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**Tarnish and Corrosion**

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## “Tarnish and Corrosion”

### *Introduction:*

In most cases corrosion is undesirable. However, in dental practice a limited amount of corrosion around the margins of dental amalgam restorations may be beneficial, since the corrosion products tend to seal the marginal gap and inhibit the ingress of oral fluids and bacteria.

A common example of corrosion is rusting of iron, a complex chemical reaction in which iron combines with oxygen in air and water to form the hydrated oxide  $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ . This oxide layer is porous, bulkier, weaker and more brittle than the metal from which it formed. Loss of non-adherent oxide exposes a fresh underlying metal surface, which enhances continuation of the corrosion process. One method to prevent this corrosion is to alloy iron with chromium forming stainless steel.

High noble alloys used in dentistry are so stable chemically that they do not undergo significant corrosion in the oral environment; the major components of these alloys are gold, palladium, and platinum. Silver is not considered noble by dental standards, since it will react with air, water and sulfur to form silver sulfide, a dark discoloration product.

Metals undergo chemical and electrochemical reactions with the environment resulting in dissolution and formation of chemical compounds. Commonly known as the corrosion products, the chemical compounds may accelerate, retard or have no influence on the subsequent deterioration of the metal surface.

A primary requisite of any metal used in the mouth is that it must not produce corrosion products that will be harmful to the body. Some metals which are completely safe in elemental state can form hazardous or even toxic ions or compounds.

Several aspects of the oral environment are highly conducive to corrosion. The mouth is warm and moist, and is continually subjected to fluctuations in temperature. Ingested foods and liquids have wide range of pH. Acids are liberated during breakdown of foods, and the resulting debris often adheres tenaciously to the metallic restoration, providing a localized condition that promotes accelerated reaction between the corrosion products and the metal or the alloy. Because it has the least tendency to become ionized, gold resists chemical attack very well. Thus, it was natural that this most noble metal was employed early in modern dental history for the construction of dental appliances.

### **Tarnish and Corrosion:-**

A differentiation should be made between tarnish and corrosion even though there is a definite technical difference. It is difficult clinically to distinguish between the two phenomenon and the terms are often used interchangeably in dental literature.

**Tarnish:** - is surface discoloration or a slight loss or alteration of the surface finish or luster. In the oral cavity tarnish often occurs from the formation of hard and soft deposits on the surface of the restoration.

Calculus is the principal hard deposit and its color varies from light yellow to brown. The soft deposits and plaques are films composed mainly of microorganisms and mucin stain or discoloration arises from pigment producing bacteria, drug

containing chemicals such as iron or mercury and absorbed food debris.

Surface discoloration may also arise on a metal from the formation of thin films such as oxides, sulfides or chlorides. Such films may even be protective however it is an early indication of corrosion.

**Corrosion:** - is defined as a physiochemical interaction between a metal and its environment to form metallic compound. The resultant changes in the metal can lead to an impairment of its function and can also change the environment in which the metal is situated.

Corrosion is to all intents and purposes the reversal of the reactions employed in extraction process. Frequently, the corrosion products of a metal are very similar to the compound from which the metal was originally extracted. Eg: Iron is extracted originally from iron oxide, and rust is simply hydrated iron oxide.

In specific sense, corrosion is not merely a surface deposit, but it is an actual deterioration of a metal by reaction with its environment. Frequently, especially with surfaces under stress or with inter granular impurities in the metal or with corrosion products that does not completely cover the substrate metal; the corrosion attack rate may actually increase with time. In addition corrosion attack that is extremely localized may cause rapid mechanical failure of a structure even though the actual loss of metal is very small.

This disintegration of the metal may occur through the action of moisture, atmosphere, acid, or alkaline solutions and other chemicals. Tarnish is often the forerunner of corrosion.

The film that is deposited and produces tarnish in time form or accumulate elements or compounds that chemically attack the metallic surface. For example: eggs and certain other foods contain significant amount of sulfur. Various sulfides such as hydrogen and ammonium sulfides corrode silver, copper and mercury, and similar metals present in dental alloy and amalgam. In addition water, oxygen and chloride ions are present in the saliva and contribute to corrosion attack. Various acids such as phosphoric, acetic and lactic acids are present at times at proper concentration and pH these can lead to corrosion.

The oral environment is an aggressive environment. Materials may dissolve in the water that is present or release soluble components. They may discolor or break down due to absorption of substances from the water or they may undergo tarnish and corrosion.

All of these possibilities can adversely affect the chemical stability of the materials and limit their durability. The products released may have an adverse effect- on the biological environment both locally and systemically.

Metals undergo chemical reactions with non-metallic elements in the environment to produce chemical compounds, commonly known as Corrosion products. These compounds may accelerate, retard or have no influence on the subsequent deterioration of the metal surface.

One of the primary requisites of any metals that are to be used in the mouth is that it must not produce corrosion products that will be harmful to the body. It is unfortunate that the oral environment is very conducive to the formation of corrosion products. The mouth is moist and continually subjected to fluctuations in temperature. The food and liquids ingested have a

wide range of pH. Acids are liberated during the breakdown of foodstuffs. This food debris often adheres tenaciously to the metallic restorations thus providing a localized condition that is extremely conducive to an accelerated reaction between the corrosion products and metal or alloys. All of these environmental factors contribute to the degrading process known as Corrosion.

### Types of Corrosion: -

There are two general types of corrosion reactions: -

- a) Chemical or dry corrosion
- b) Electrochemical or wet corrosion.

### Chemical (Dry) Corrosion: -

In this type of corrosion there is a direct combination of metallic and nonmetallic elements to yield a chemical compound through a process such as oxidation, halogenation, or sulfurization reactions.

A good example is the discoloration of silver by sulfur, where silver-sulfide forms by corrosion reaction. It can also be a corrosion product of dental gold alloys that contain silver. This mode of corrosion is also referred to as *Dry Corrosion*, since it occurs in the absence of water or another fluid electrolyte.

### Electrochemical (Wet) Corrosion: -

Chemical corrosion is seldom isolated and is invariably accompanied by *Electrochemical Corrosion*, which is also known as *Wet Corrosion*, since it requires the presence of water or some other fluid electrolyte. This mode of corrosion is much more important for dental restorations than dry corrosion.

### Types of Electrochemical corrosion: -

- a) Galvanic corrosion – Electrogalvanism / Dissimilar metals

- b) Heterogeneous surface composition
- c) Stress corrosion.
- d) Concentration cell corrosion.

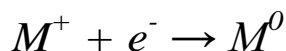
The starting point for discussion of electrochemical corrosion is the electrochemical cell. Such a cell is composed of three essential components, namely the *Anode*, *Cathode* and *Electrolyte*.

An apparatus is employed to measure the voltage and current between the two electrodes. In this example the dental amalgam restoration can be the anode and a gold alloy restoration can represent the cathode, and the saliva may act like the electrolyte.

The anode is the surface or sites on a surface where positive ions are formed (i.e. the metal surface that is undergoing *oxidation* and *is corroding*) with the production of free electrons: -



At the cathode or cathodic sites, a *reduction reaction* must occur that will consume the free electrons produced at anode.



The electrolyte supplies the ions needed at the cathode and carries away the corrosion products at the anode. The external circuit serves as the conduction path to carry electrons from the anode to the cathode.

If a voltmeter is placed into the circuit instead of an ammeter, an electric potential difference may be measured. It should be pointed out that this simple electrolytic cell is in principle of a battery. Since the flow of electrons in the external circuit is capable of lighting a bulb in a flashlight.



It is also capable of producing a physiological sensation in the tooth i.e. pain. In order for electrolytic corrosion to be an ongoing process the production of electrons by oxidation reaction at the anode must be exactly balanced by the consumption of electrons in the reduction reaction at the cathode. Normally, a single anode reaction is balanced by any number of cathode reactions. Hence, the cathode is considered to be primary driving force in electrolytic corrosion.

The basis for any discussion of electrochemical corrosion of dental alloys is the electromotive series of the metals, which classifies the metals by their equilibrium values of electrode potential, thereby arranging them in the order of their dissolution tendencies in water. Each of these standard half-cell potentials may be considered as the voltage of an electrochemical cell in which one electrode is the hydrogen electrode designated arbitrarily as zero potential, and the other electrode is the element of interest. The sign of the electrode potential in Electromotive Series indicates the polarity in such a cell, and metals with more positive potential have a lower tendency to dissolve in aqueous environments.

This is very important consideration in determining the rate of corrosion and can be used to reduce or eliminate corrosion. If any two metals are immersed in an electrolyte and are connected by an electrical conductor, an electric couple is formed in such condition metal with the lowest electrode potential goes into the solution. The strength and direction of the current thus depends primarily on the electrode potential of the individual metals.

The position of any of the elements in the electromotive series is dependent not only on the inherent solution tendencies but also on the effective concentration of ions of that element that are present in the environment as the ionic concentration increases in the environment, the tendency for that element to dissolve decreases. The EMF series provides information only about whether a given corrosion reaction can occur. In actual situation, it predicts neither the occurrence nor the rate of corrosion.

The increase in the metal content in the environment may eventually prevent further corrosion. Metal sometimes cease corroding merely because their immediate environment have become saturated with ions of the metals. Such a situation does not occur in a dental restoration because the dissolving ions are removed by foods, fluids, and tooth brushing. Thus, the corrosion continues.

Provided that an electrolyte is present, many types of electrochemical corrosion are possible and all may occur to some extent in oral cavity because with its salts is a weak electrolyte. The electrochemical properties of saliva depend on the composition, concentration of its components, pH, surface tension, and buffering capacity. All these factors may influence the strength of any electrolyte and thus the magnitude of the resulting corrosion process.

An anodic reaction, then is one that produces electrons, where as a cathodic process consumes electrons, this process can be used for electroplating or electro deposition in which the material to be coated is made of an electrolytic cell and the anode is made of the metal to be deposited onto the cathode. The electrolyte serves to transport ions from anode to cathode.

**Galvanic corrosion / Dissimilar metals:-**

An important type of electrochemical corrosion occurs when combinations of dissimilar metals are in direct physical contact. Here the dental reference is to two adjacent restorations where the metal surfaces have different compositions. The alloy combinations that may produce galvanic corrosion or electrogalvanism through the flow of galvanic currents may or may not be in intermittent contact.

The effect of galvanic shock is well known in dentistry. For example, assume that a dental amalgam restoration is placed on the occlusal surface of a lower tooth directly opposing a gold inlay in an upper tooth. Because both restorations are wet with saliva, an electrical circuit exists, with a difference in potential between the dissimilar restorations. When the two restorations are brought into contact, there is a sudden short-circuiting through the two alloys, which may result in the patient experiencing a sharp pain.

When the teeth are not in contact, there is still an electrical circuit associated with the difference in potential or electromotive force between the two restorations. The saliva forms the electrolyte, and the hard and soft tissues can constitute the external circuit, although the electrical resistance of the external circuit is considerable in comparison with that which exists when the two restorations are brought into contact. The current generated is inversely related to the electrical resistance of the metal.

The electric currents measured under these conditions between a gold crown and an amalgam restoration in the same mouth, but not in contact, appear to be approximately 0.5 to 1 microampere ( $\mu\text{A}$ ) with a corresponding difference of approximately 500 millivolts ( $\text{mV}$ ).

A current is present even in a single isolated metallic restoration, although it is less intense. In this situation the electrochemical cell is generated as a electrical potential

differences created by the two electrolytes: saliva and tissue fluids. The term "tissue fluids" is used to denote the dentinal fluid, soft tissue fluids and blood that provide the means for completing the external circuit.

Although the magnitude of these currents usually diminishes somewhat as the restoration ages, it remains indefinitely at the approximate value cited. Coating with a varnish tends to eliminate galvanic shock.

### Heterogeneous Surface Composition:-

Another type of galvanic corrosion is associated with the heterogeneous com the surfaces of dental alloys. Examples include the eutectic alloys and peritectic alloys.

The reason for the previous statement that the corrosion resistance of multiphase alloys is generally less than that of a single-phase solid solution should now be evident. For example, when an alloy containing a two-phase eutectic microstructural constituent is immersed in an electrolyte, the lamellae of the phase with the lower electrode potential are attacked, and corrosion results.

Nominally pure metals, which do not contain significant quantities of impurities or secondary microstructural phases acting as miniature electrodes with different potentials, corrode at much slower rates than alloys.

### Stress corrosion:-

Since the imposition of stress increases the internal energy of an alloy, either through the elastic displacements of atoms or the creation of microstrain fields associated with dislocations the tendency to undergo corrosion will be increased. The deleterious effects of stress and corrosion, called stress corrosion, are most

likely to occur during fatigue or cyclic loading in the oral environment. Small surface irregularities, such as notches or pits, act as sites of stress concentration so that ordinary fatigue failure occurs at nominal stresses below the normal elastic limit of the alloy.

### Concentration Cell Corrosion:-

An important type of electrochemical corrosion is called concentration cell corrosion, which occurs whenever there are variations in the electrolytes or in the composition of the given electrolyte within the system. For example, there are often accumulations of food debris in the interproximal areas between the teeth, particularly if oral hygiene is poor. This debris then produces an electrolyte in that area, which is different from the electrolyte that is produced by normal saliva at the occlusal surface. Electrochemical corrosion of the alloy surface underneath the layer of food debris will take place in this situation.

A similar type of attack may occur from differences in the oxygen concentration between parts of the same restoration, with the greatest attack at the areas containing the least oxygen. Irregularities, such as pits, on restorations provide important examples of this phenomenon. The region at the bottom of such concavity has a much lower oxygen concentration than that at the surface of the restoration, because the pit will be typically be covered with food debris and mucin. The alloy at the bottom of the pit becomes the anode, and the alloy surface around the rim of the pit becomes the cathode. Consequently, metal atoms at the base of the pit ionize and go into solution, causing the pit to deepen.

The rate of such corrosion may be very rapid, since the area of the anodic region is much smaller than that of the cathodic region and there must be a balance of charge transport in both regions.

Consequently, failure may occur much more rapidly than what would be anticipated from uniform surface attack. For this reason, all metallic dental restorative materials should be polished.

An important category of concentration cell corrosion is crevice corrosion, in which preferential attack occurs at the crevices in dental prostheses or at the margins between the tooth structure and restorations because of changes in electrolyte and oxygen concentration caused by the presence of food debris and other deposits.

### Corrosion of dental restorations:-

It is apparent from this discussion that the oral environment and dental structures present complex conditions that can promote corrosion and discoloration. The variables of diet bacterial activity drugs, smoking and oral hygiene habits unquestionably account for a great portion of the differences in corrosion often noted in different patient in whom the same dental alloy, handled in the same manner, has been employed.

**Amalgam:** Both low copper, and high copper dental amalgams undergo, two kinds of corrosion, i.e. chemical corrosion and electrochemical corrosion. Chemical corrosion occurs most notably on the occlusal surface and produces a black Ag<sub>2</sub>S tarnish film. This reaction is limited to the surface and does not compromise any properties, except for esthetics. These amalgams with very high copper also are capable of producing a copper oxide film but that is relatively uncommon.

Electro chemical corrosion is an important mechanism of amalgam corrosion has the potential to occur virtually any where on or with in a set dental amalgam, electrochemical corrosion occurs when ever chemically different sites act as an anode and

cathode. This requires that the sites be connected by an electrical circuit in the presence of the electrolyte, typically saliva. The anode corrodes; producing soluble and insoluble reaction products.

If a dental amalgam is in direct contact with the adjacent metallic restorations such as a gold crown. The dental amalgam is the anode in the circuit. This is called galvanic corrosion i.e. macroscopically different electrode site.

It may also occur when an area is covered by food debris, calculus etc. This area has a locally lowered oxygen and/or high hydrogen ion concentration making it behave more anodically and corrode.

- Cracks and cervical areas produce similar conditions and preferentially corrode
- Regions within a dental amalgam that are under stress also display a greater propensity for corrosion i.e. stress corrosion.

Corrosion of newly placed amalgam restorations occurs within the interface between tooth and restoration. The space between the tooth and alloy permits microleakage of electrolyte i.e. due to percolation and concentration cell occurs.

**Percolation:** One of the consequences of thermal expansion and contraction difference between a restorative material and adjacent tooth structure.

During electrochemical corrosion of low copper dental amalgam the Sn-Hg phase is oxidized to Sn-O and or Sn-O-Cl. The oxychloride species is soluble. The oxide precipitates as crystals and tends to fill up the spaces occupied by the original Sn-Hg phase. Along the margins of the amalgam, Sn Electrochemical

corrosion of Sn - Hg does not release free mercury into the oral environment. Rather mercury immediately reacts with the locally available Ag and Sn from residual amalgam alloy and is reconsumed to form more reaction products.

The ceramic employed in composite material as resin forcing fillers, and as inlay and crowns are corroded by saliva. In the composites, water is absorbed by the resin and comes into contact with the filler. Metallic ions pass from the glass and the accumulation of corrosion products causes stress cracking in the resin, long term immersion studies have shown dramatic decreases in strength of conventional composites. Glasses containing barium, strontium or zinc salts to confer radio opacity are more vulnerable than alumino silicate combination.

However, the microfine materials are more resistant to corrosion because the filler particles are surrounded by heat cured resin that exhibits a lower water uptake. The clinical durability of the microfine is greater than would be expected from simple mechanical properties tests and this illustrates another problem in predicting clinical performance. Their performance clinically is very similar to the more highly filled composite resins.

**Stainless steel:** Steel is an iron based alloys that usually contain less than 1.2% carbon. When 12 % to 30% chromium is added to steel the alloy is commonly called stainless steel.

These steels resist tarnish and corrosion primarily because of the passivating effect of chromium. For passivation to occur a thin, transparent, but tough and impervious oxide layer of  $\text{Cr}_2\text{O}_3$  forms on the surface of the alloy when it is subjected to an oxidizing atmosphere such as room air. This protective oxide layer prevents further tarnish and corrosion, if the oxide layer is ruptured by mechanical or chemical means, a temporary loss of protection



against corrosion will occur. However the passivating oxide layer eventually forms again in an oxidizing environment.

**Nobel Metals:** High gold alloys contain a high percentage of nobel metal elements and thus have an inherent resistance to corrosion because of their low reactivity to oxygen in the atmosphere. Elements in some base metal alloys have a high affinity for oxygen but the oxide film formed can serve as a protective layer against further oxidation and corrosion. This formation of protective film by a reactive substance is called passivation, and metals are well known for their passivation potential are aluminium, chromium and titanium. The most corrosion resistant of these is titanium, which is used for surgical implants, partial denture frameworks and most recently for crowns and bridges.

For alloys to be protected from corrosion they must contain a minimum of 12% chromium. Thus base metal alloys are resistant to tarnish and corrosion because not of their low reactivity but because of their passivity when produced by a chromium oxide layer.

**Silver points:** Used for endodontic filings also undergo corrosion, it may corrode by oxidation reaction to form surface compound on the point of silver amine surface anhydrate. This has cytotoxic effect on tissue.

Although deformation by cutting and trimming the silver points could cause the initiation of some corrosion noted. It was necessary to have some sulfur present to react with the silver to form the cytotoxic product. Sulfur is present in amino acids heparin, thiamine and other compounds in blood, cementum, bone and saliva. Therefore corrosive product probably resulted from an inadequate apical seal of the canal.

## PROTECTION AGAINST CORROSION: -

It has been suggested that for dental casting a coating of a noble metal may be applied to the surface of a second metal for instance a base metal.

However the noble metal is soft and when its surface becomes scratched or pitted to such a depth that the base metal is exposed to the environment, the base metal will be corroded at a rapid rate. This occurs for three reasons: -

- a) A surface defect is created that could set up a concentration cell.
- b) 2 dissimilar metals are in direct contact thus producing a galvanic cell
- c) There is an unfavorable anode-cathode surface area ratio.

Thus rapid corrosion is expected where the coating has been scratched.

When paint or other types of inorganic or organic coating are used for protection any pit or scratch in the protection layer may lead to the rapid corrosion of the base metal. In case of two dissimilar metals paint or other non-conductive film can be used to advantage if it is applied to the nobler of the two metals. The corrosion rate of the more active metal is reduced because the surface area for reduction reaction has been decreased, a scratch in this type of coating does not lead to rapid attack on the active metal.

Metallic and non-metallic coating have been attempted on dental gold alloys. They were ineffective because they were too thin and did not adhere to underlying metal.

Certain metals develop a thin highly protective film by reaction with the environment such metal is said to be passive. Eg: Chromium.

Passivating metals are not without drawbacks. Tensile stresses and certain ions such as chloride can disrupt the protective film and rapid corrosion may ensure. Chromium passivated metals can be susceptible to stress corrosion and pitting corrosion. For this reason patients are advised not to use household bleach for cleaning RPD's or removable ortho appliances.

Antirust / chemical corrosion inhibitors used in autoclave to prevent corrosion are dicyclohexylammonium nitrate.

### CLINICAL SIGNIFICANCE OF GALVANIC CURRENTS:-

As long as metallic dental restoration materials are employed there seems to be little possibility that the galvanic currents can be eliminated. The cement base itself although it is a good thermal insulator, has little effect in minimizing the current that is carried into the tooth and through the pulp.

Although the post operative pain caused by galvanic shock is not a common occurrence in the dental office. It can be a real source of discomfort to an occasional patient. Such post operative pain usually occurs immediately after insertion of a new restoration and generally is gradually subsides and disappears in a few days. It is likely that the physiologic condition of the tooth is the primary factor responsible for the pain resulting from this current flow. Once the tooth has recovered from the injury of preparing the cavity and has returned to a more normal physiological condition the current flow then produces no response.

Practically the best method of reducing the galvanic shock is by painting an external varnish on the surface of the restoration. It seems that the conservative procedure would be to avoid situation that might obviously produce an exaggerated condition. By the insertion of an amalgam restoration directly in contact with gold crowns seems to be contraindicated although it is often done. Mercury released from the corroding amalgam (anode) certainly interacts with gold alloy and weakens it. A discoloration of both restorations will probably occur.

### Minimization of clinical corrosion:

Using the principles just discussed a number of general rules may be formulated to minimize corrosion in the clinical situation. The dental student or dentist applying these rules to his particular situation can no doubt increase the list.

1. Always avoid restoring teeth in opposition with the mixed metals, where even practical, avoid using mixed metals within the same mouth, since the restored tooth is open to the biological system through the dentinal tubules, an electrical connection through the extra cellular fluid is established for mixed metals even if they are not in opposition. The associated galvanism is of course accelerated if mixed metals are placed in opposition.

2. Use an appropriate insulating base when seating a metallic restoration. Electrical contact with the extra cellular fluid may be minimized or eliminated by using an insulating base such as copal varnish for amalgam or a cement base for gold casting.

3. Avoid conditions conducive to plaque buildup in selected areas of metallic restorations. Establishment of areas of plaque will lead to decreased pH and oxygen tension in areas covered by plaque. As indicated in the previous section, both of these manifestations will enhance corrosion phenomena.

4. As a logical consequence of the above all appliances should be designed as smooth and self cleansing as possible in order to decrease plaque build up and retention. Amalgam restorations in particular should be routinely polished

5. Copper chromium partial denture clasps should be either cast integrally with the frame work or else spot welded. Soldering clasp with either a gold or silver solder is to be avoided since it produces a galvanic mixed metal couple. Silver solders which may contain up to 50% Cu and Zn may be quickly corroded when coupled with Co - Cr alloys. Many commercial cleansers will attack such a solder joint.

6). be alert to the development of new dental materials technology in supplying improved corrosion resistant materials.

### Conclusion:

It is apparent that the oral environment and the oral structures present various situations that promote discoloration and corrosion. The variables of diet, bacterial activity, drugs, smoking, and oral hygiene habits produce different rates of corrosion in different patients.