CHEMICAL PROPERTIES
Corrosion

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While there are many different chemical properties, one of the most important for dental materials trying to survive in the mouth is corrosion. We will focus on that property for this module.

Corrosion can involve any class of materials (metals, ceramics, polymers, composites) depending on the bonding states, but it primarily affects metals. Unfortunately most naturally occurring metals are exposed to air, water, or something else and react to form a ceramic ore. To collect the metal from the ore, we mine the ore, heat it up to drive off the other part of the compound, and then we are left with the metal. Unfortunately, the environment immediately starts to convert it back into the ore. So, it is important to select metals for which we can protect or limit the corrosion.

[CLICK] There are two types of corrosion, chemical and electrochemical ones. CHEMICAL corrosion occurs by familiar bimolecular reactions. An example is oxygen in the air coming in contact with iron and producing iron oxide. The surface of a dental amalgam can become black if has chemically reacted with sulfur compounds in the air (as part of pollution) that tarnishes the amalgam.

Most reactions that are possible occur by both chemical and electrochemical paths. The environment will determine which one is more likely. In the body, and particularly the mouth, most metallic reactions occur by electrochemical corrosion. For electrochemical corrosion, the reaction occurs via two half-cell reactions separated at a distance but connected by a conducting circuit. Next, let's look at those details.

ELECTROCHEMICAL CELL

Components = anode, cathode, electrolyte, and circuit.

CIRCUIT

Nernst Equation
$$\Delta E = (E°_a - E°_b) + (0.0592/n)\,(\ln\,[C]/[A])$$

H
↑
H$^+$ ← e$^-$

e$^-$
↑
M → M$^+$

ANODE   CATHODE
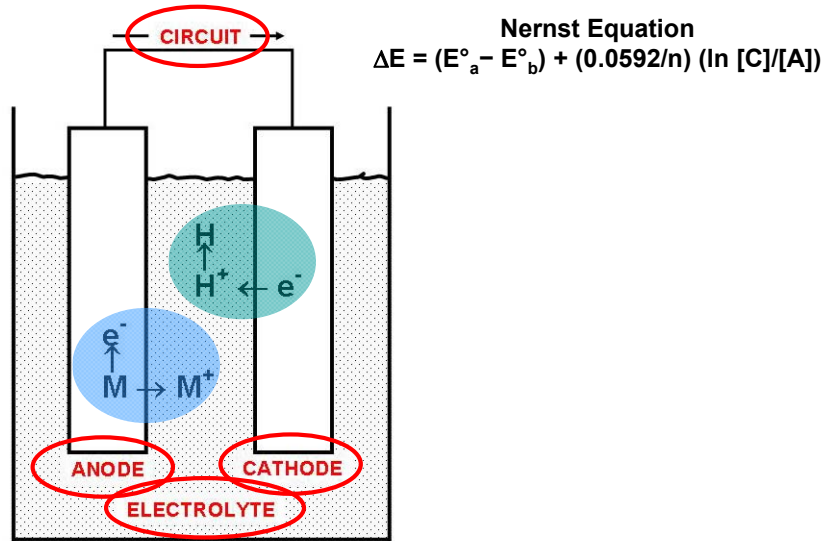
ELECTROLYTE

Electrochemical corrosion requires the presence of an identifiable **[CLICK]** anode, **[CLICK]** cathode, **[CLICK]** electrical circuit, and **[CLICK]** electrolyte. If any one is missing, there will be no electrochemical corrosion. **[CLICK]** Thermodynamics predicts the likelihood or electrochemical potential for an atom of metal (or alloy) at the anode to go into solution as an ion. The other metal (or alloy) electrode behaves as a cathode. This half-cell reaction generates an electron which flows through the circuit from the anode to the cathode where undergoes a second half-cell reaction that consumes it. **[CLICK]** The cathodic reaction could involve any process but usually involves formation of hydrogen. As corrosion occurs, the anode become consumed. That is the site where changes are observed.

Anodes and cathodes may be large (e.g., restorations) or small (e.g., adjacent crystals that are different phases). They usually represent different materials but can be made of the same material and simply be seeing different local conditions. If a single phase material is covered partially on its surface, the composition of the electrolyte will be different under its film (e.g., lower oxygen concentration) and that makes that portion of the surface behave as an anode. Also, part of a restoration could be under more local stress than another. The stressed region behaves as an anode.

[CLICK] The entire electrochemical cell equilibrium can be described by an equilibrium equation modified in terms of half-cells. You are NOT responsible for knowing this equation, other than it is called the **Nernst Equation** and may arise in your studies of human physiology.

THERMODYNAMICS

Corrosion potentials for half-cell reactions (electrochemical series) .

GALVANIC SERIES

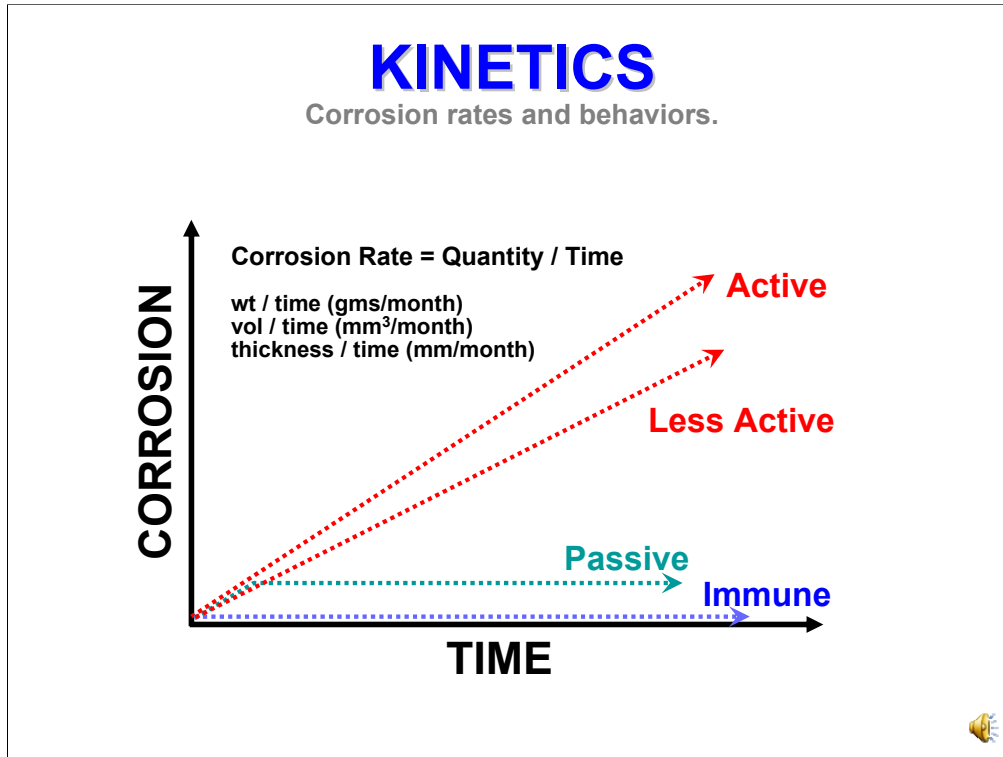| Electrode Reaction	E_0 (volts)		Electrode Reaction	E_0 (volts)
Au → Au+	+1.68		Cr → Cr+++	- 0.913
Au → Au+++	+1.50		Nb → Nb+++	- 1.1
Pt → Pt++	+1.19		Mn → Mn++	- 1.18
Ir → Ir+++	+1.000		V → V++	- 1.18
Pd → Pd++	+0.987		Ti → Ti+++	- 1.21
Hg → Hg++	+0.857		Pu → Pu++++	-1.28
Rh → Rh+++	+0.80		Np → Np++++	-1.354
Ag → Ag+	+0.799		U → U++++	-1.50
Hg → Hg++	+0.789		Zr → Zr++++	-1.53
Cu → Cu+	+0.521		Ti → Ti++	-1.63
Cu → Cu++	+0.337		Al → Al+++	-1.66
H₂ → H+	0.000		Hf → Hf++++	-1.70
D₂ → D+	-0.0034		U → U+++	-1.80
Fe → Fe+++	-0.036		Be → Be++	-1.85
Pb → Pb++	-0.126		Np → Np+++	-1.86
Sn → Sn++	-0.136		Th → Th++++	-1.90
Ge → Ge++++	-0.15		Pu → Pu+++	-2.07
Mo → Mo+++	-0.2		Am → Am+++	-2.32
Ni → Ni++	-0.250		Mg → Mg++	-2.37
Co → Co++	-0.277		La → La+++	-2.52
Mn → Mn+++	-0.283		Na → Na+	-2.714
Tl → Tl+	-0.336		Ca → Ca++	-2.87
In → In++	-0.342		Sr → Sr++	-2.89
Cd → Cd++	-0.402		Ba → Ba++	-2.90
Fe → Fe++	-0.440		Ra → Ra++	-2.92
Ga → Ga++	-0.53		Cs → Cs+	-2.923
Cr → Cr++	-0.74		K → K+	-2.925
Zn → Zn++	-0.762		Rb → Rb+	-2.925
V → V+++	-0.876		Li → Li+	-3.045

For any particular electrolyte (at any temperature and pressure), there is a series of electrochemical potentials for each possible half-cell reaction that predict the propensity for reaction of metallic elements into ions. The table above is for seawater at 1 atmosphere and at room temperature. It is a particular ELECTROCHEMICAL SERIES called the GALVANIC SERIES and is used to estimate the half-cell reactions in the mouth. Seawater is very close to the electrolytes found in the body.

Let's examine the table. Half-cell reactions are shown in 2 columns for most of the metals of interest. **[CLICK]** Run down the left-hand side and then restart at the top. The values are reported with respect to a standard half-cell reaction for hydrogen which is defined as zero. **[CLICK]** Values that are positive represent half-cells that require more energy than the standard. Values that are negative, require less energy. The difference between the values for the electrodes tells you the relative propensity to corrode. Large values indicate stronger corrosion potentials. To use the table, you look up the 2 half-cells of interest for the metals behaving as the electrodes. The one that is more electronegative will be the anode and the other the cathode.

For example if we had 2 electrodes of Ag and Cu **[CLICK] [CLICK]**, then Ag is the cathode and Cu is the anode. If you had 2 half-cells involving Pd **[CLICK] [CLICK]** and Ni **[CLICK] [CLICK]** , then Ni would be the cathode and Pd would be the anode. If you had 2 half-cells involving Fe **[CLICK] [CLICK]** and Mg **[CLICK] [CLICK]** , then Fe would be the cathode and Mg would be the anode. In commercial systems in which a lot of Fe is involved, Mg is attached as a sacrificial anode to protect the Fe from initial corrosion. There is a huge potential difference and so Mg is strongly anodic.

Ideally, all half-cells for all possible combinations of alloys (not just metals) should be shown in the chart. We use the present ones as initial estimates based on the dominance of elements in alloy phases. For real systems, we measure the values as needed by running corrosion tests.

KINETICS
Corrosion rates and behaviors.

Corrosion Rate = Quantity / Time

wt / time (gms/month)
vol / time (mm^3/month)
thickness / time (mm/month)

CORROSION

Active

Less Active

Passive

Immune

TIME

For any corrosion reaction, **[CLICK]** the corrosion rate reveals the amount of material that is converted into corrosion product per unit of time. You can report the weight, the volume, or the thickness of material involved. A typical corrosion rate could be 1 mm per month. The units are corrosion/time.

[CLICK] As corrosion proceeds, it could occur steadily with time. Materials that are corrosion prone and continue to corrode are called ACTIVE. Th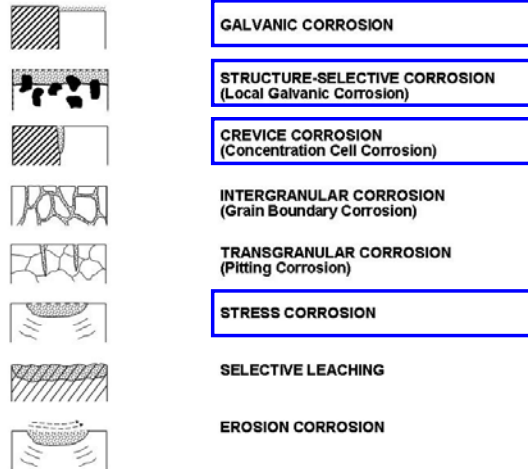e slope of the line is the actual corrosion rate. **[CLICK]** Materials that corrode at a slower rate will have a lower slope.

[CLICK] If systems in which corrosion product accumulates on the exposed surface, continued corrosion will substantially impede or prevent further corrosion. These materials are called PASSIVE. Their passivating film stops corrosion even if the material initially corrodes at a high rate. An example of this process is stainless steel.   Chromium is included in stainless steels because it quickly forms an oxide that creates a protective surface film. The film forms almost instantaneously, is extremely thin, and is transparent.

[CLICK] Systems in which the metal or alloy are not corrosion prone are called IMMUNE. Remember that these classifications are relative to the temperature, pressure, electrolyte, and electrode combinations. Gold alloys are IMMUNE under most circumstances, However, under certain intraoral conditions, they will behave as ACTIVE materials. Immune or passive materials at room temperature often become active at higher temperatures.

MECHANISMS

Major classifications of electrochemical corrosion mechanisms.

- GALVANIC CORROSION
- STRUCTURE-SELECTIVE CORROSION (Local Galvanic Corrosion)
- CREVICE CORROSION (Concentration Cell Corrosion)
- INTERGRANULAR CORROSION (Grain Boundary Corrosion)
- TRANSGRANULAR CORROSION (Pitting Corrosion)
- STRESS CORROSION
- SELECTIVE LEACHING
- EROSION CORROSION

There are a tremendous number of possible corrosion situations in the real world. A few are illustrated. The four principal ones that affect materials in dentistry are indicated. **[CLICK]**

In the first schematic, two different large electrodes are shown touching. The left is the cathode. The right is the anode. Both are presumed to be immersed in electrolyte. The fact that they are touching creates a circuit. The dotted surface represents anodic material being lost to corrosion. This is called GALVANIC CORROSION and is the classic macro-corrosion situation.

A smaller version of the same thing occurs when there are 2 different phases in the same material. Different grains (representing different phases) act as local anodes and cathodes. This is called LOCAL GALVANIC CORROSION or structure-selective corrosion.

Any crevice or crack that exists either between a restoration and tooth structure, or between grains, or between a portion of plaque on the surface and the restoration, creates a locally different electrolyte composition and changes the electrochemical potentials. This is called CREVICE CORROSION or concentration cell corrosion. It is due to the fact that locally different concentrations in the electrolyte create different half-cells with the same material. This is extremely common in dentistry.

Finally, STRESS CORROSION occurs when different parts of a restoration are under different levels of stress. This also produces different local electrochemical potentials or half-cells. Portions under higher stresses are more corrosion prone (or anodic).
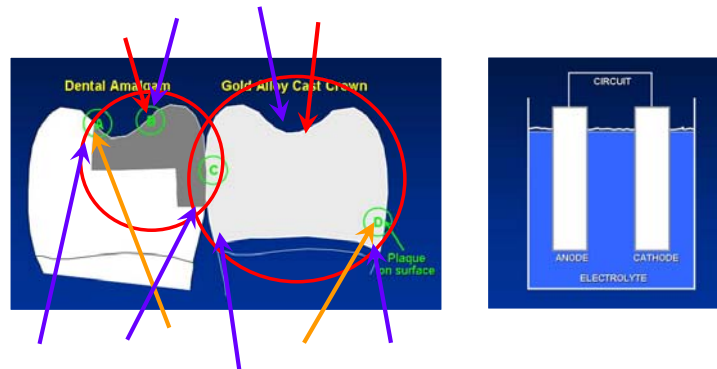
Be able to recognize these 4 corrosion situations and know their names.

6

INTRAORAL CORROSION

Chemical and electrochemical cells and corrosion types.

Electrochemical Corrosion Mechanisms:
a. **Galvanic Corrosion** (macro-galvanic corrosion)
b. **Structure-Selective Corrosion** (**local galvanic corrosion**)
c. **Concentration Cell Corrosion** (**crevice corrosion**)
d. **Stress Corrosion**

Dental Amalgam Gold Alloy Cast Crown

Plaque on surface

CIRCUIT
ANODE CATHODE
ELECTROLYTE

Now let's see if you can recognize each type of corrosion situation **[CLICK]** in a complex clinical situation **[CLICK]** involving of a cast gold crown adjacent to a dental amalgam restoration. We are assuming everything is bathed in saliva. An electrochemical cell is shown for reference. Remember that the relative rate of corrosion will always depend on the magnitude of the electrochemical potential difference between the half-cells. If these are small, then corrosion will occur very slowly.

Identify **galvanic corrosion. [CLICK]** Where the gold restoration and amalgam alloy touch (letter C) is an electrical circuit and potential corrosion. Gold alloys are strongly electropositive and typically are cathodes. Under most circumstances, gold alloys are fabricated with only one microstructural phase present. All the phases in amalgam are more electronegative than gold phases and behave as anodes. Saliva acts as the electrolyte. This is macro galvanic corrosion. **[CLICK]**
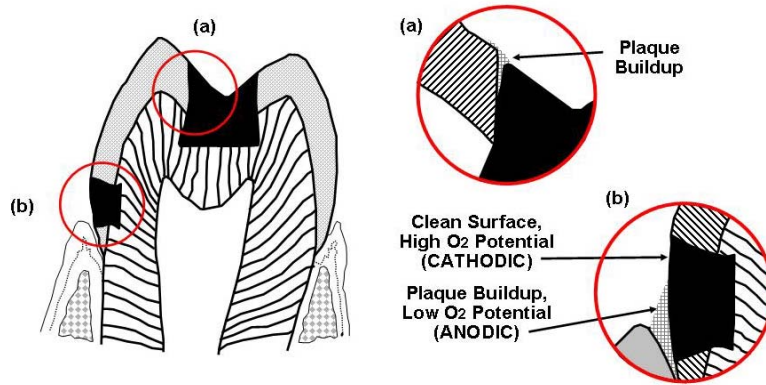
Where does local galvanic corrosion occur? [CLICK] (It occurs at letter B and all exposed surface on the amalgam). As you will learn later, amalgam is composed of several phases, and the gamma 1 or 2 phases are anodic compared to the gamma phase. The gold alloy may also undergo local galvanic corrosion. When we take advantage of precipitation hardening during fabrication to make the alloy stronger and better able to resist more extreme mechanical loading situations (e.g., some bridges and partial dentures), the special gold alloy composition which is used allows a second phase to be precipitated. The two phases are not electrochemically the same. One phase acts as a local anode, while the other functions as the local cathode. This leads to pitting. While it does not occur quickly, it will affect the gold alloy restoration over the long term. **[CLICK]**

Find examples of **crevice corrosion**. (Look at letters D and A) **[CLICK]** Plaque encourages crevice corrosion and causes pitting. Quite often the facial surfaces of a cast crown, especially near gingival margins, begin to looks dull over 15 to 20 years due to the effects of pitting. Plaque suppresses the local pH and pO_2 in comparison to other uncovered portions of the restoration surface. Since the local electrolyte varies in composition. The surface under the plaque behaves as an anode and undergoes corrosion. The same thing also happens anywhere on the amalgam surface that plaque might occur. Finally, if there is a gap at the margin of the amalgam restoration, as indicated by A, where another concentration cell can occur. This is another type of crevice corrosion. **[CLICK]**

Where does **stress corrosion** occur? (Look at letter B) **[CLICK]** During function, mechanical stresses often are not distributed uniformly throughout the restoration. Higher stresses tend to occur at points of occlusal contact or near margins where the stresses are higher and being transferred to tooth structure. Higher-stress regions behave as anodes and are more prone to electrochemical corrosion.

Now let's see if you can recognize the corrosion shown in (a) and (b). Correct. **[CLICK]** Crevice corrosion. This is very common in dental situations, especially when patients do not maintain good oral hygiene.

QUICK REVIEW

Review of terminology and concepts for corrosion.

- **What are the 2 major TYPES of corrosion?**
  CHEMICAL, ELECTROCHEMICAL

- **What COMPONENTS are required for electrochemical corrosion?**
  ANODE, CATHODE, ELECTROLYTE, CIRCUIT

- **What is the name of the TABLE of electrochemical potentials (half-cell reactions) for sea water as the electrolyte?**
  GALVANIC SERIES

- **What terms are used to describe CORROSION RATES?**
  ACTIVE, PASSIVE, IMMUNE

- **What corrosion TYPES are normally encountered in dentistry?**
  GALVANIC CORROSION, LOCAL GALVANIC CORROSION, CREVICE CORROSION, STRESS CORROSION.

- **What is another name for CREVICE CORROSION?**
  CONCENTRATION CELL CORROSION

Here is a quick review of the concepts from this module.

[CLICK] (1) What are the 2 major types of corrosion?
[CLICK]

[CLICK] (2) What components are required for electrochemical corrosion?
[CLICK]

[CLICK] (3) What is the name of the table of electrochemical potentials (half-cell reactions) for sea water as an electrolyte?
[CLICK]

[CLICK] (4) What terms are used to describe corrosion rates?
[CLICK]

[CLICK] (5) What corrosion types are normally encountered in dentistry?
[CLICK]

[CLICK] (6) What is another name for crevice corrosion?
[CLICK]

THANK YOU

THANK YOU.