Influence of oral cavity environment on various dental materials

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Oral cavity

Complex and aggressive environment acting on the hard tooth tissues and reconstruction materials:

- Saliva, water, enzymes, ions,
- Plaque, bacteria and products of their metabolism,
- Changes of pH and temperature,
- Food components, exogenous and endogenous chemical substances,
- Mechanical stresses.
Saliva

- Water: 99 %
- Ions: Na\(^+\), K\(^+\), Ca\(^{+2}\), Mg\(^{+2}\), Cl\(^-\), F\(^-\), HCO\(_3\)\(^-\) (maintains pH by neutralization of acids in dental plaque), PO\(_4\)\(^{3-}\),
- pH: 6.5-6.9 (normal level); 7.0-7.5 (after stimulation),
- Enzymes (alfa amylase, lysozymes, lipase), proteins (glycoproteins-mucines).
Plaque

- Bacteria (streptococcus mutans, s. sobrinus, lactobacillus),
- Extracellular polysaccharides forming a dental plaque **matrix**, intracellular polysaccharides which fermentation makes it possible continuous production of acids even in the lack of an exogenous substrate,
- Bacterial metabolic products - **organic acids** (acetic, formic, propionic, lactic) **decreasing pH** even to **4.5**.
Food and chemical substances

• Drinks such as „soft drinks“ with a high content of organic acids (pH frequently below 2.0, citric, phosphoric acids) and simple saccharides, energetic drinks, foodstuff, sweets..,

• Acids from fruits (citric acid) with the chelating effect,

• Alcohol, cigaretts,

• Mouth rinses and toothpastes components (surfactants, abrasives), fluorides, 

• Disinfectants – chlorhexidine,

• Cosmetic products – bleaching gels containing peroxides and other substances,

• Drugs (solutions of acetylsalicylic acid), multivitamin supplements....
Mechanical stresses

- Forces during chewing/biting 100-400 N (up to app. 50-200 MPa), compressive, tensile, flexural or shear,

- Forces arising from various habits (biting pipe or pencil, nail biting but also bruxism).

- Forces acting during tooth cleaning.
Dental materials are influenced in the oral cavity environment by:

- **Chemical** reactions – *corrosion* (hydrolysis, oxidation), polymer chain degradation/scission with decrease in the polymer chain length),

- **Dissolution** of materials, water sorption, swelling microfracture initiation,

- **Mechanical failure** – abrasion, attrition, fracture, fatigue, creep.
Few **terminological** notes:

**Aging/ageing** – processes that occur in a material during a period of time, and that usually result in *changes* in physical and/or chemical structure and the *values (positive/negative)* of the *properties* of the material. If the changes in material properties are *negative* a term **degradation** can be used.

**Abrasion, attrition and fatigue** – defined as the progressive loss of a material arising from contacting surfaces, in some literature appointed as **wear**. However, it may include also a chemical attack – erosive wear. In this presentation abrasion, attrition and fatigue will be used for a long-term mechanical effects.

As erosion in dentistry is related to a chemical dissolution of hard dental tissues, **corrosion** instead of erosion will be used to describe chemical or electrochemical changes of dental materials in the oral cavity environment.
Consequences of material aging:

• **Loss of anatomical shape** (abrasion or fracture), marginal fracture,

• Decrease in aesthetic properties,

• Decrease in mechanical resistance and durability,

• **Release of the material components and their corrosion products in the human body.**
Corrosion of dental materials

Chemical or electrochemical attack of dental materials in the oral cavity

What does it cause??

1. Dissolution of material surface, water sorption, swelling, but with some metallic materials formation of protective passivation layer,
2. Release of constituent substances and their degradation products, corrosion products,
3. Decrease in abrasion, fracture resistance and increase in the surface roughness.
Mechanical failure - abrasion

„Abrasion“ - the loss of material by mechanical forces usually on the occlusion surfaces, proximal or in the cemento-enamel junction due to micro movement of teeth in the periodontium.

1. Three-body abrasion, e.g:

**Restoration** – **abrasive particles** (from food or a toothpaste) – opposing tooth/restoration

![Diagram of abrasion process](attachment:image.png)
Proximal abrasion:

- Abrasive particles
- Direction of movement
- Contact point
- Contact area
2. Two-body abrasion - attrition:

*Example: an opposing ceramic crown – enamel

Characterized by a flat surface circumscribed with a well defined border
Mechanical failure - fracture

Usually brittle materials which mechanical resistance is controlled by the presence of various defects (voids, composition inhomogeneity, sharp edges...).

Material fracture may result from:

• Random forces exceeding strength limit (compression, tension, shear) of the material,

• Repeated small stresses — material fractures after many cycles - fatigue.
Corrosion and mechanical loads of dental materials are acting in the oral cavity synergetically and accelerate material aging.
Ageing of composite materials in the oral cavity environment

Heterogeneous materials consisting of a polymer matrix and particulate fillers or fibre reinforcement.

Main components of particulate composites:

- Matrix,
- Filler particles,
- Coupling agents.
Corrosion of composite materials

- Disintegration of filler particles,
- Decomposition of filler to matrix bond,
- Degradation of polymer matrix.

Depends on water diffusion rate into the matrix and thus on its composition and polymerization degree.
1. Disintegration of filler particles

**Hydrolytic degradation** - depends on glass particle composition and its surface treatment. **Starts** at the composite surface but due to water diffusion includes also inner particles.

- It results in:
  - leaching of cations (Na, **Ba**, **Sr**, **Zr**, Yb, Si but traces of Ti, Pb, Co ...) into saliva,
  - Due to alkaline nature of the cations - pH in the neighbourhood of particles increases to app. 9.0-9.5 which further accelerates particle disintegration (autocatalytic mechanism).
Reaction with F\(^-\) ions from concentrated (Acidulated Phosphate Fluoride, APF) gels with Si leads to glass particle disintegration.

- Replacement of \textbf{large} cations with small H\(^+\) ions induces \textbf{stress} in the superficial particle layer – \textbf{accelerates} their disintegration – \textbf{stress corrosion effect}.

\textbf{Chemical substances}, e.g. \textbf{from peroxide} gels – may disintegrate and release glass particles from a composite surface.
2. Decomposition of filler particle – matrix bond

Hydrolytic degradation:
1. Ester bond in the silane molecule (1),
2. Degradation of -Si-O-Si- bond between glass surface and silane molecules (2).

Very destructive – strongly affects strength and durability of a composite material.
Surface of a filler particle

\[ CH_2=CH(CH_3)CO_2(CH_2)_3-Si \]

\[ CH_2=CH(CH_3)CO_2(CH_2)_3-Si \]

\[ O-Si- \]

(1) (2)
3. Polymer matrix degradation

- Release of free-residual monomers, components of initiating systems and other substances used in its formulation,
- Hydrolytic decomposition of monomer units (ester bond) – into alcohols, methacrylic/acrylic/trimellitic acid, Bisphenol A (from bis-GMA, bis-EMA), polymer chain scission.

Water diffusion in a composite matrix starts:

Depends on degree of matrix polymerization – the higher it is, the harder is a composite matrix and lower diffusion and water sorption.
- Plasticization of polymer matrix causes:
  - deterioration of composite mechanical resistance,
  - increase rate of composite degradation,
  - increase release of residual monomers, oligomers, additives and composite degradation products into saliva.

**Mind thermal degradation**

During composite **finishing** and **polishing** without proper **water cooling** local temperature may increase 200°C which starts thermal decomposition of polymer matrix. Decomposition **products** (e.g. formaldehyde) are released and composite is prone to faster **degradation**.
Abrasión de materiales compuestos

Frecuente razón para restauración de composite refurbishing o reemplazo.

Resistencia al desgaste:
1. Aumenta con la dureza de la superficie del composite, i.e. carga de relleno,
2. Disminuye con la dureza del partículas y su irregulares,
3. Proporcionalmente directa a la dureza del matrix composite – i.e. grado de polymerización,
4. Disminuye debido a la corrosión de la superficie del composite.
Resistance to mechanical loads

Brittle materials liable to fracture under load.

High compression strength (app. 350 MPa) but low tensile and flexural strength (app. 120 MPa).

Critical factor controlling resistance to mechanical stresses is the presence of superficial defects (voids, finishing grooves, sharp edges) or inner (air bubbles, voids) which acts as stress raisers initiating fractures.
**Defects/flaws** – by grinding/polishing composite surfaces with course diamond burs – producing typical cutting grooves acting as stress raisers initiating fractures.

Do not forget polishing with fine grained burs.
Fatigue

Local stresses well **below the yield stress** generated in the restoration due to its contact with an opposing tooth/other restoration/hard food particles and **acting repeatedly** may **drastically reduce** strength of the material.

**Fatigue fractures** propagate from small defects (**microcracks, voids, etc**) in the material. They cause sudden catastrophic fracture of the material **at small stresses**.
Propagation of fatigue microcracks
Ageing of glass-ionomer cements in the oral cavity environment

Corrosion

Solubility of GIC is much higher than that of composite materials due to crosslinking by ionic species (Ca/Al), hydrolytically unstable glass particles and water content.

Water penetration and sorption induce:

1. Hydrolysis of glass particles and cross-linked polymer matrix (polyacid salts) — release of Na, Ca, Al, Si, Sr .. cations, mainly in the acidic environment even at pH close to 4.5 (e.g. soft drinks).
2. With **classical** types release of **residual monomers**, oligomers and substances used in the **polyacid production**.

3. With **hybrid** types release as from (2) and:

   - **HEMA** and other monomers (crosslinking dimethacrylates e.g. **TEGDMA, EGDMA**),
   - components of photoinitiating system: CQ, acyl phosphine oxides, diphenyljodonium chloride, amines etc.

   **Controlled by water diffusion – GIC surface should be coated with a protection glaze immediately after the placement.**

   Note: high water sorption mainly with hybrid types leads to volume expansion by up to 5 %. It seals the margins but water sorption from dentinal tubuli is reported a reason for increased postoperative sensitivity.
Abrasión y resistencia mecánica

La naturaleza britálica y la menor resistencia a la tracción \(\rightarrow\) GIC son propensas a un alto abrissionamiento. Sin embargo, depende del nombre de la marca, la composición, el \textit{recomendado P/L ratio} y con tipos de mezcla manual, se producirán variaciones en P/L y defectos (burbujas de aire) presentes en la cementación.

\begin{quote}
Abrasión y resistencia mecánica de GIC \textbf{depende} fuertemente de su \textit{maturation} – extremadamente \textbf{alta} con \textbf{blísteres} de cimentos (horas y días) después de la colocación \textit{直到} hasta alcanzar su maturation completa.
\end{quote}
Ageing of dental amalgams in the oral cavity environment

Setting reaction of low-copper amalgams:

\[ \text{Reaction of Ag} \]
\[ \text{Ag}_3\text{Sn(}\gamma\text{)} + \text{Hg} \rightarrow \text{Ag}_2\text{Hg}_3(\gamma_1) + \text{Ag}_3\text{Sn(}\gamma\text{)} \]

Alloy particles

-less than stoichiometric amount

Amalgam matrix

Non-amalgamated alloy particles

Reaction of Sn

\[ \text{Sn}_8\text{Hg(}\gamma_2\text{)} \]

App. 10 vol. % of amalgam, soft phase, prone to corrosion
Setting reaction of high-copper amalgams:

Amalgamation of „unicompositional“ typ:

\[
\text{AgSnCu+Hg} \rightarrow \text{Ag}_2\text{Hg}_3 (\gamma_1) + \text{Cu}_6\text{Sn}_5 (\eta_1)
\]

Great number of small particles of
\(\eta_1\) (corrosion resistant) in \(\gamma_1\)
matrix+unconsumed alloy particles

Note: \(\gamma_2\) phase is sometimes formed in these amalgams but in a low quantity.

After initial setting – content of \(\text{Ag}_2\text{Hg}_3(\gamma_1)\) phase of all amalgams increases as well as strength, hardness and resistance to creep (plastic deformation at long-term mechanical load).
Corrosion of amalgams

Phase $\text{Ag}_2\text{Hg}_3(\gamma_1)$ is stable, covers with the passivation layer of $\text{SnO}_2$ arising from a small amount of Sn dissolved in this phase.

Phases $\text{Ag}_3\text{Sn}(\gamma)$ and $\text{Cu}_3\text{Sn}$ are stable as well.

**Low-copper** amalgams - $\text{Sn}_8\text{Hg}(\gamma_2)$ surface of this phase is covered with the layer of $\text{SnO}_2$ but:

It has a low strength and can be therefore easily removed by abrasion forces or may be decomposed by unreacted Hg.

This phase with a high concentration of Sn is **the most liable to corrosion**.
Reactions of $\text{Sn}_8\text{Hg} (\gamma_2)$ phase with the oral cavity environment produce $\text{SnO}_2$, Sn chlorides, oxychlorides, CuCl, CuSCN, AgSCN and other salts. Particles of amalgam were found in enamel, dentin and pulp but also as pigmentation "amalgam tattoo" in the soft tissues in the areas close to amalgam fillings.

**High-copper** amalgams – phase $\text{Cu}_6\text{Sn}_5 (\eta_1)$ is more mechanically and chemically resistant than $\text{Sn}_8\text{Hg} (\gamma_2)$ which results in a higher corrosion resistance of these amalgams. Their corrosion products contain mainly Cu salts.
Electrochemical/galvanic corrosion

It occurs in the oral cavity due to:

1. **Dissimilar** metals are present or are in a **direct** contact when **electrochemical/galvanic couple** is formed. Amalgam restoration is usually an **anode** and **oxidizes** (dissolves) in the presence of noble metals (Au, Ag, Pd) a **cathode** (reduces) but also some predominantly base metals (Ni-Cr alloys).

2. **Differences in the electrolyte composition:**
   - in the gap between the amalgam-tooth tissues and in saliva (**crevice corrosion**).
- in the **interproximal** areas with plaque/food debris and **saliva**.

3. Differences in oxygen concentration between the rim and bottom of **concavities leading to pits on amalgam surface** - **pitting corrosion**.

To minimize pitting corrosion - all metallic dental restorations should be polished.
Corrosion of amalgams leads to:

1. **Tarnish** – observable *surface discoloration*, loss of finish and luster occurring soon after placement – *caused by Sn sulfides* produced in the presence of bacteria, *or by corrosion products of Cu*.

2. **Pitting** corrosion – its extension to the depth of a restoration – *crevice* corrosion in the *bulk of restoration* with a *catastrophic effect on restoration durability* (fractures).
Pitting and crevice corrosion

The rim of a pit or crevice – cathode

Crevice bottom – anode

electrolyte

Amalgam with typical surface pits (holes) caused by corrosion: a) low 35, b) high magnification 250x.

Amalgam ditching
3. Corrosion increases **surface roughness** which supports bacteria adhesion, plaque and food debris accumulation, decreases surface **hardness and amalgam strength**.

4. Ions of amalgam metals (Hg, Ag, Sn, Cu, Zn and others) are released in to saliva and hard and soft dental tissues.

Electric current produced by or electrochemical/galvanic couples may cause patient subjective discomfort, e.g. sharp pain when restorations from dissimilar metals touch.
Abrasion and strength of amalgams

1. In the course of setting (hours, days) the amount of Ag$_2$Hg$_3(\gamma_1)$ phase increases – better hardness, strength and abrasion resistance, but increased brittle character,

2. Fully set – higher strength and abrasion resistance than composites and GIC,

3. Due to creep (mainly in contact areas) the margins of amalgam filling are „lifted“ over tooth tissues forming marginal gaps „marginal ditching“ where food debris and plaque may accumulate,

4. Due to electrochemical/galvanic corrosion deep cracks which decrease strength maybe formed.
# Mechanical properties of restorative materials

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Amalgam</td>
<td>380-420</td>
<td>120</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Composite</td>
<td>280-350</td>
<td>120</td>
<td>50-80</td>
<td>200-300</td>
</tr>
<tr>
<td>GIC</td>
<td>200&lt;sup&gt;2&lt;/sup&gt;</td>
<td>40</td>
<td>20-30</td>
<td>500</td>
</tr>
<tr>
<td><em>Enamel</em></td>
<td><em>384</em></td>
<td>-*</td>
<td><em>310-360</em></td>
<td><em>50-80</em></td>
</tr>
<tr>
<td><em>Dentin</em></td>
<td><em>297</em></td>
<td>-*</td>
<td><em>50-60</em></td>
<td>&gt;<em>enamel</em></td>
</tr>
</tbody>
</table>

<sup>1</sup>Knoop hardness (Knoop hardness number), <sup>2</sup>measured after 7 days.
Aging of Dental Casting Alloys in the oral cavity environment

Classification of dental alloys (metals):

1. High Noble Alloys,
2. Noble Alloys,
3. Predominantly Base Metal Alloys.
Corrosion of casting alloys

It leads to tarnishing, pitting and crevice corrosion.

Galvanic couple can originate also from heterogeneous alloy composition or impurities concentrated e.g. at the grain boundaries of castings.

Stress corrosion

More mechanically deformed metal regions are prone to anodic dissolution than less deformed. At these regions may corrosion start first.
Corrosion of the alloys is controlled by:

**Alloy type** (noble alloys are the most stable), processing, **microstructure**, presence of **other metals** in the oral cavity, saliva **composition** and the **surface roughness**.

**Adverse effect of corrosion**

Dissolution and release of various metals in the human body (allergenic effect of Ni, Pd), tarnishing, surface roughness, decrease in mechanical resistance.

But also risk for technicians/dentists when finishing the casting.
Corrosion resistance depends on the position of a metal in the "electrochemical/electromotive series of metals"

- Metals are arranged in the order of their electrode potential against hydrogen electrode. Metals on the left to H are nonprecious while those on the right to H are precious or noble (in dentistry) metals.

- Metals in the series are able to reduce those metals on their right (while they oxidise and usually dissolve).
• On the other hand, metals can oxidise those on their left (while being reduced).

• The reducing or oxidising ability of metals increases as you go left and right of the series.

Electrochemical series of metals:

Li  K  Ca  Na  Mg  Al  Mn  Zn  Cr  Fe  Sn  Pb  H  Cu  Ag  Hg  Pt  Au
< - non precious metals | precious/noble metals ->
Electrochemical series of metals with electrode potentials against the hydrogen electrode.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electrochemical potential [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>-2.9</td>
</tr>
<tr>
<td>Al</td>
<td>-1.7</td>
</tr>
<tr>
<td>Ti</td>
<td>-1.6</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.8</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.7</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.4</td>
</tr>
<tr>
<td>Co</td>
<td>-0.3</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.3</td>
</tr>
<tr>
<td>Sn</td>
<td>-0.1</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
</tr>
<tr>
<td>Cu</td>
<td>+0.2</td>
</tr>
<tr>
<td>Ag</td>
<td>+0.8</td>
</tr>
<tr>
<td>Hg</td>
<td>+0.8</td>
</tr>
<tr>
<td>Pt</td>
<td>+1.2</td>
</tr>
<tr>
<td>Au</td>
<td>+1.5</td>
</tr>
</tbody>
</table>

Metals with high negative potential (at the top) are prone to corrosion, while those with high positive potential (at the bottom) are more resistant.

Typical electrode potentials of few dental alloys in the artificial saliva

Dle Craig´s Restorative Dental Materials, 12th. Edition

<table>
<thead>
<tr>
<th>Slitina</th>
<th>Electrochemical potential [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0</td>
</tr>
<tr>
<td>Amalgam</td>
<td>-1.7</td>
</tr>
<tr>
<td>Low-copper</td>
<td>0.02</td>
</tr>
<tr>
<td>High-copper</td>
<td>0.10</td>
</tr>
<tr>
<td>Ni alloys</td>
<td>0.12-0.25</td>
</tr>
<tr>
<td>Co alloys</td>
<td>0.30</td>
</tr>
<tr>
<td>Au-Cu-Ag alloy</td>
<td>0.35</td>
</tr>
<tr>
<td>Au-Pt-Pd-Ag alloy</td>
<td>0.35-0.45</td>
</tr>
</tbody>
</table>
Ageing of ceramic materials in the oral cavity environment

A two-phase (glass matrix and „dispersed“ crystalline phase – „Glass-ceramics“) or „homogeneous“ polycrystalline structure without a glass phase.

Matrix – feldspathic glass (KAlSi$_3$O$_8$)

Crystalline phase:

<table>
<thead>
<tr>
<th>Crystalline phase</th>
<th>Flexural strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>leucite</td>
<td>KAlSi$_2$O$_6$</td>
</tr>
<tr>
<td>alumina</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>lithiumdisilicate</td>
<td>Li$_2$Si$_2$O$_5$</td>
</tr>
<tr>
<td>spinel</td>
<td>MgAl$_2$O$_4$</td>
</tr>
<tr>
<td>zirconia</td>
<td>ZrO$_2$</td>
</tr>
</tbody>
</table>
Very brittle materials – which stability in the oral cavity is controlled by:

1. **Defects** – voids, cracks, inhomogeneities in composition, surface scratches or sharp edges originating **from processing** (firing, grinding, air-abrasion) or **preexisting** in the material. Upon loading (mastication) they act as **stress raisors** initiating **fracture**,

2. Resistance to water and to acidic environment – release of various constituent ions from glassy and crystalline phase.
3. Specific properties, e.g. „low temperature ageing„ of zirconia (ZrO$_2$) ceramics.

ZrO$_2$ – high strength ceramics with high fracture resistance.

**Complicated crystallographic structure:**

ZrO$_2$ – monoclinic (m) to 1170°C
tetragonal (t) to 2370°C
cubic at even higher temperatures

Transformation (t-m) is accompanied with the volume expansion by app. 4.5% - **retards fracture propagation.** To **stabilise t** modification at normal temperatures **Y, Mg, Ca, Ce** are added.
Transformation t-m generates compression stresses which decrease stress at the crack tip and retards propagation of fracture.

But t-m transformation starts also due to grinding, air-abrasion but also water sorption (so called low temperature aging) resulting in decrease in mechanical resistance of zirconia ceramics.
Corrosion of dental ceramics

- Excellent **resistance** against chemical **substances** (2% NaF, 0.4% SnF₂) and **acids**. However, surface of e.g. **feldspathic** ceramics may be attacked by **APF** gels (**Acidulated Phosphate Fluoride**, 1.2 % F⁻) or (8 %) **SnF₂**. Selective dissolution of glass matrix – increases surface **roughness** (staining, plaque accumulation or increased abrasion).

- „Soft drinks“ or some cosmetic preparations (peroxide bleaching gels) may release other ions, e.g. Y³⁺, Al³⁺, Ca²⁺, Li⁺, however, in much **lower concentrations** than from **other** restorative **materials**.
Mechanical strength and abrasion resistance

Surface microcracks may cause localized fractures and asperities strongly increasing abrasivity of ceramic materials.

Brittle fracture of a glass matrix with crystal phase projecting out of the surface.