic protection rectifier on some other line, a street car system, or an electric railway.

Stray current corrosion due to the return path of an electric railway

The corrosion effects of stray current can be easily demonstrated with a simple laboratory set-up such as shown in part a) of the following Figure. After only a few minutes of passing a small DC current in the cell containing a dilute
saline solution, the formation of hydrogen bubbles is readily visible on the steel nail connected to the negative post of the DC power supply (b) while the nail connected to the positive post shows signs of rapid corrosion a few minutes later (c).
Stray Current Corrosion Cells

b)
c)

Experiments to illustrate the effects of stray current showing a) the experimental set-up containing a DC power supply plus two steel nails partially immersed in a dilute saline solution and connected to the positive (left) and negative (right) posts of the DC supply; the effects of imposing a DC current the nails b) after five and c) ten minutes.
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Stress Corrosion Cells

If an ordinary nail is dropped into a vessel of salt water, it will be attacked, and, after some time, rust will be observed discoloring the water. The initial points of attack will be, in almost every case, the point and the head. This is an example of a type of cell known as a stress cell. The following Figure shows how dramatic this effect can be on the heads and nuts used to hold fire hydrants on their base in the soil.

![Severe corrosion of fire hydrant bolts and nuts due to stress cells. (Courtesy of Drinking Water Services, City of Ottawa)](image)

In these cases the two electrodes are of the same metal and the electrolyte is uniform. The difference lies in that one electrode is more mechanically stressed than the other. The area of high stress is always the anode of the cell, made that way by the extra energy supplied by the stress itself. Stress cells can take on two basic forms. One, like the nail just described, has its anode established by residual internal stress or stress left because of something which has happened to the metal. In the case of the nail, the stress was caused by cold-forming of the head and point. If these stresses had been relieved by heating the nail at a moderate temperature[1] and letting it cool slowly, the stresses will disappear and this type of stress cell will be eliminated.
In the other type of stress cell, the metal is part of some kind of structure which is under stress. The most highly stressed part of the metal becomes the anode, with the less stressed or unstressed metal acting as the cathode. [1] For carbon steels this temperature would be 75-80°C below the $A_t$ transformation temperature, which is about 727°C. Therefore stress relieving is done at approximately 650°C for about one hour or until the whole part reaches the temperature.
Surface Film Corrosion Cells

The surface of a metallic object can be easily reacted in normal atmospheres making it behave quite differently from a piece of unreacted metal, a situation closely related to dissimilar metal corrosion. A film may be formed which is invisible, actually only a few molecules in thickness, but which may have a potential as much as 0.3 V different from the unfilmed metal. Naturally, such a potential difference is enough to create an active corrosion cell. Steels in soil have a tendency to film with time. ‘Old’ steel, i.e. steel which has been in the ground for several years may then become cathodic with respect to ‘new’ steel, even when the two are identical in composition pipe as shown in the following Figure. It is thus strictly a surface phenomenon.

A common occurrence of surface film cell is found in older distribution piping systems where a section of pipe has been replaced because of corrosion damage. The new piece of pipe, exposed to the same corrosion conditions, logically would be expected to last as long as the original section. However, the new section will usually fail sooner than expected unless it is electrically insulated from the remainder of the system.
Microbial Corrosion Cells

As illustrated in the following Figure, microorganisms tend to attach themselves to solid surfaces, colonize, proliferate, and form biofilms which may in turn produce an environment at the biofilm/metal interface radically different from the bulk medium in terms of pH, dissolved oxygen, organic and inorganic species.
Different stages of biofilm formation and growth

Since the biofilm tends to create non-uniform surface conditions, localized attack might start at some points on the surface leading to localized corrosion, usually in the form of pitting [11]. Industrial systems are likely to contain various structures where microbiologically induced corrosion (MIC) and biofouling can cause problems: open or closed cooling systems, water injection lines, storage tanks, residual water treatment systems, filtration systems, different types of pipes, reverse osmosis membranes, and potable water distribution systems.

Current conceptual models concur that there are three stages in the pitting corrosion: initiation, metastable pitting, and active pitting. When microorganisms are involved in the corrosion of metals, the situation is more complicated than it is in an abiotic environment, because microorganisms not only modify the near-surface environmental chemistry via microbial metabolism but also may interfere with the electrochemical processes occurring at the metal-environment interface.
The anaerobic corrosion of iron was noted in the 19th century and many theories were proposed about its mechanism. Decades of scientific research projects and investigations on the complex influence of microbes on increasing or decreasing corrosion rates have provided a much deeper insight in the role microorganisms play on the life of systems exposed to waters and grounds where they proliferate. The mechanisms potentially involved in MIC are summarized as:

- Cathodic depolarization, whereby the cathodic rate limiting step is accelerated by micro-biological action;
- Formation of occluded surface cells, whereby microorganisms form "patchy" surface colonies. Sticky polymers attract and aggregate biological and non-biological species to produce crevices and concentration cells, the basis for accelerated attack;
- Fixing of anodic reaction sites, whereby microbiological surface colonies lead to the formation of corrosion pits, driven by microbial activity and associated with the location of these colonies;
- Underdeposit acid attack, whereby corrosive attack is accelerated by acidic final products of the MIC "community metabolism", principally short-chain fatty acids.

Certain microorganisms thrive under aerobic conditions, whereas others thrive in anaerobic conditions. The pH conditions and availability of nutrients also play a role in determining what type of microorganisms can thrive in a particular soil environment. Microorganisms associated with corrosion damage are classified as:

- Anaerobic bacteria that produce highly corrosive species as part of their metabolism;
- Aerobic bacteria that produce corrosive mineral acids;
- Fungi that may produce corrosive by products in their metabolism, such as organic acids. Apart from metals and alloys these can also degrade organic coatings and wood;
- Slime formers that may produce concentration corrosion cells on surfaces.

MIC is responsible for the degradation of a wide range of materials. A useful representation of materials degradation by microbes was made in the form of a pipe cross section as in the following Figure[12].

Schematic illustration of the principal methods of microbial degradation of metallic alloys and protective coatings.
Microbial Corrosion Cells

coatings. 1 - Tubercle leading to differential aeration corrosion cell and providing environment for “2”; 2- Anaerobic sulfate reducing bacteria (SRB); 3- Sulfur-oxidizing bacteria, producing sulfates and sulfuric acid; 4- Hydrocarbon utilizers, breaking down aliphatic and bitumen coatings and allowing access of “2” to underlying metallic structure; 5- Various microbes producing organic acids as end-products of growth, attacking mainly non-ferrous metals/alloys and coatings; 6- Bacteria and molds breaking down polymers; 7- Algae forming slimes on above-ground damp surfaces; 8- Slime forming molds and bacteria (which may produce organic acids or utilize hydrocarbons), providing differential aeration cells and growth conditions for “2”; 9- Mud on river bottoms, etc., providing matrix for heavy growth of microbes (including anaerobic conditions for “2”); 10- Sludge (inorganic debris, scale, corrosion products, etc.) providing matrix for heavy growth and differential aeration cells, and organic debris providing nutrients for growth; 11- Debris (mainly organic) on metal above ground, providing growth conditions for organic acid-producing microbes.

Most metals and their alloys (including stainless steel, aluminum and copper alloys), polymers, ceramic materials, and concrete can be attacked by microorganisms. The synergistic effect of different microbes and degradation mechanisms should be noted in the Figure above.

The muddy bottom of any relatively stagnant body of water with a high biological oxygen demand often supports massive growth of sulfate reducing bacteria (SRB), as may waterlog soils. The following Figure shows the pitted area of a 15 cm circulating water line from the supply to the auxiliary vacuum pumps.

Circulating water MIC cell corrosion footprint. (Courtesy of Russ Green, TMI)

Note the cluster of hemispherical pits and the long striated grooves due to the MIC attack. Each pit represents a localized cluster of anaerobic bacteria that have become destructive and begun damaging the pipe wall. The grooves are the results of bacteria attacking along the steel structure probably due to the drawing process in manufacturing the pipe. Any metallic installations buried or immersed in such environments can be expected to suffer badly from microbiological corrosion.
The most serious economic problem is to pipelines as in the example shown in the following Figure, although sheet piles, hulls of ships, piers, and so on are frequently attacked. In some instances, cast iron pipes of **6.3 mm thickness** have become perforated within 1 year under such conditions, while perforation in 3 years is common.

Pit and perforation of 6.3 cm internal diameter carbon steel pipe carrying heavy oil. The pit morphology is typical of sulfate reducing MIC attack [13]. (Courtesy of Kingston Technical Software)
Simple Corrosion Experiments

The Corrosion Doctors Web site contains a wide spectrum of theories about corrosion phenomena and ways to apply protective measures. The present module describes simple experiments that have been carried out to illustrate the principles behind these concepts. While most of the experiments presented here do not require special chemical handling skills, SOME STILL DO!

The experimental results presented in this module often require patience more than any other ingredients. We have tried to illustrate the results of these experiments so that students taking our distance learning course, for example, would be able to visualize the effects of corrosion without actually performing the experiments themselves, more or less as virtual experiments. However, you are greatly welcomed to join the club of fanatics that enjoy testing the insolence of metallic materials to their limit.
Corrosion in Action

By LaQue, May, & Uhlig

The text of this book is essentially the narrative of the motion picture "Corrosion in Action". In its present form this narrative is supplemented by appropriate references to literature which will provide more detailed information on particular points. In addition, there is a description of the experiments shown in the film so that these can be undertaken by any students who may have an opportunity to study the subject in the laboratory. (reference)

The film itself was produced by Inco as an aid to the understanding of some of the electrochemical processes that result in corrosion. It was felt that ad knowledge of these principles would improve the basis for action in avoiding corrosion by choosing the proper materials and using them to best advantage. As stated in the final paragraph, the goal is to have the right metal used in the right way in the right place. It is hoped that making the substance of the film available for ready reference in this form will prove to be a useful supplement to the motion picture itself in achieving this objective.

In nature the forces that cause corrosion are as constantly in action as the sea. Everyone has seen corrosion turn useful structures into crumbling skeletons, productive machines into frozen hulks, automobiles into piles of junk. It costs more than 6 billion dollars in a year. It dissipates our resources and the fruits of our labor. It interrupts production. It causes accidents.

Different metals are affected to different degrees and corrosive attack takes many different forms. Attack may be by general tarnishing or rusting with occasional perforations in especially affected areas (1). Corrosion may develop preferentially near the junction of two different metals (2). The metal may suffer highly localized attack by pitting (3). The strength of a metal may be destroyed by cracking induced by corrosion (4). We are all too familiar with corrosion in action in these ways. Corrosion may also be confined to crevices, under gaskets or washers, or in sockets (5). It may have the effect of removing one of the constituents of an alloy so as to leave a weak residue (6).

The study of corrosion considers reactions between a metal and its environment (7). It also concerns the suppression of corrosion by changing the characteristics of metals and their environments. The great progress in the battle against corrosion has been based on a better understanding of the natural forces concerned and on the development of the scientific principles upon which effective control of corrosion must be based. It is possible to explain how this action occurs and what can be done to reduce it by illustrating some of these principles.

Module Seven of CCE 281 Corrosion: Impact, Principles, and Practical Solutions

A Classic Corrosion Experiment : Anodes and Cathodes in Corrosion Reactions

Purpose

- To show the existence and location of anodes and cathodes in corrosion processes.
Apparatus & Materials

- Agar agar gel containing 3% sodium chloride 5% potassium ferricyanide solution 1% phenolphthalein solution Three iron nails
- Three iron nails with point half copper plated One iron nail with point half plated with zinc One milliammeter, 0-10 ma., D. C., range
- Two strips of thin sheet zinc, 1/2" x 6" x .04" (approximate)
- Wires and clamps for connecting nails and zinc strips to milliammeter
- Three or more Petri dishes large enough to accommodate nails (about 50-60 mm. diameter)

Procedure

a. Prepare 250 ml. agar agar gel containing 3% sodium chloride. To do this, dissolve 7.5 g sodium chloride in 250 ml. distilled water. Add 5 g powdered agar agar and boil the mixture until the agar is dispersed. Then add 5 ml of the potassium ferricyanide solution and 1 ml. of the phenolphthalein solution.

b. To demonstrate the accumulation of alkali at cathode areas and corrosion at anode areas, fill a Petri dish with the hot gel solution and allow to cool without disturbance until it begins to set. At this point place one of the partially copper plated nails in the gel and observe the subsequent color developments over a period of several hours. The red color develops along the copper surface because it is performing as a cathode and the blue color develops on the bare iron surface that is the anode in the copper-iron galvanic couple. The red color results from the accumulation of alkali on cathode areas and the blue color reveals the presence of ferrous ions at the iron anode surface. Save for comparison with experiment (f).

c. Repeat experiment (b) using a nail that is partially plated with zinc. Note the color development over several hours. In this instance no blue coloration appears because zinc is more active than iron and performs as the anode in the zinc-iron galvanic couple. Zinc ions form at the anode but they do not form a colored compound with the indicators used. Hence, no color develops on the zinc area.
d. To demonstrate the existence of and to locate anodes and cathodes on a single metal surface, repeat experiment (b) using a plain bare iron nail. Note the development of blue and red colors at different places on the nail. (Most frequently the blue color develops on the cold worked head and point while the red develops on the shank.) Save for comparison with the results in experiment (e).

![Image of anodes and cathodes](image1.png)

e. To demonstrate the role of galvanic anodes in cathodic protection, solder a wire connection onto the head of a bare iron nail and clip a second wire on a strip of zinc. Bend the zinc strip so that it will rest in a Petri dish without support. Connect the nail and strip of zinc to a milliammeter. Then pour warm gel solution into a Petri dish and allow to cool as in experiment (b). As the gel begins to set, place the nail and zinc strip in the gel. Note that iron is not corroding and forming iron ions. The development of a red color on the iron surface shows that it is now acting entirely as a cathode. (A local red coloration that may develop on the zinc strip where it comes out of the gel is due to a secondary oxygen concentration cell effect on the
zinc. This is to be distinguished from the reactions of the zinc-iron nail galvanic couple. Compare with the results of experiment (d).

f. To demonstrate that galvanic anodes through cathodic protection may also eliminate destructive galvanic corrosion, repeat experiment (e) using a partially copper plated nail in place of the bare iron nail. Compare the results with those of experiment (b). Note again that a red color develops on the nail receiving protection from the sacrificial zinc anode.

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**Answers to example problems**

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