

Experimental Study and Mathematical Modeling for Corrosion of Amalgam at Different Periods

Rana A. Majed BSc, MSc., Ph.D. ⁽¹⁾

Khawla Abdul kathem Ali BSc, MSc. ⁽²⁾

Hind B. Al-Atrakchy BSc, MSc. ⁽³⁾

Hawraa D. Al-Deen BSc ⁽⁴⁾

Key words

corrosion of amalgam, artificial saliva, modeling for amalgam.

Abstract

This work involves experimental study for corrosion of amalgam as filling material after different period time (0, 7, 14, 21, 35, 42 days) in artificial saliva by electrochemical method to estimate corrosion parameters such as corrosion potential E_{corr} , corrosion current density i_{corr} , and Tafel slopes b_c & b_a . The results of polarization resistance which calculated according to Stern- Geary equation indicates that the resistance of amalgam was increased during the experimental period due to stable phases which produced between mercury and other powders in amalgam such as Sn-Hg and Ag-Hg, in addition to Ag-Cu and Ag-Sn phases. Cyclic polarization test shows that the reverse scan curves meet the forward scan curve along the passive range. Numerical modeling was achieved to estimate the corrosion behavior of amalgam in artificial saliva through longer period time, the results of this modeling shows that values of polarization resistance for amalgam at long time of filling decreases with time, but after 2200 days of filling, i.e. after at least 6 years.

Introduction

Dental amalgam, in widespread use for over 150 years, is one of the oldest materials used in oral health care. Its use extends beyond that of most drugs, and is predated in dentistry only by the use of gold. Many blended or dispersed phase high Cu amalgams show excellent clinical performance in long term clinical trials ⁽¹⁾. However, little is known concerning the microstructural changes that occur during clinical use of these systems ⁽²⁾. The corrosion and wear resistance of dental amalgams has been of much interest in recent years as a result of increased concern regarding toxicity arising from

amalgam particles and corrosion products in the oral cavity. A further concern results from the possible release of mercury and mercury vapour as well as the effect that mercury can have on antioxidant activity and neurotoxicological effects ⁽³⁾. A number of factors can influence the rate of corrosion. These include acidity of the contacting medium and temperature, which can both undergo sharp variations in a short period of time in the oral cavity, as well as the effective potential of the amalgam. For these reasons, a full understanding of the electrochemical and corrosion behavior of the amalgams can be of much benefit in taking appropriate measures to reduce amalgam corrosion as well as ensuring complete amalgamation such that there is no free mercury that can be vaporized ⁽⁴⁾. Many authors were investigated about various properties of

(1) Ass. Prof., Department of Materials Engineering, College of Engineering, University of Technology.

(2) Lecture, Department of Chemical Engineering, College of Engineering, University of Technology.

(3) Lecture, Department of Materials Engineering, College of Engineering, University of Technology.

(4) Engineer, Department of Materials Engineering, College of Engineering, University of Technology.

amalgam especially corrosion behavior. Jaro studied corrosion attacks on twenty-two dental amalgam restorations after in vivo service by Scanning Electron Microscopy together with the Energy Dispersive X-Ray Technique, and by optical microscopy. From the measured depth and type of corrosion attack, estimates of released mercury amounts are made. Model calculations of released mercury, based on previously published measurements of corrosion currents with and without abrasion are also given ⁽⁵⁾. Heloí'sa et al. observed that corrosion is a complex process, which involves contributions from each of the phases present as well as intergranular corrosion. It is thus of interest to investigate the corrosion of individual phases present in dental amalgams. In this work the corrosion behavior in 0.9% NaCl solution of Ag-Hg, Ag-Sn and Sn-Hg phase components of dental amalgams was investigated by electrochemical methods⁽⁶⁾. Chang et al. studied electrochemical behavior on microbiology-related corrosion of metallic dental materials. They showed that the corrosion behavior of dental metallic materials in the presence of streptococcus mutants and its growth by products is increased ⁽⁷⁾. Christopher et al. studied an electrochemical impedance study of the corrosion of Tytin dental amalgam in electrolytes similar to artificial saliva with or without lactic acid, and in standard inorganic artificial saliva with higher ionic concentration. Spectra were recorded in the presence and absence of dissolved oxygen to show the importance of the formation of oxide film and the adsorption of the organic component, as well as the exposed surface microstructure. The data, supported by open circuit potential and polarization curve experiments, obtained in the presence and absence of dissolved oxygen are interpreted in the light of possible corrosion mechanisms ⁽⁸⁾. Maruthamuthu studied the electrochemical behavior of microbes on orthodontics wires in artificial saliva with or without saliva, and he showed that bacteria slightly reduce the resistance and increase the corrosion current ⁽⁹⁾. Van Vuuren et al. studied galvanic corrosion due to release

elements from the alloy into the oral cavity with possible harm to the patient. This in vitro study was conducted to determine the extent of galvanic corrosion where different dental amalgams and Co-Cr alloy combinations were placed in contact with artificial saliva as an electrolyte. The tests were conducted with potential measurements as well as potentiodynamic and potentiostatic polarisation techniques. Results showed that the galvanic corrosion current density is much lower than the corrosion current density, indicating that galvanic coupling of the samples does not have a substantial effect on the overall corrosion of the samples⁽¹⁰⁾. Mahler et al. observed that amalgam restorations, when first placed, have been shown to exhibit a gap at the amalgam/tooth interface. With time in service, this gap fills with corrosion products that have the potential to "seal" the restoration. With the advent of high-copper, more corrosion-resistant amalgams, there has been concern that the time required to create this seal would be increased significantly when compared with low-copper traditional amalgams. The current study was designed to address this concern. Analysis of a tooth extracted after 16 years of clinical service that had been restored with an amalgam-containing zinc was also shown to contain zinc corrosion products in the occlusal marginal area. This could explain the reported reduction in marginal fracture of clinically placed amalgam restorations made from zinc-containing alloys⁽¹¹⁾. Zhang et al. studied effect of silver on corrosion behavior of Ti-Ag alloys in artificial saliva solutions. They showed that addition of silver to titanium is effective in reducing the corrosion current density and increasing the open circuit potential of Ti-Ag alloy in artificial saliva environment. The presence of fluoride leads to higher corrosion current densities and lower open circuit potential for the alloys ⁽¹²⁾. Mareci et al. studied electrochemical behavior of two Ag-Pd alloys in Carter-Brugiard/ AFNOR/NF artificial aerated saliva at pH 8.1. Electrochemical measurements were carried out at 25°C under static conditions. They concluded that the open circuit

potential of Ag–Pd are attributed to dealloying followed by surface enrichment with Ag and the possible formation of an insoluble AgCl surface film on the respective alloy surfaces⁽¹³⁾. This work investigates the corrosion behavior of amalgam after preparation for different period (0, 7, 14, 21, 35 and 42). The electrical potential at the metal electrolyte surface is strongly dependent on the nature and the concentration of the electrolyte, pH and surface conditions. As a result, the electrochemical reactions at this interface vary with time.

Experimental Procedure

Materials and Chemicals

The used alloy in this study was high copper amalgam which obtained from Megalloy EZ spherical alloy (high strength and high copper) ; the specimens were made by triturating 0.7 gm of powder alloy and the corresponding weight of mercury by amalgamator type (YDM-Pro) for 15 seconds at high speed. The specimens were prepared according to A.D.A. specification No.1; after the triturating, the amalgam paste was immediately inserted into the cavity of the die with several thrusts of an amalgam condenser, and then a compressive stress has applied by inserting a punch in the die and applying 80 Kg/m² over the punch for 15 seconds. The chemical composition of this alloy is shown in Table (1). Cold mounted using pyrax polymers to obtain only surface area for corrosion test. All experiments were carried out at 37±1 °C by using water bath. The open side was polished mechanically to a mirror finish, rinsed in distilled water and stored in desiccators. The electrolyte reference used was modified Fusayama artificial saliva^(14,15), which closely resembles natural saliva, with composition of (0.4 g/L KCl, 0.4g/L NaCl, 0.906 g/L CaCl₂.2H₂O, 0.69 g/L NaH₂PO₄.2H₂O, 0.005g/L Na₂S.9H₂O and 1g/L urea). pH of this electrolyte was 5.3 .

Corrosion Test

Polarization experiments were performed in (WINKING M Lab 200

Potentiostat/Galvanostat from Bank-Elektronik) with electrochemical standard cell with provision for working electrode (amalgam), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with saturated calomel electrode SCE reference electrode. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate 3 mV.sec⁻¹. The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) in addition to measure the Tafel slops by Tafel extrapolation method.

Results and Observations

Corrosion Behavior

Fig.(1) shows the variation of open circuit potential (ocp) with time, from which several deductions can be made. The first is that the initial potential in artificial saliva vs. SCE. This could be due to the mixed potential resulting from the ionic constitution of the solutions. This figure indicates that through the time the E_{oc} shifts to nobler values. The polarization curves, (Fig. 2), show, in general, that the anodic and cathodic region shifted to the lower current densities and more noble potentials, the data are listed in the Table (2). In these curves can be seen the anodic reactions which represent the dissolution of metals in amalgam, while at cathodic sites reduction of hydrogen and oxygen can occur. The polarization resistance (R_p) can be determined from the Tafel slopes and according to Stern- Geary equation:

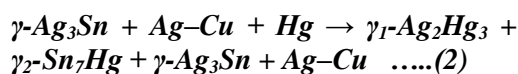
$$R_p = \left(\frac{dE}{di} \right)_{i=0} = \frac{b_a b_c}{2.303(b_a + b_c) i_{corr}} \dots\dots(1)$$

The values of R_p which have been calculated from above equation are presented in table (2). These data indicate that the polarization resistance values of amalgam were increased when the time of filling increased. Cyclic polarization curves as shown in Fig.(3) show that after 7, 14 and 21 days of filling, the reverse scan shifted to lower current densities and the better behavior was noted after 14

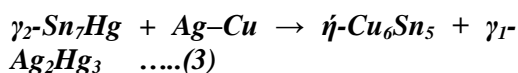
days, as well as disappear the small hysteresis loop in scan of 0 days. Cyclic polarization of amalgam after 35 and 42 days show wide reverse scan and shifted to lowest current densities. This type of cyclic polarization curve is known to resist localized corrosion. It is also observed that the reverse scan curves meet the forward scan curve along the passive range. The potentials for the reverse scan curves are more positive than those for the forward scan.

Discussion and Interpretation

Mercury diffuses into the alloy particles and reacts with silver, tin and copper, forming various compounds. The exact compounds formed depend on the chemical composition of the powder and on particle shape (which can be spherical or irregular) but are mainly phases of the systems Sn–Hg, Ag–Hg, with Ag–Cu and Ag–Sn phases remaining from the reactants. For the currently used, high copper amalgams, the main reaction is ⁽¹⁶⁾:

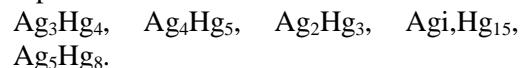


The Sn–Hg phase, which has a relatively low corrosion resistance, then undergoes further reaction, according to



The microstructure of the dental amalgam is complex, consisting of new microphases, as produced in the reactions above, and the remains of the powder alloy particles, within the $\gamma_1\text{-Ag}_2\text{Hg}_3$ matrix phase⁽¹⁶⁾. For this reason, and in order to understand better the role of the various phases, individual phases have electrochemical measurements can lead to an improved understanding of the processes that take place at the amalgam electrode surface as well as the influence of surface oxide. The conventional silver amalgam consists of several metallographic phases, mainly gamma, gamma-1 and gamma-2. In literature, the composition of the phases is often given as

Ag_3Sn , Ag_3Hg_4 and Sn_7Hg , respectively. However, the composition of gamma-1 and gamma-2 does not seem to be the same in various fillings. For gamma-1 phase the following formulas have been reported:



The gamma-2 has been described as Sn_7Hg , Sn_8Hg , $\text{Sn}_{7.8}\text{Hg}_2$ and Sn_6Hg . Apparently, the structure of a fresh amalgam filling can vary considerably. Hypothesis has also been proposed, that the released mercury may partly react with Ag_3Sn , to produce additional Sn_7Hg , so that the corrosion cycle can continue. The filling becomes porous and can lose most of its strength. Absorption of released mercury by Ag_3Sn requires the absorbing phase in close vicinity of the corroding Sn_7Hg -phase, otherwise there is no thermodynamical reason for mercury to diffuse into the filling with high mercury content. Rather, it will evaporate. The content of Ag_3Sn may vary depending on amalgam composition and working methods of the particular dentist. As the amount and distribution of Ag_3Sn cannot be controlled, the hypothesis about Ag_3Sn as a sink for all mercury released by corrosion is not substantiated. In particular, surface corrosion will result in evaporation and abrasion of major part of free mercury, rather than its diffusion into the filling. As has been shown by Brecht-Bergen ⁽¹⁷⁾ the partial pressure of mercury over amalgam is 11–25% of that over pure liquid mercury, and increases with increasing mercury concentration and temperature. The corrosion products found on amalgam surfaces are mainly tin oxide and hydrochloride ⁽¹⁸⁾ and silver chloride ⁽¹⁹⁾. Instead, as reported by Brune ⁽²⁰⁾ silver has been found in the solution already after a few days exposure to artificial saliva. Though ionized mercury also has been found among the dissolved corrosion products by radioactive tracer method ⁽²¹⁾ the main part is released as metallic mercury, which can be found as droplets on freshly corroded amalgam surfaces ⁽²²⁾. The evaporated mercury can be measured in expired air ^(23, 24).

Mathematical Modeling

Mathematical calculations were achieved to predict the corrosion behavior of amalgam for long-term as shown in the Figs. (4) and (5) using Mat Lab analysis. Table (3) shows the predicted values of long time and corrosion parameters. Fig. (4) shows the predicted values of open circuit potential and corrosion potential for amalgam at long time, this figure indicates that these potentials became more negative. Fig. (5) shows the

predicated values of polarization resistance for amalgam at long time and the results of this figure indicates that the resistance decreases with time, but after 2200 days, i.e. after at least 6 years. These results agreement with the investigations that show the long-term release of mercury from a few amalgam fillings will often reach or exceed the recommended limits for daily intake of mercury. Hence, mercury from corroding amalgam fillings represents a potential health hazard⁽⁶⁾.

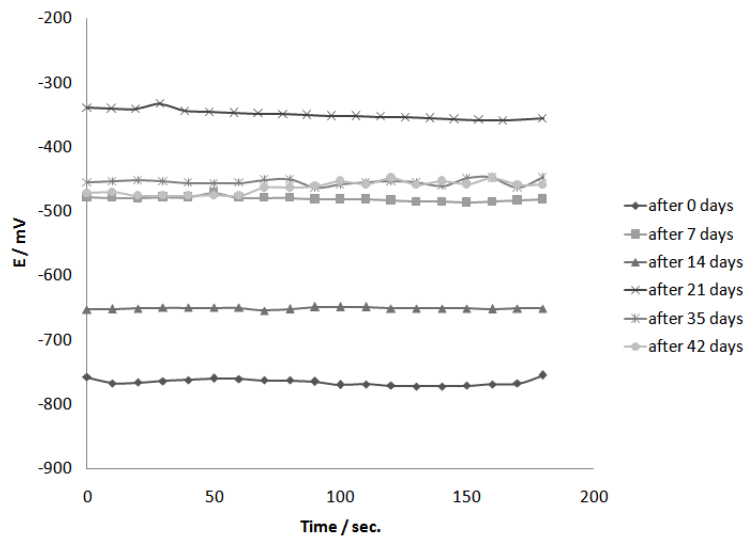


Fig.(1):- The variation of open circuit potential – time for amalgam in artificial saliva.

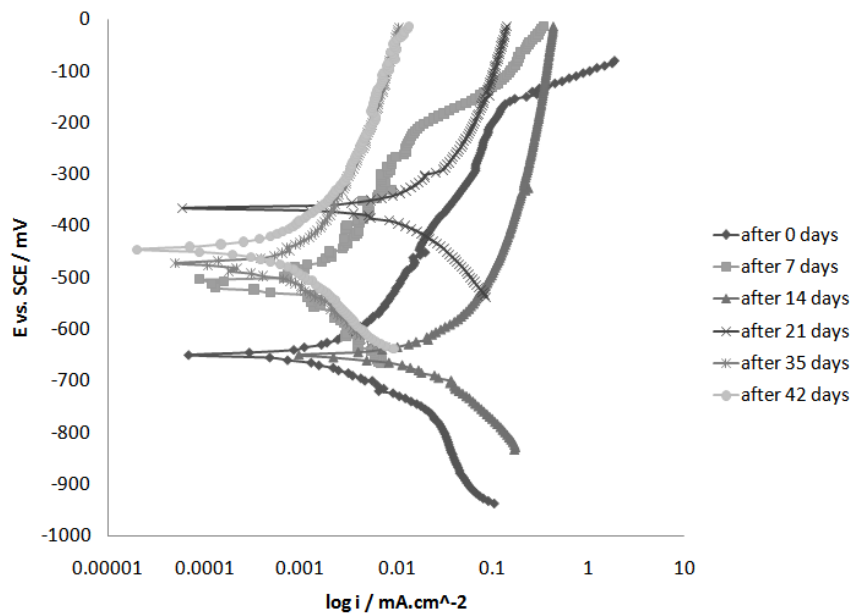


Fig. (2):- Potentiodynamic polarization for amalgam in artificial saliva at different time after filling.

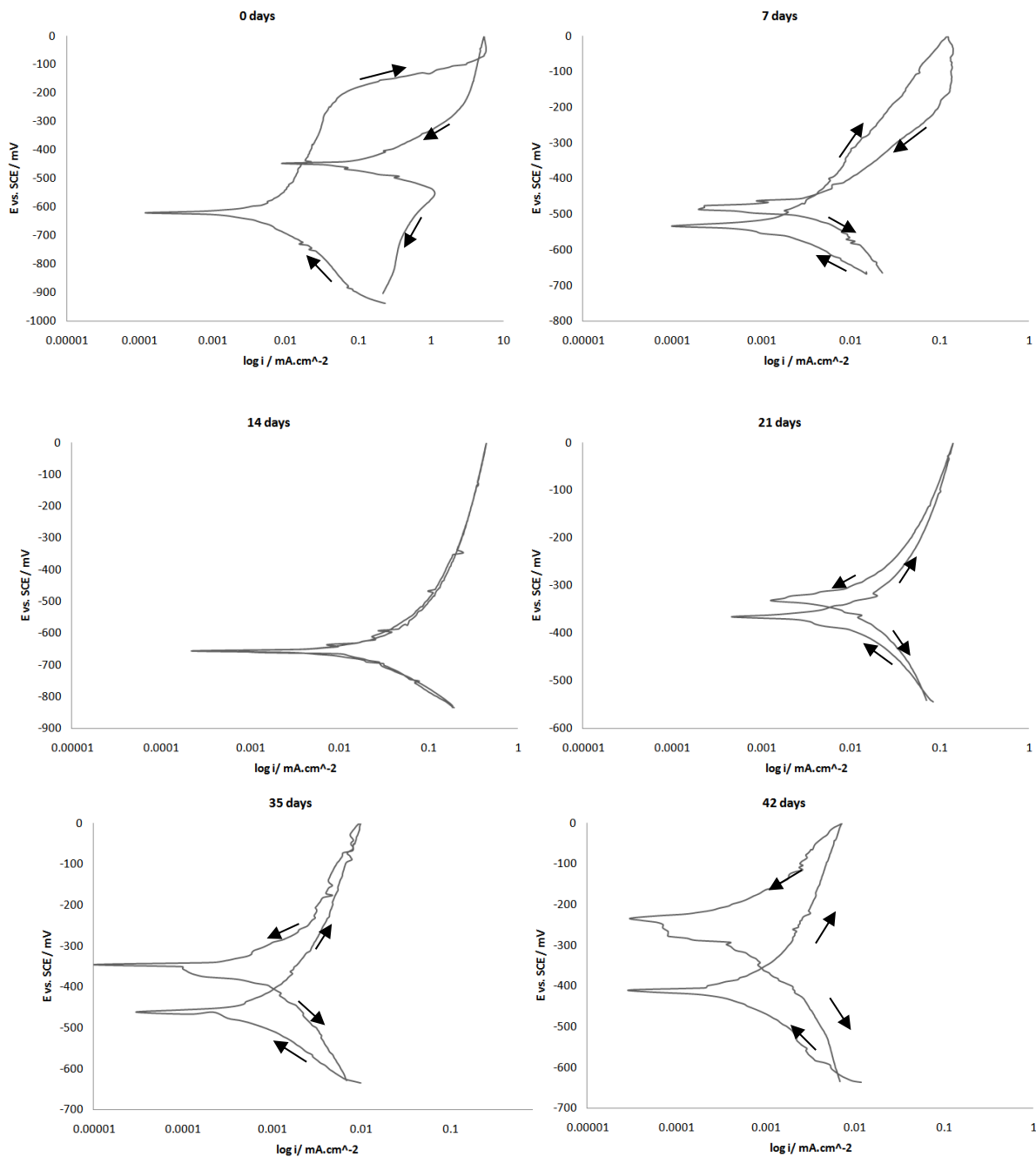


Fig. (3):- Cyclic polarization for amalgam in artificial saliva at different time after filling.

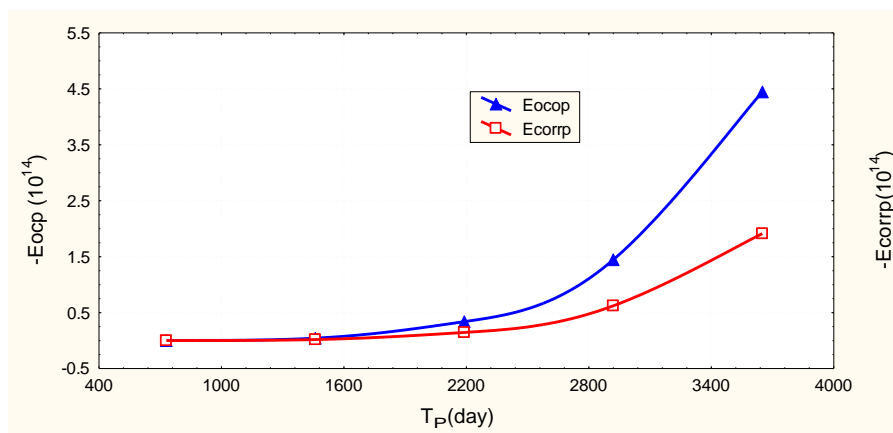


Fig. (4):- Predicted values of E_{oc} and E_{corr} for amalgam in artificial saliva at long time after filling.

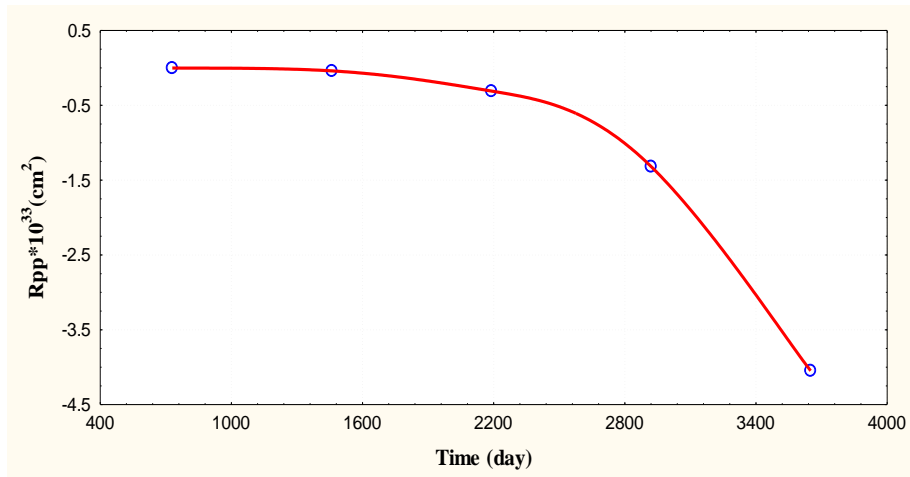


Fig. (5):- Predicted values of R_p for amalgam in artificial saliva at long time after filling.

Table (1):- Chemical composition of amalgam.

Metal	Ag	Sn	Cu
Wt%	56.7	28.6	14.7

Table (2):- Corrosion parameters of amalgam in artificial saliva during different periods.

Time Day	$-E_{oc}$ mV	$-E_{corr}$ mV	i_{corr} nA.cm ⁻²	$-b_c$ mV.dec ⁻¹	b_a mV.dec ⁻¹	$R_p \times 10^{+6}$ Ω.cm ²
0	755	653.0	1100.0	68.6	94.8	0.0157
7	482	496.0	569.40	126.0	111.9	0.0453
14	652	512.3	371.31	60.9	69.4	0.0380
21	356	367.0	355.42	104.7	112.1	0.0662
35	447	475.0	581.29	153.9	160.3	0.0587
42	459	444.5	380.26	115.0	131.5	0.0701

Table (3):- Predicated corrosion parameters of amalgam in artificial saliva during long different periods.

Time Day	$-E_{oc} \times 10^{14}$ mV	$-E_{corr} \times 10^{14}$ mV	$R_p \times 10^{+33}$ Ω.cm ²
730	0.0013	0.0005	-0.0012
1460	0.0436	0.0188	-0.0399
2190	0.3391	0.1459	-0.3095
2920	1.4462	0.6222	-1.3177
3650	4.4458	1.91221	-4.0468

References

- 1-M.L. Swartz, Ralph W. Phillips, and Mohamed Daoud EL Tannir, Tarnish of Certain Dental Alloys, *J Dent Res*,(1958); 37 (5): 837-847.
- 2-M.Marek, Corrosion Test for Dental Amalgam, *J Dent Res*, (1980);59(1):63-69.
- 3-R.S. Mateer and C.D. Reitz, Corrosion of Amalgam Restorations, *J Det Res*, (1970);49(2): 399-407,.
- 4-M. Fathi, and V. Mortazavi, A Review on Dental Amalgam Corrosion and Its Consequences, *Journal of Research in Medical Sciences*,(2004);1:42-5.1
- 5-Jaro Pleva, Ph.D., “Corrosion and Mercury Release from Dental Amalgam”, *Journal of Orthomolecular Medicine*, (1989);4(3):141-158.
- 6-Heloi’sa A. Acciari, Antonio C. Guastaldi, Christopher M.A. Brett, “Corrosion of dental amalgams: electrochemical study of Ag–Hg, Ag–Sn and Sn–Hg phases”, *Electrochimica Acta*, (2001); 46:3887–3893.
- 7-Chang JC, Oshida Y, Gregory RL, Andress CJ, Thomas M, Barco DT, “Electrochemical study on microbiology- related corrosion of metallic dental materials”, *Biomed. Mater. Eng.* , (2003); 13:281-95.
- 8-Christopher M.A. Brett , Florin Trandafir, “The corrosion of dental amalgam in artificial salivas: an electrochemical impedance study”, *Journal of Electroanalytical Chemistry*, (2004);572:347–354.
- 9-Maruthamuthu S, “Electrochemical behavior of microbes on orthodontics wires”, *Curr. Sci.* , (2005);89:988-1005.
- 10-Van Vuuren L.J., Odendaal JS., Pistorius PC., “Galvanic corrosion of dental cobalt-chromium alloys and dental amalgam in artificial saliva”, *Journal of the South African Dental Association*, (2008);63(1):34-38.
- 11-Mahler D. B., Pham B. V., and Adey J. D., “Corrosion Sealing of Amalgam Restorations In Vitro”, *Operative Dentistry*: (2009);34(3) May:312-320.
- 12-Zhang B.B., Zheng Y.F., Liu Y., “Effect of silver on the corrosion behavior of Ti-Ag alloys in artificial saliva solutions”, *Dental Materials*, (2009); 25:672-77.
- 13- Mareci D., Sutiman D., Caliean A. and Bolat G., “Comparative corrosion study of Ag-Pd and Co-Cr alloys used in dental applications”, *Bull. Mater. Sci.*, (2010);33(4):491-500.
- 14-Geis- Gerstorfer J , Weber H. "Effect of potassium thio cyanate on corrosion behavior of non- precious metal dental alloys", *Dtsch Zahnärztl*, (1985);40:87-91.
- 15-Zhang B.B., Zheng Y.F., Liu Y., "Effect of silver on the corrosion behavior of Ti-Ag alloys in artificial saliva solutions", *Dental Materials*, (2009) ;25:672-77.
- 16-H.A. Acciari, A.C. Guastaldi, C.M.A. Brett, *Electrochim. Acta*(2001);46:3887.
- 17-Brecht-Bergen N: Korrosionsuntersuchungen an Zinn-Silber-Amalgamen. *Zeitschr. Elektrochem.* (1933);39(12):927-935.
- 18-Sarkar NK, Marshall GW, Moser JB, Greener EH: In Vivo and in Vitro Corrosion Products of Dental Amalgam. *J. Dent. Res.* (1975);54: 1031-1038.
- 19-Guthrow CE, Johnson LB, Lawless KR: Corrosion of Dental Amalgam and its Component Phases. *Dent. Res.* (1967);46(6):1372-1381.
- 20-Brune D, Evje DM: Initial Corrosion of Amalgams in Vitro. *Scand. J. Dent. Res.* (1984); 92:165-171.
- 21-Brune D, Evje DM: Man's Mercury Loading From a Dental Amalgam. *Sci. Total Environ.* (1985);44:51-63.
- 22- Fredin B: Studies on the Mercury Release From Dental Amalgam Fillings. Univ. of Lund, Dept. Physiol. Chemistry, Sweden, (1985).
- 23-Sware CW, Peterson LC, Reinhardt JW, Boyer DB, Frank CW, Gay DD, Cox RD: The Effect of Dental Amalgams on Mercury Levels in Expired Air. *Dent. Res.* (1981);60:1668-1671.
- 24-Patterson JE, Weissberg BG, Dennison PJ: Mercury in Human Breath from Dental Amalgams. *Bull. Environ. Contam. Toxicol.* (1985);34:459-468.