

BR-392

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 02/08/94

Project No. E-18-667 _____

Center No. 10/24-6-R6363-7A0_

Project Director MAREK M I _____

School/Lab MSE _____

Sponsor DHHS/PHS/NIH/NATL INSTITUTES OF HEALTH _____

Contract/Grant No. 2 R01 DE07754-07 _____

Contract Entity GTRC

Prime Contract No. _____

Title DISSOLUTION OF MERCURY FROM DENTAL AMALGAMS _____

Effective Completion Date 940131 (Performance) 940430 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	N	_____
Final Report of Inventions and/or Subcontracts	N	_____
Government Property Inventory & Related Certificate	N	_____
Classified Material Certificate	N	_____
Release and Assignment	N	_____
Other _____	N	_____

Comments CONTINUED BY E-18-699. _____

Subproject Under Main Project No. _____

Continues Project No. _____

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Management	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other CARL BAXTER-FMD _____	Y
_____	N

PROGRESS REPORT SUMMARY		GRANT NUMBER DE07754-08	
PRINCIPAL INVESTIGATOR OR PROGRAM DIRECTOR MAREK, MIROSLAV I		PERIOD COVERED BY THIS REPORT	
APPLICANT ORGANIZATION Georgia Tech Research Corporation, Georgia Institute of Technology		FROM 02/01/94	THROUGH 01/31/95
TITLE OF PROJECT (Repeat title shown in item 1 on first page) DISSOLUTION OF MERCURY FROM DENTAL AMALGAMS (SEE INSTRUCTIONS)			

1. SPECIFIC AIMS

The goal of the program is an understanding of the release of mercury from dental amalgam restorations, including the mechanism, kinetics and effects of variables. The study is performed *in vitro*. The 3-year research program has been planned with the following Specific Aims:

1. To determine the kinetics of formation of an oxide film (repassivation) after a mechanical generation of a film-free surface.
2. To determine the kinetics of chemical transformations of mercury in simulated oral fluids.
3. To determine the kinetics of mercury dissolution from a mechanically generated film-free surface.

In the reported project period Specific Aim No. 1 was addressed. It was expanded and modified as a study of the mercury emission from a mechanically-generated, film-free surface of dental amalgam, and includes determination of the kinetics of oxide film formation on such surfaces. The objective is to determine if there is an enhanced mercury emission from mechanically generated surfaces, and if there is, what is the cause of the enhancement, how the emission rate varies with time, and what is the effect of atmosphere, especially oxygen, on the emission rate.

The hypotheses tested in this study is that a mechanical generation of a film-free surface, such as by fracture, results in an instantaneous formation of a thin film of liquid mercury covering part of the surface, which results in a substantially enhanced mercury emission. Liquid mercury evaporation, liquid mercury absorption in the amalgam, and oxide film formation are then the competing processes, which decrease with time the mercury release.

2. STUDIES AND RESULTS

The study was designed to take advantage of the analytical capability of Atomic Absorption Spectrophotometry (AAS), which allows a very sensitive detection of mercury vapor in a gas stream. A special test setup, which was built for this study, contains a small volume, glass flow-through cell, in which a notched amalgam specimen can be fractured by an impulse application of tensile force. The fracture load is generated by an electromagnet, which is momentarily connected to a DC power source. The mercury emitted from the fracture surfaces into a stream of gas flowing through the cell is passed through a flow-through cell of the AAS. The absorbance of light at the mercury wavelength (253.7 nm) produces a signal proportional to the concentration of mercury in the gas. The signal is monitored as a function of time and recorded, providing a measure of the time-dependent emission rate of mercury. Calibration of the output has been accomplished by a calibration bypass of the fracture cell, in which saturated mercury vapor is generated in a series of flasks with liquid mercury on the bottoms, maintained at constant temperature. The vapor from the flasks is mixed at known proportions with a mercury-free gas stream, using accurate flowmeters, providing a stream of gas of known mercury concentration. The fracture surface area has been estimated using quantitative stereology to allow calculation of the emission rate per unit area. For a comparison, mercury evaporation rate from pure liquid mercury was measured under the same conditions of gas flow. The mercury drop was generated in the flow-through cell in the given carrier gas stream to avoid any interaction with the laboratory air. All the tests were performed at 20°C, using as a carrier gas either ultra-high purity argon, or oxygen, at 100 mL/min. The tests to date have been performed using specimens of a low-copper amalgam.

All the results obtained to date have shown a very high initial rate of mercury following the fracture, reaching $15 \mu\text{g cm}^{-2} \cdot \text{min}^{-1}$. There has been no significant difference between the rates of initial mercury

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emission in argon and oxygen ($p < 0.05$). Following the initial peak the rate of emission slowly decreased with time for about 15 minutes, after which a sharper drop in the emission rate occurred. The drop was slightly sharper and reached a lower value in oxygen than in argon. The evaporation rate from liquid mercury was remained virtually constant in high purity argon, but started to decrease after about 15 minutes in oxygen, indicating formation of an oxide film on the liquid mercury surface.

The results of mercury emission from the fracture surfaces have been attributed to the formation, by the mechanical processes of fracture, of a thin film of mercury liquid on a portion of the surface. The comparison with the emission from the liquid mercury drop indicated that about 10-20% of the fracture surface of the mercury-containing may be covered with liquid mercury. The preliminary quantitative analysis has indicated that only a portion of this film evaporates, suggesting that part of the mercury diffuses back into the γ_1 phase. A combination of evaporation and absorption by diffusion is believed to explain the drop in the emission rate in the inert gas (argon). In oxygen, the decrease in the emission is further accelerated by on oxide film formation. The kinetics of the oxide formation on the mercury film is slow; when the liquid film is depleted by vaporization and absorption, tin oxide film formation further decreases the mercury emission to negligible values.

3. SIGNIFICANCE

The release of mercury from dental amalgam restorations continues to be controversial. Although the released amounts seem to be small, it is prudent to minimize the release of any toxic element into the human body. To be able to evaluate the potential physiological effects, and to find ways to minimize the release, the mechanism, kinetics, and effects of variable must be known. An *in vitro* study allow a measurement under controlled conditions.

The mercury release in the oral cavity involves mostly atomic mercury dissolution from the amalgam in oral liquids; mercury then either evaporates, or is oxidized to the ionic form. The volatile atomic mercury seems to be of greatest physiological concern. Mercury release is enhanced substantially by abrasion of the amalgam during chewing and brushing. The release of mercury from an amalgam surface that has been stripped of the surface oxide barrier and activated by a very localized surface deformation is thus the very important step the mercury release process, which probably contributes most to the total release. Although dry mercury evaporation may not be a significant event in the oral cavity, an understanding of the mercury emission from a mechanically generated, film-free, dry amalgam surface is a first step towards an understanding of the atomic mercury dissolution from surface abraded in the presence of oral fluids.

4. PLANS

In the proposed project period the study will be focused on achieving Specific Aim No. 2, *i.e.*, determination of the kinetics of mercury dissolution from a mechanically generated film-free surface. This phase of the program will be a logical extension of the study performed during the reported period. Armed with the knowledge of the conditions existing on the dry surface a fractured dental amalgam, the alteration of these conditions due to the presence of simulated oral fluids will be examined. The standard environment will be synthetic saliva of the composition, used in the previous studies (KCl: 1.5 g/L; $\text{NaHPO}_4 \cdot \text{H}_2\text{O}$: 0.5 g/L; KCSN: 0.5 g/L; Lactic acid: 0.9 g/L; NaHCO_3 : 1.5 g/L). All tests will be performed at 37°C.

The research program will include to types of test. In the first type, the electrode properties of the freshly generated fracture surface will be examined, using a high-speed data acquisition system. These tests will complement previous preliminary work, performed in this laboratory using a slower speed setup. The higher data acquisition speed will allow a better determination of the electrode properties and their changes under the conditions immediately following the fracture surface generation. The objective will be to

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determine if the same condition as in dry fracture tests, *i.e.*, formation of a film of liquid mercury, and formation of oxide films, exists in the presence of an electrolyte, and to determine the rates of the surface changes. Since the basic setup for amalgam specimen fracture in an electrochemical cell is available from previous studies, this phase of the research is not expected to meet unusual difficulties.

In the second type of tests the mercury dissolution rate from the fracture surface and its changes with time will be determined. For this purpose a special setup will be built, in which a small amount of simulated oral fluid will be sprayed on the fracture surface immediately after fracture, and its mercury content will be determined by AAS. The electrolyte access to the fracture surface will be repeated to obtain dissolution rate vs. time data. This part of the proposed research present a substantial challenge and is experimentally very demanding, and its chances of success cannot be reliably predicted. If successful, however, it will provide a very useful information on the mercury release during the most important phase of the release process.

Although the proposed test involves film-free surface generation by fracture, while the release under clinical conditions involves mainly abrasion, the fundamentals under both conditions are believed to be very similar. In both fracture and abrasion a film-free surface if generated by mechanical forces, and the surface suffers very localized deformation. The surface generation by fracture offers substantial advantages over abrasion in the speed of the surface creation and absence of filmed surface, which allows a more accurate determination of the time-dependent events.

5. HUMAN SUBJECTS

None

6. VERTEBRATE ANIMALS

None

7. PUBLICATIONS

Marek, M. "The Effect of the Electrode Potential on the Release of Mercury from Dental Amalgam: ," *Journal of Dental Research* vol. 72, 1315-1319, 1993.

8. INVENTIONS AND PATENTS

None