Experiments in Natural and Synthetic Dental Materials
A Mouthful of Experiments

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Key Words: Biomaterials, dental, corrosion, composite, amalgam.

Prerequisite Knowledge: The student should be familiar with the basics of materials science, metallography, and chemistry. Levels at which these experiments are performed are second semester junior year and either semester senior year. The students are first given lectures on fracture mechanics, metals, alloys, and composites. They should have already had a laboratory experiment on metallography and sample preparation. A video on the deterioration of restorative materials in the oral environment is used as a backdrop for the experiments.

Objectives

The objectives of these experiments are to show that the area of biomaterials, especially dental materials (natural and synthetic), contain all of the elements of good and bad design, with the caveat that a person’s health is directly involved. The students learn the process of designing materials for the complex interactions in the oral cavity, analyze those already used, and suggest possible solutions to the problems involved with present technology. The N.I.O.S.H. Handbook is used by the students and judgments are made, even without extensive biology education.

Equipment and Supplies

(1) Metallurgical preparation and polishing apparatus (eg. Buehler Co.),
(2) Amalgam triturated samples (Johnson & Johnson, Inc., Degussa Chemical, etc.),
(3) Titanium, gold crowns, graphite, and stainless steel (316L) posts and fixtures (J. & J.),
(4) Teeth with amalgam, ceramic, and composite restorations (heal dentists),
(5) Selenium oxychloride (Hg stain from Fisher Scientific.),
(6) Metallurgical microscope (Olympus, Zeiss, etc.), and
(7) SEM with EDAX (optional).

Introduction

There are few materials which capture the essence of materials science as dental materials and the amazing, adaptive natural dental materials. In the same vein, these materials are all subject to the same mechanical, electrical, chemical, and biological laws as all other materials. Certain of these synthetic materials are now deemed potentially harmful in the human bio-system. Newer materials have shown promise of solving the restoration problem. At Western New England College, two senior projects and some extensive research have led to the development of a two-part experiment involving natural and synthetic materials such as actual previously extracted teeth, amalgam filled teeth, stainless steel orthodonture material, gold alloy crowns, composite restoration material, titanium implants, and graphite endodontics posts. Tests involving corrosion couples, sectioning and microscopic investigation of alloys and composites, and bond strength of polymer adhesives.

The problem of restoration of carious regions, the materials used, and the associated appliances employed in orthodonture and implantology provide a complex electrochemical scenario to be sorted out by the practitioner and patient alike. Add to this the fact that many scientists cannot even agree on the cause/effect relationships associated with pathologies resulting from the release of...
ions, metallic vapors, and molecules from the man-made materials placed in the oral cavity, and the problem of fact vs fiction eludes even the more astute practitioner, much less the patient.

These experiments detail the basics of corrosion and material function and failure in the oral environment, listing many of the possible combinations of materials that could be and are employed in the practice of oral restorations, implants, and orthodonture. Known facts will be isolated from conjecture, while visual observations and measurement techniques will be explained in the light of good electrochemical practice and common sense approaches. Standard tests, ranging from expensive and highly sophisticated ones to simple, inexpensive tests will be enumerated, while less expensive ones will be employed. Bases for agreement on fundamental starting points for future “good practice” techniques will be discussed as part of the experimental writeup. Some of the materials covered will be: mercury amalgams (redundant: amalgam means “with mercury”), noble metal inlays, appliances, posts, fixtures, implants, ceramics, and polymeric composites. Background theory is given in the Appendix for use as a pre-lab lecture/reference for the student and laboratory instructor.

Experiment

The specific aims of these experiments are to classify these mechanical effects, thermodynamic phase diagram realities, electrochemical and corrosive effects, identify the species involved, use certain measurement devices, and show the physical data associated with the actual restorations, appliances, and implants and their attendant biodental engineering effects.

Phases in amalgam and their electrochemical potentials:

The student should refer to the Appendix in Figure A3 to observe the ternary phase diagram for mercury-silver-tin. This will serve to help the student identify the polished samples produced by the following procedures. Samples of high copper amalgams are prepared by trituration according to the specifications of the manufacturer/supplier. Typical mixture morphologies and trituration apparatus are shown in Figure 1. These samples are then mounted in phenolic or suitable cold mounting polymers and observed under a suitable optical microscope or electron microscope at magnifications appropriate for phase detection. A typical polished sample is shown in Figure 2. Make sure that the students note the “droplets” of free mercury which result.

Figure 1
Mixed Amalgams and Triturator
If a potentiostatic or potentiodynamic apparatus is available, measurements can be made on the electrochemical potentials and anodic polarization curves of restoration alloys with amalgams. Phases can be made "from scratch, using standard alloying techniques. Potentiometric corrosion curves typical of some of the restoration materials, appliances, and implant materials are shown in Figure 3.

These curves verify the degree of corrosion under given corrosion potentials. Note the consideration of area in the current density on the ordinate of the graph. Area of the anode and cathode influence greatly the rate of corrosion of the materials involved. For instance, if the area of the cathode is much larger than the anode, the corrosion reaction will proceed at a much faster rate than if the areas of the two are the same.

Obtaining freshly extracted teeth from a local dental practitioner, the laboratory instructor may wish to show the microstructure of natural teeth and cracking from restorations. If EDAX is available on an SEM, then diffusion of Hg and Ag can be made visible on polished teeth (see Appendix).
Composites and Polymers, mostly composed of bis-GMA with fillers and colorants, are easy to prepare for observation. Samples from Companies such as Bisco and Denmat provide a basis for observing some of the most high-tech, durable materials of this experiment. Taking a small sample from the hypodermic dispenser (Figure 4), prepare a mounted sample as in the earlier part of the experiment (setup time is less than 10 minutes). Polish and prepare teeth, from the dental practitioner, which contain composite restorations and/or endodontics posts (root canal filler posts). Observe (as in the Appendix) the structure and topographies of these restorations.

Figure 4
Composite Dispensers and Sections

Reporting

Reports should be made on preparation and observations regarding the above experiments and procedure. Judgments based on corrosion and durability, as well as structure of the materials should be detailed by the students. A “white paper” to the ADA may be composed based upon both background material and the information gleaned from the experiments. These experiments are easy beginnings for senior capstone design projects. The experiment is taken quite seriously and personally, and the comments are very positive to date. The student should be allowed to suggest other experiments to clarify concepts, both in their minds and in the scientific community. The experiments detailed here will be broken up into five distinct stand-alone modules.

APPENDIX

BACKGROUND/THEORY:

Techniques and materials for dental restorations have advanced greatly over the past decade with improved dental metals, ceramics, and polymeric composites. The mechanical properties and ease of fabrication of restorative fillings of mercury-silver amalgams have undoubtedly been the strong driving force for the retention of this practice in modern dentistry. The reality of the electrochemistry of “oral galvanism” first appeared in 1754 with a paper by Sulzer (1). It was later, in 1879, that Chase (2) called this new “oral electricity”, associated with the dental amalgam, hazardous. Dental amalgams have been employed in the United States as restorative materials since 1832 and, according to the American Dental Association and others (3,4,5), no cases of well-documented “patient toxicity” have been reported in the scientific literature. This view is in sharp contrast to other researchers(6,7,8,9), to mention a few, documenting literature and physico-chemical effects of the vapor and corrosive release of mercury in the oral environment. Work has been done to elaborate on the degradation of amalgams and the implications of this degradation in the oral environment (4). The purpose of these experiments is not to discuss the medical or physiological effects of the restorations or possible etiology of other pathologies, but to explain and document the mechanical, materials science, electrochemical, and chemical phenomena attendant to the placement and use of many of these materials alone or together in the oral environment.

Corrosion

Corrosión can be defined as the destruction or deterioration of a material because of its reaction with its environment (10). This definition includes both metals and non-metals. The general classifications of corrosion are wet or dry, direct combination or electrochemical.

For the purpose of this study, wet electrochemical corrosion occurring in electrolytes is considered. The principles underlying corrosion state that there are two basic requirements for electrochemical corrosion: at least one anode and one cathode must be present to forma cell, and direct currents must flow. Anodes and cathodes may be near to each other (local cell) or farther apart. The current (ion and electron flow) may be self-generated (as in the case of two dissimilar metals in solution) or maybe impressed from an outside source (as in plating, for example). The anode is the area where corrosion occurs, current leaves the metal in the form of dissolved ions, and enters the electrolyte solution. The cathode is the area where no corrosion occurs and current enters the metal. Two basic diagrams show the requirements for metallic corrosion, as seen in Figure A1.
Note the separate and same surface scenarios for corrosion between two different materials. The governing factor for the corrosion of one material in the presence of another has to do with the Nernst equation

\[ E = E_o + 2.3 \frac{RT}{nF} \log \frac{a_{\text{red}}}{a_{\text{ox}}} \]  

(Eq. A1)

where \( E \) is the half-cell potential, \( E_o \) the standard half-cell potential, \( R \) is the gas constant, \( T \) is the absolute temperature, \( n \) is the number of electrons transferred, \( F \) is the Faraday constant, and \( a_{\text{ox}} \) and \( a_{\text{red}} \) are the activities (concentration) of the oxidized and reduced species. Table A1 shows a series of half-cell potentials measured by potentiometric means, using a standard calomel electrode (SCE) as a reference in saline solution. The more active (anodic) metals corrode at the expense of the less active (more noble or cathodic) metals. For instance, mercury would be corroded (release ions into solution) in a couple with titanium or gold. Simply stated: “In any electrochemical reaction, the most negative or active half cell tends to be oxidized, while the most positive or noble half-cell tends to be reduced” (11). These determinations were made for pure metals and phases of amalgam as part of this work. Figure A2 shows a typical potentiometric setup for the determination of the corrosion (galvanic) potential between metallic species in an electrolyte.
Table A1: Potentials of phases and alloys vs SCE

<table>
<thead>
<tr>
<th>PHASE/METAL</th>
<th>(av.) POTENTIAL(V) vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure gold (Au)</td>
<td>+0.26 (cath.)</td>
</tr>
<tr>
<td>titanium (Ti)</td>
<td>+0.05</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>+0.01</td>
</tr>
<tr>
<td>316 stainless steel</td>
<td>-0.05</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>-0.10</td>
</tr>
<tr>
<td>alpha Ag/Sn (100-89/0-11)</td>
<td>-0.10 to -0.12</td>
</tr>
<tr>
<td>gamma Ag/Sn (74/26)</td>
<td>-0.13</td>
</tr>
<tr>
<td>gamma 1 Ag5g (40/60)</td>
<td>-0.14</td>
</tr>
<tr>
<td>beta Ag/Sn (84/16)</td>
<td>-0.14</td>
</tr>
<tr>
<td>mercury (Hg)</td>
<td>-0.16</td>
</tr>
<tr>
<td>copper (Cu)</td>
<td>-0.30</td>
</tr>
<tr>
<td>epsilon Cu/Sn (75/25)</td>
<td>-0.31</td>
</tr>
<tr>
<td>eta Cu/Sn (54/46)</td>
<td>-0.32</td>
</tr>
<tr>
<td>gamma 2 Sn/Hg (88/12)</td>
<td>-0.33</td>
</tr>
<tr>
<td>Tin (Sri)</td>
<td>-0.35 (anodic)</td>
</tr>
</tbody>
</table>

Biodental Engineering Factors

Previous work (11, 12) has identified several factors acting alone or in concert to produce a variety of corrosive, fracture, physico-mechanical, and electrical effects in the oral environment. These factors are shown below in Table A2.
Table A2. Biodental Engineering Factors

Biomechanical: Column loading
- Compressive and tensile forces
- Stress concentration

Biochemical:
- Stress and fatigue corrosion
- Crevice corrosion
- Ionic transport
- Saliva - pH flow rate, buffering capacity

Bioelectrical:
- Piezoelectric, Hydro-electrodynamic
- Electrochemical potential difference between different materials
- Electrolysis

Combined effects of the above mentioned biodental engineering factors have been shown to exacerbate the release of metallic vapors, ions, and tooth material, both natural and man-made substitutes. Only with metallic restorations, implants, and appliances do the bioelectrical effects become dominant causal factors in the ionic release. It should also be noted that the underplay of Hg$^+$ mercury vapor and particulate Hg$^+$ by many is seldom if ever accompanied by a mention the more vitally active ionic Hg$^+$ free to combine thermodynamically in a wide variety of species. The abfraction (11) of both natural and man-made tooth substance due to bruxing, abrasion, clenching (squeezing), and malocclusive forces serves only to make the scenario an unquestionable multifactorial maze in which the scientist must “sort out” cause and effect and take proper corrective actions. Shown in Figure A3, for the purpose of basic illustration, is a ternary phase diagram(13) of the alloys of Silver (Ag), Mercury (Hg), and Tin (Sn). More complex quaternary and pentenary diagrams are not possible due to the multidimensionality of the drawing and the enormity of the data.

Figure A3

Ternary Phase Diagram for Hg-Sn-Ag

The multiplicity of phases and the fact that these phases are formed, not from room temperature amalgamation, but from standard elevated temperature techniques further complicates the scenario.

The overall simplified reaction (14) for the phases in amalgams can be written in general for high copper (non-gamma 2 phase materials):

$$\text{Ag}_x\text{Sn} + \text{Hg} + \text{AgCu} \rightarrow \text{Ag}_y\text{Sn} + \text{Ag}_z\text{Hg}_3 + \text{Cu}_b\text{Sn}_n + \text{(unreacted) (other phases)}$$

Ignoring the minor phases, noting that the gamma 2 phase is no longer present in high copper amalgams, and applying the same criteria for corrosion to the phases (15) as to the bases for local and separate cathodes and anodes, the conditions for corrosion in the oral environment with mixed metals as well as the local anode-cathode areas on the amalgam itself (due to its phases) become apparent. Amalgams, due to the many phases forming local anodes and cathodes, are self-corroding.
Experimental methods for determinations of mercury

There are a variety of methods of determining the presence of mercury and detecting ionic current flow. Among these are methods ranging from high cost and high sophistication to lower cost and less sophistication of technique. The most sophisticated of the methods for analyzing Hg and other metals in saline and saliva is Atomic Absorption Spectroscopy (A.A.S.). This method utilized the injection atomized species into a flame with the attendant absorption (from an Hg discharge lamp, for example) or emission from the flame of certain wavelengths characteristic of the metal to be detected. The basis of this work utilized both FAAS and GFAAS with detection limits of 0.3 to 1 ng/L, dependent on whether or not gold amalgamation concentration techniques (16) were used. A second method involves a slightly less expensive gold film technique called Differential Pulse Anodic Stripping Voltammetry (17), with detection capabilities down to 1 ppb (1 pg/L).

A third, less expensive method for detection in vivo is a potential, current, energy meter, shown in Figure A4, which measures the potential, current, and energy between two metallic restorations.

An inference regarding the ion exchange, anodic and cathodic regions, and possible excessive galvanic effects can be made simply, as follows: Polarity indicates cathode vs anode; voltage gives the magnitude (driving potential) for the electrochemical reaction; and current gives the number of ions per second transferred.

eg. Hg vs Au, Au is positive, approximately 0.4 volts, with respect to Hg, at 10 microampere (typical of measured values using this method). If \( N \) is the number of ions per second of the species, \( I \) is the current in amperes (Coulombs/second), \( q \) is the electronic charge (coulombs), \( n \) is the valence of the species (eg. +2 for Hg), then

\[
N = \frac{I}{nq}
\]

or \( N = 10 \times 10^4/(2 \times 1.6 \times 10^{-19}) \times 3.12 \times 10^9 \) ions/sec, assuming Hg is available in an electrolytic environment. Further calculations lead to removal of approximately 10 ng/sec for a constant current as measured.

Measurements made on the saliva of thirty subjects with mixed metals in the mouth (eg. combinations of one or more pairs of orthodontic stainless steel, amalgams, gold inlays, titanium posts, base metal posts, graphite composite endodontics posts, etc.) were made by A.A.S., stripping voltammetry, and potential meter. Since the A.A.S. and stripping voltammetry were ion specific (Hg), these results correlated well in total Hg concentration in the saliva. No attempt was made to mechanically disturb the restorations by chewing or similar disruption. Saliva was retained in the mouth without swallowing for a period of 30 seconds and then released into a vial four times for testing. The tests showed that the A.A.S. and the stripping voltammetry correlated within thirty percent in ranges tens to hundreds of parts per million (ppm). The measurement of ionic flow between suspected anodes and cathodes, as an estimate of Hg ion concentration, was consistently higher than predicted by the A. A. S., by a factor of two or more, probably due to the fact that the ions detected by this method were not solely mercury, but included other ions anodic with respect to the cathode chosen.

Scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDXA) of sectioned teeth with amalgams

Over sixty samples of amalgam restorations in their host tooth were mounted and polished using standard metallurgical techniques. SEM photomicrographs and EDXA scans were made to observe some of the phenomena associated with these restorations, cracking, mercury migration, and effects of mechanical pressure on the surface of the amalgam. Ten of the specimens were scanned to study the concentration of Hg vs distance from the restoration. Three notable commonalities were seen on almost all of the samples studied: (a) The samples all showed some degree of micro-cracking; (b) Migration of mercury through the dentin.
occurred and was accelerated down the micro-cracks; and (c) Mechanical pressure of less than 2000 Pa on the amalgam surface always produced "droplets" of mercury, exclusive of the age of the restoration. Figure A5 below shows electron micrographs of lingual and occlusal restorations along with a magnified view of a region on which a pressure of approximately 1900 Pa was applied. Note the regions of microcracking, voids, and Hg droplet formation. Mercury relative concentration analyses were made on the teeth from the margin of the amalgam restoration to both the pulpal region and to the lateral extremity of the dentin.

Figure A5

Restoration and EDXA measurement of Hg vs distance from the restoration margin

Figure A5 shows a tooth measured and the plot of relative Hg concentration vs distance both toward the outer extremity of the dentin and in the direction of the pulpal region. As can be seen from the plots and from the map of Hg in and around cracks, mercury migrates in the tooth material, most likely driven by combinations of concentration gradients and electrochemical potentials existing in the oral cavity prior to extraction. Figure A6 shows possible scenarios of corrosion (ionic current paths) in the oral environment and oxygen deprived anodic regions on the tooth (18). These paths further enhance the probability of anodic dissolution in both tissue and saliva. Some researchers (14) have found that scaling the amalgam with polymeric sealers retards evaporation of the highly volatile mercury vapor. Add to this the possibility of crevice and oxygen deprivation corrosion, and the use of mixed metals appears to be less than ideal in the oral environment, at least from a materials science perspective.

Figure A6

Possible paths of corrosion (ion flow) and oxygen cathode
Polymers and ceramics

Polymers used as restorations with and without fillers are composed of a number of materials, some of which (19) are shown in Table A7a. These polymers combined with fillers such as Si$_3$N$_4$, SiO$_2$, Al$_2$O$_3$, calcium hydroxyapatite, glass, glass ionomers, phosphates, etc. make up classes of materials called restorative dental composites. These composites, when cured with zero residue promoter or when light cured to full polymerization, possess good properties mechanically and no electrochemical ion transfer effects in the oral cavity. The strength of the materials, though falling short of amalgams for occlusal restorations, wear well. Adhesives, available from a number of manufacturers, perform very well in securing the restorations and in minimizing marginal leakage. The materials themselves are non toxic and present no reported hazard. The wear mechanism is clearly visible on filled composites, however, showing bonding failure after seven months between the filler and the matrix, leading to cracking in the restoration, as shown in Figure A7b. Also shown is a margin of a restoration fabricated from both a composite and amalgam (19). There is great promise for further work in the successful development of strong, long-lasting restorations made from combinations of polymers and inorganic fillers.

Table A7a. Some monomers used in dental restorations

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Structure</th>
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<tbody>
<tr>
<td>BISMA</td>
<td><img src="image" alt="BISMA Structure" /></td>
</tr>
<tr>
<td>HEMA</td>
<td><img src="image" alt="HEMA Structure" /></td>
</tr>
<tr>
<td>TEGDMA</td>
<td><img src="image" alt="TEGDMA Structure" /></td>
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<tr>
<td>EGDMA</td>
<td><img src="image" alt="EGDMA Structure" /></td>
</tr>
<tr>
<td>OFDMA</td>
<td><img src="image" alt="OFDMA Structure" /></td>
</tr>
<tr>
<td>UDMA</td>
<td><img src="image" alt="UDMA Structure" /></td>
</tr>
</tbody>
</table>

Figure A7

Seven month views of polymeric composites showing filler picking and marginal terracing

It should be noted that even occlusal regions in natural tooth enamel (a natural composite) crack and fail (20).

Ceramics Composed of aluminum oxide, glass ceramic phases, hydroxyapatites, sapphire single crystals, etc., are extremely durable and inert as implant materials, but have shortcomings as restoration materials. They are mostly very hard materials and offer an abrasive surface to opposing natural teeth or other restorations. In addition, they may fracture, presenting a danger of swallowing sharp debris or cutting oral tissue near the remaining restoration. As work proceeds with these highly inert, non-ion releasing materials, it is hoped that biomimetic analogs can be developed.
REFERENCES: