Long-term corrosion studies in vitro of amalgams in contact

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Three types of amalgams, one conventional and two with a high copper content, were stored in phosphate-buffered 0.9% NaCl solution, at pH 6, for 35 weeks. Every 7 weeks the solutions were changed and analyzed with regard to Cu, Zn, Sn, Hg, and Ag. In one of the amalgam combinations, the conventional amalgam and one of the copper-rich amalgams in an area ratio of 2:1, contact between the amalgams clearly increased the amounts of Cu, Hg, and Ag released the first 14 weeks compared with when immersed in separate solutions. With the reversed area relation, Cu, Hg, and Ag decreased when they were in contact. The conventional amalgam in contact with the other copper-rich amalgam, in an area ratio of 2:1, reduced the amount of Cu but increased the Zn released. Polishing initially decreased the amounts of Cu and Zn released compared with the unpolished amalgams. □ *Crevice corrosion; dental alloys; metal release; microstructure*

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The γ_2 phase in conventional amalgams has been identified as the most corrosion-prone phase (1, 2). In amalgams containing a high content of copper, the Cu-rich phases have shown to be most prone to corrosion (3). Cu-containing corrosion products are formed on the surface of high-copper amalgams (4), and the release of Cu from some amalgams has been reported to be substantial (5). When the corrosion of amalgams extends into the amalgam body, the release of corrosion products from the surface, in a saline solution, has been shown to increase (6).

The corrosion of the heterogeneous structure of amalgam depends on both the corrosion properties of the individual phases and the electrochemical interaction between them in an electrolyte (3). Common situations in clinical practice are amalgam restorations in close contact with each other. Under these circumstances a galvanic cell is formed which might alter the corrosion of the amalgams.

In a short-term study highly polished amalgam surfaces were shown in vitro to have a low current density when coupled to gold compared with non-polished amalgams (7). The elimination of porosities related to the condensation technique is of importance in reducing the corrosion of amalgams (8).

The long-term effect on the release of corrosion products from the surfaces of amalgams coupled together has not previously been investigated. The aim of the present investigation was therefore to study the corrosion effect, by measuring the amount of elements released from the amalgams into a saline solution and by analyzing the microstructure of the amalgams.

Materials and methods

Three types of amalgam were used in the study, one conventional amalgam (ANA 68) and two amalgams with a high copper content (Table 1). One of the latter was a blended alloy (Dispersalloy) and the other a single-composition alloy (ANA 2000).

Two of the amalgams, ANA 68 and Dispersalloy, were made in the shape of plates with three holes, and all three amalgams were made in the shape of plugs. The surface of the plates was 6.7 cm^2 and of the

Table 1. The amalgam alloys used in the investigation, their compositions, in percentage by weight, according to the manufacturers, and recommended mercury to alloy ratio

Metal	ANA 68*	Dispersalloy†	ANA 2000*
Mercury	1.5	—	1.6
Silver	68	70	42
Tin	26	18	29.4
Zinc	0.3	0.9	0.2
Copper	5.5	12.4	25
Mercury/ alloy ratio	1/1	1/1	1.1/1
Batch no.	7903	OC 703	7-194

* Nordiska Affineriet ANA, Helsingborg, Sweden.
† Johnson & Johnson Dental Products Co., East Windsor, N.J., USA.

plugs 1 cm^2 each. The plates were mounted in acrylic holders, and three plugs were inserted in the holes of each plate. Because of some conicity, the plugs were stuck to the plates by friction. A plate with plugs is shown in Fig. 1. The ANA 68 plates were combined with Dispersalloy and ANA 2000 plugs and the Dispersalloy plates with ANA 68 and ANA 2000 plugs. Five specimens were made of each combination. Five plates of ANA 68 and Dispersalloy, without amalgam plugs in contact, and five acrylic plates for each type of amalgam plugs were also made.

The amalgam plugs were made in a steel mold, and the condensation was done by hand for 60 sec, starting 30 sec after trituration. The mean pressure applied was 10 N/mm^2, and the thrusts were given with a frequency of 1/sec. Excess of amalgam was brushed away 120 sec after the end of trituration, and the specimens were separated from the mold. The plates were made in an acrylic mold in a similar manner. To evaluate the effect of hand condensation, plugs were also made in a standardized manner with a constant pressure of 14 N/mm^2 in a machine (Zwick 1454, Zwick Werkstoffprufmaschinen, Zwick GmbH & Co., Ulm, FRG) according to ADA specification no. 1 (9).

All specimens were polished with a silicon-carbide wheel with intermittent soaking in water 24 h after condensation. The effect of polishing was evaluated by immersion of plugs that had not been polished.

Twenty-four hours after condensation each specimen was placed in a glass beaker (25 ml) with 23 ml of sterilized 0.9% NaCl solution (made of deionized double-distilled water) buffered to pH 6.0 with phosphate (NaH_2PO_4, 8.8 mM, and Na_2HPO_4, 1.2 mM). The beakers were stored at 37°C and shaken for a few seconds once a day. The experiment was in progress for 35 weeks. Every 7 weeks the solutions were renewed and analyzed. The corrosion products that precipitated on the surface of the specimens were removed by light brushing with a soft toothbrush in the solution. The solutions were analyzed by means of an atomic absorption spectrophotometer (Pye Unicam SP 190, Pye Unicam Ltd.,

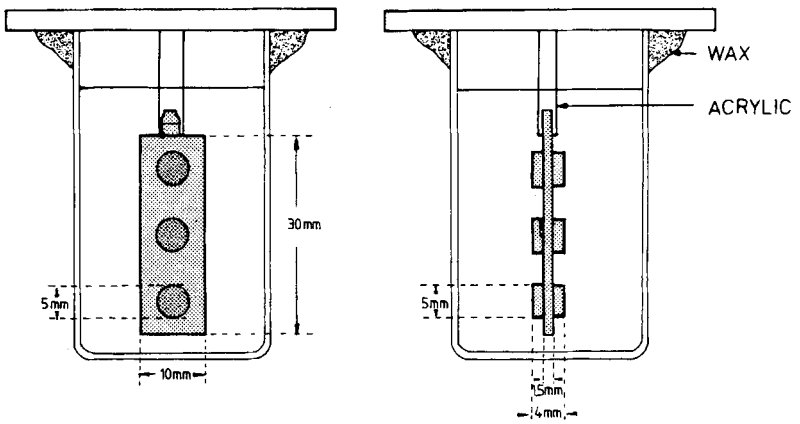

Fig. 1. A plate with three plugs in phosphate-buffered saline solution.

Cambridge, England) with regard to Cu, Zn, Ag (air/acetylene flame), Sn (nitrous oxide/acetylene flame), and Hg (cold vapor). The methods of analysis used were the same as described previously (10).

The microstructure of the amalgams was examined in a scanning electron microscope (Philips SEM 501, Philips, Eindhofen, Holland) operating in a secondary and back-scattered electron mode. The different phases were identified with an energy-dispersive detector (EDAX). Cross-sections of the specimens were polished by standard metallographic techniques.

Statistical analysis

To obtain homogeneity of the variances, the amounts of elements measured were transformed into logarithms, and differences were tested by Student's *t* test for two means. $p < 0.01$ was chosen as the level of statistical significance.

Results

The amounts of elements released from the amalgam plates and plugs when immersed in separate solutions and in contact with each other are presented in Tables 2–5. The release of Cu, Zn, Hg, and Ag was larger per unit area from the plugs (3 cm^2) than from the plates (6 cm^2), for both ANA 68 and Dispersalloy. However, the Dispersalloy plugs released less Sn than the plates, whereas no such difference was found for ANA 68.

ANA 68 plates in contact with Dispersalloy plugs

A comparison of the amounts of elements released from the amalgams showed that the release of Cu, Hg, and Ag was clearly increased during the first 14 weeks when the amalgams were stored in contact with each other, compared with when separately immersed in different solutions (Fig. 2). However, these differences leveled out during the rest of the experimental period. After 35 weeks, when measurements every 7 weeks were accumulated, only Cu was found in larger amounts (Table 2).

When the amalgams were in contact, ANA 68 was less rough and tarnished and the cross-sections showed less subsurface corrosion than the amalgams stored separately. Dispersalloy, in contrast, showed pronounced subsurface corrosion, sometimes in connection with expansion near the crevice between the amalgams, when they were in contact (Fig. 3). The crevices were filled with corrosion products, predominantly Sn and Cl. The subsurface corrosion in the crevice was less, compared with outside the crevice. The γ_2 phase in ANA 68 was also sparse in this region.

Dispersalloy plates in contact with ANA 68 plugs

With the reversed area relation the contact between ANA 68 and Dispersalloy resulted in smaller amounts of elements released into the solutions (Table 3). The amalgams in contact released less Cu than the Dispersalloy plates immersed without plugs. The reduction of Cu was therefore mainly due to a decreased release from Dispersalloy. In the same manner it can be established that the decreased release of Hg and Ag mainly depended on ANA 68.

When immersed in contact, the amalgams, particularly ANA 68, where brighter and more shiny and showed less subsurface corrosion than those immersed separately. The crevice between the amalgams showed the same appearance as with the reversed area ratio.

ANA 68 plates in contact with ANA 2000 plugs

Contact between the amalgams decreased the Cu released from ANA 2000 (Table 4), whereas Zn increased.

The cross-sections showed no differences between amalgams in contact or not in contact. However, contact between the amalgams resulted in less tarnish being formed on ANA 68. The crevices were only partly filled with corrosion products, mainly Sn and Cl (Fig. 4).

Table 2. The amounts of metals released from ANA 68 plates and Dispersalloy plugs when immersed in separate solutions during 35 weeks (accumulated values from measurements every 7 weeks) and immersed in contact with each other. The mean and standard deviation (SD) for five specimens are presented

	Amounts of metals released (μg)									
	Cu		Zn		Sn		Hg		Ag	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
ANA 68 plates	122	179	56.7	26.4	3707	4470	124	147	59.6	71.7
Dispersalloy plugs	4810	1066	1256	190	291	101	283	76	137	34
Total	4932	1245	1313	216	3998	4571	407	223	197	106
In contact	10,400*	5408	1493	260	1157	613	564	471	324	177

* Statistically significant difference, $p < 0.01$, between the sum of amounts obtained from the plates and the plugs stored in separate solutions and the amounts released when they were in contact.

Table 3. The amounts of metals released from Dispersalloy plates and ANA 68 plugs when immersed in separate solutions during 35 weeks (accumulated values from measurements every 7 weeks) and immersed in contact with each other. The mean and standard deviation (SD) for five specimens are presented

	Amounts of metals released (μg)									
	Cu		Zn		Sn		Hg		Ag	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Dispersalloy plates	2904	2302	1084	487	1485	76	203	67.5	111	44.9
ANA 68 plugs	962	650	66.3	20.0	1664	517	445	169	284	118
Total	3866	2952	1150	507	3149	593	648	237	395	163
In contact	1102*	2421	633	314	941*	190	122*	122	58.1*	52.0

* Statistically significant difference, $p < 0.01$, between the sum of amounts obtained from the plates and the plugs stored in separate solutions and the amounts released when they were in contact.

Table 4. The amounts of metals released from ANA 68 plates and ANA 2000 plugs when immersed in separate solutions during 35 weeks (accumulated values from measurements every 7 weeks) and immersed in contact with each other. The mean and standard deviation (SD) for five specimens are presented

	Amounts of metals released (μg)									
	Cu		Zn		Sn		Hg		Ag	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
ANA 68 plates	122	179	56.7	26.4	3707	4470	124	147	59.6	71.7
ANA 2000 plugs	4482	1989	43.2	14.8	530	81	537	170	241	72
Total	4604	2168	99.9	41.2	4237	4551	661	978	301	144
In contact	816*	1451	631*	194	1545	1115	504	705	251	333

* Statistically significant difference, $p < 0.01$, between the sum of amounts obtained from the plates and the plugs stored in separate solutions and the amounts released when they were in contact.

Table 5. The amounts of metals released from Dispersalloy plates and ANA 2000 plugs when immersed in separate solutions during 35 weeks (accumulated values from measurements every 7 weeks) and immersed in contact with each other. The mean and standard deviation (SD) for five specimens are presented

	Amounts of metals released (μg)									
	Cu		Zn		Sn		Hg		Ag	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Dispersalloy plates	2904	2302	1084	487	1485	76	203	67.5	111	44.9
ANA 2000 plugs	4482	1989	43.2	14.8	530	81	537	170	241	72
Total	7386	4291	1127	502	2015	157	740	238	352	117
In contact	8424	5434	1785	878	913*	196	762	356	309	131

* Statistically significant difference, $p < 0.01$, between the sum of amounts obtained from the plates and the plugs stored in separate solutions and the amounts released when they were in contact.

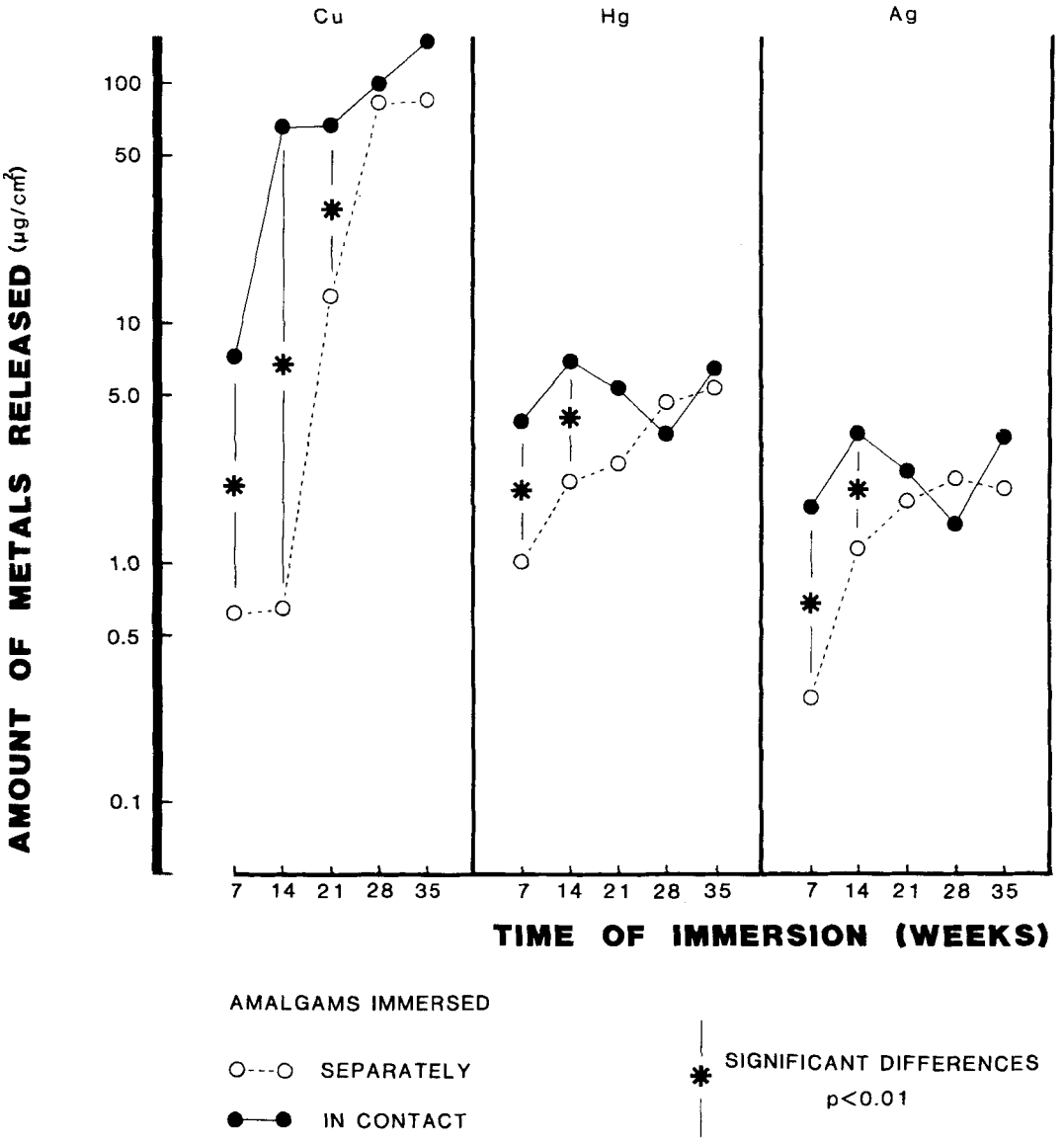

Fig. 2. Amounts of metals released from ANA 68 plates and Dispersalloy plugs immersed separately and in contact with each other during 35 weeks. The circles represent mean amounts of corrosion products released every 7 weeks. The mean values for immersed 'separately' represent the sum of the mean values obtained from the plates and plugs stored in separate solutions.

Dispersalloy plates in contact with ANA 2000 plugs

Contact between the amalgams decreased the release of Sn from Dispersalloy (Table 5).

Contact between the amalgams made the Dispersalloy plates more rough and tarnished than those not in contact. However, no differences were found in the microstructure as seen in cross-sections. The crevices showed heavy corrosion, but no specific corrosion product layer was formed, in con-

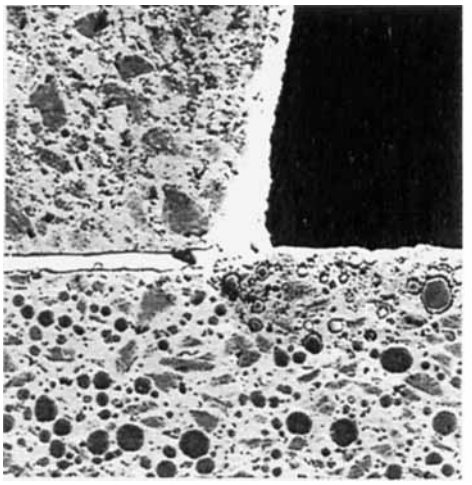

Fig. 3. Cross-section of an ANA 68 plate (upper) and Dispersalloy plug (lower) after 35 weeks in saline solution. The crevice is filled with corrosion products, and expansion of the Dispersalloy plug can be observed just outside the crevice.

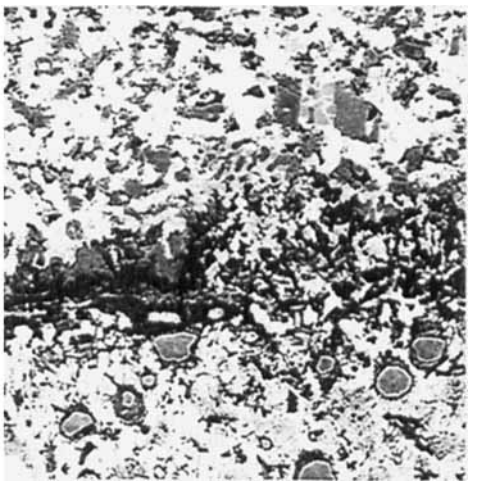

Fig. 5. Cross-section of a Dispersalloy plate (lower) and ANA 2000 plug (upper) after 35 weeks in saline solution. The amalgams are heavily corroded in the crevice, and the original structure is almost completely broken down.

trast to the other combinations in the study (Fig. 5).

Condensation

Condensation by hand, compared with the standardized condensation procedure used, gave no significant differences in the release of elements. No differences in the microstructure were observed in specimens condensed by the two methods.

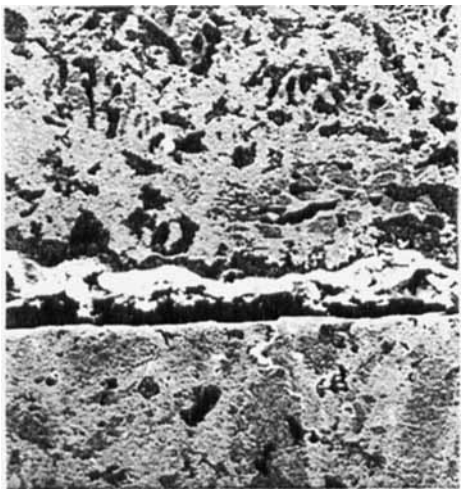

Fig. 4. Cross-section of an ANA 68 plate (upper) and ANA 2000 plug (lower) after 35 weeks in saline solution. The crevice is only partly filled with corrosion products.

Polishing

The release of Cu and Zn in the initial 14 weeks was lower for all the polished amalgams than for the unpolished ones. However, this difference leveled out during the rest of the experimental period, and after 35 weeks only the release of Cu from ANA 2000 showed clearly lower values for the polished amalgams. No such differences were observed for Sn, Hg, and Ag.

Discussion

The method used in this study and its clinical relevance have been discussed in a previous paper (10). To reduce the number of factors that could influence the corrosion process and to make comparisons with other published data possible, the relatively aggressive 0.9% NaCl solution was used. This Cl^- concentration is about six times as great as the concentration in saliva.

The results obtained confirmed the previous findings that the release rate of cor-

rosion products into an NaCl solution increases with time (10, 11). This increase is probably due to subsurface corrosion (6).

The standardized condition of machine-made amalgam specimens did not decrease the variations in the amounts of corrosion products released compared with those condensed by hand with a condenser.

The release of Cu and Zn was less after polishing. This seems to be in agreement with the results reported for amalgam in contact with gold (7), in which the current density measured was lower for polished surfaces than for unpolished.

In one of the amalgam combinations studied, ANA 68 plates and Dispersalloy plugs, contact between the amalgams clearly increased the amounts of Cu, Hg, and Ag released during the first 14 weeks. The corrosion products released, the microstructure of the cross-sections, and changes in surface texture indicated that Dispersalloy was the origin of the major part of these elements. The Cu_6Sn_5 phase of Dispersalloy probably was the most anodic phase in this combination, and ANA 68 was cathodically protected. However, when ANA 68 was in contact with ANA 2000, the reduction of Cu from ANA 2000 and increase of Zn released probably from ANA 68 suggest a protection of the Cu phases of ANA 2000. Zn has been shown to be liberated earlier than Cu from amalgams (12) and seems to be less dependent on galvanic action from a cathode to be released (10).

The reduction of corrosion products released into the solutions when amalgams were in contact with each other could to some extent be due to the volume of the saline solutions. This was smaller per unit area of the specimens when the plates and plugs were in contact in the same solution instead of stored in separate solutions not in contact. This smaller release is in accordance with the finding that less Cu, Zn, Hg, and Ag were released, per unit area, from ANA 68 and Dispersalloy when plates (6 cm^2), as compared with plugs (3 cm^2), were immersed in the 23 ml of solution.

The reduction of corrosion products released into the solutions could also be due to anodic protection as a result of another amalgam placed in contact (13). Strong cathodes, such as gold alloys, favor the formation of hydroxides in an NaCl solution (6). However, the corrosion potentials of the various amalgams are relatively close (3). If the influence from the alloy introduced is only slightly cathodic, this might cause anodic protection; that is, the corrosion products formed are retained on the surface, making the amalgam more passive. It has been shown that the insoluble oxides of Cu and Sn formed on the surface of amalgams show a higher degree of adhesion than the hydroxychlorides (4, 14).

The subsurface corrosion in the crevice was reduced compared with the subsurface corrosion outside the crevice when the conventional amalgam was in contact with the high-copper amalgams. Sn from the γ_2 phase in ANA 68 may have diffused into the crevice to form insoluble Sn compounds that retarded diffusion of the Cl^- into the crevice. When high-copper amalgams were in contact with each other, the acidity in the crevice probably favored dissolution of Cu and reduced the formation of a corrosion layer. The high anodic activity inside these crevices could result in cathodic protection of the surfaces outside.

The tarnish observed may, especially on ANA 68, illustrate specific characteristics of the compounds formed on the surface, such as low solubility and strong adhesion to the surface.

In the oral cavity the environment, with regard to corrosion, is complex. Both aggressive and inhibitory agents act on the amalgams. However, in a corrosive environment the tendency of copper-rich amalgams to form easily dissolvable copper compounds increases. The Cu release in particular seems to be susceptible to the influence of other amalgams in contact.

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