Long-term corrosion studies in vitro of amalgams and casting alloys in contact

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One conventional amalgam and two amalgams with higher copper content were stored in contact with various dental casting alloys in phosphate-buffered 0.9% NaCl solution, pH 6, at 37°C during 35 weeks. Every 7 weeks the solutions were changed, and the corrosion was measured by analyzing the solutions for the amount of Cu, Zn, Sn, Hg, Ag, Co, Cr, and Ni. In the first 7 weeks the amalgams immersed in contact with acrylic or Co–Cr alloys released small amounts of elements, whereas the release was larger when the amalgams were in contact with the gold alloys. During the rest of the experiment the release of elements tended towards the same level, independent of the casting alloy in contact. In general, the high copper amalgams released more corrosion products into the solutions than the conventional one. The release of corrosion products was strongly pH-dependent. Changing the solutions more often and saturating the solutions with oxygen decreased the amounts of Hg and Ag released.

☐ *Copper; dental alloys; mercury; metal release*

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Corrosion of dental alloys in the oral cavity may be influenced by the presence of other types of alloys. Dissimilar alloys placed in contact in the mouth may create galvanic currents, and elements may be released from the alloys. This in turn may lead to adverse effects on the patient (1–4). The elements released could cause allergy, lichen planus, and pain (5–10).

The corrosion of amalgam and gold when placed in contact in a 1% KCl solution has been studied in short-term (3 h) experiments and gave a high initial current (11). This current decreased with time due to formation of corrosion products on the amalgam surface. However, the galvanic action between gold and amalgam may be so strong that a protective film is not produced (12). Von Fraunhofer & Staheli (11) also found that a large cathode (gold) coupled to a small anode (amalgam) produced intense anodic attack. This was confirmed by Holland (13); the current density increased with an increased ratio between the gold and the amalgam surface area. Non-γ_2 amalgams, when measured in combination with gold during 1 h in an artificial saliva solution, gave much lower current density than conventional amalgams in contact with gold (13). Changes in the solution from pH 7 to pH 3 also increased the current density (11). Gjerdet (14) studied the potentials of dental Co–Cr and Ni–Cr alloys and amalgams after 1 h in an artificial saliva solution. These experiments indicated that the corrosion of amalgams, at least initially, may accelerate when Co–Cr and Ni–Cr alloys are placed in contact with amalgams.

The corrosion process of amalgams is not only limited to the outer area of the amalgam surface. After some time, the corrosion process involves also the subsurface area (15–17), which may influence the corrosion and the corrosion products released.

Chloride ions have been shown to play an important role in the corrosion of amalgams in vitro and in vivo (15, 18), and phosphates have been shown to inhibit the corrosion of amalgams in the presence of the chloride ion (19). Chlorides and phosphates are constituents found in various concentrations in natural saliva (20), at the tooth–amalgam interface and in food. In the present study a relatively aggressive solution with a Cl^- concentration six times that in saliva was chosen.

Table 1. The dental casting gold alloys used in the plates and their compositions according to the manufacturers, expressed in percentage by weight. Within parentheses the abbreviations used in the study

Metal	24k gold	Sjödings C* (JSC)	Sjödings M† (JSM)	Matticraft G‡ (MG)	Herador G§ (HG)	Jelenko 'O'¶ (Jel 'O')
Gold	99.9	76.5	87.8	86.0	82.64	87.5
Platinum		2.95	4.3	10.6	16.02	4.5
Palladium			5.8	0.1		6.0
Copper		11.5			0.18	
Silver		8.5	0.8	0.2		1.0
Zinc		0.5				
Iron			0.4			0.25
Indium			0.4	2.0	0.86	0.25
Iridium		0.05	0.1	0.1	0.17	
Tin			0.4			0.5
Rhodium				1.0		

* Conventional type III dental casting gold alloy. Sjödings, Spånga, Sweden.
† Gold alloy for ceramic fused to metal restorations. Sjödings, Spånga, Sweden.
‡ Gold alloy for ceramic fused to metal restorations. Johnson Matthey Metals Limited, London, UK.
§ Gold alloy for ceramic fused to metal restorations. Heraeus Edelmetalle GmbH, Hanau, FRG.
¶ Gold alloy for ceramic fused to metal restorations. J. F. Jelenko & Co., Armonk, N.Y., USA.

Studies concerning the effect of galvanic action between dental alloys over an extended time have not been published. This study is part of a larger project examining long-term corrosion effects of dental alloys by measuring the amounts of elements released into the electrolyte, and with particular reference to the effect of placing different alloys in contact. The aim of the present investigation was to study the corrosion effect, over several months, of combining dental gold, Co–Cr, and Ni–Cr alloys in contact with various amalgams.

Materials and methods

The specimens

The casting alloys and amalgams used in the investigation are presented in Tables 1–3. The compositions of Co–Cr and Ni–Cr alloys were not declared by the manufacturers, and the surfaces of the castings were therefore analyzed in a scanning electron microscope (Philips SEM 501, Philips, Eindhofen, The Netherlands) with an energy dispersive detector (EDAX). Constituents with low atomic number, such as boron and

Table 2. The cobalt–chromium and nickel–chromium dental casting alloys used in the plates and their compositions according to scanning electron microscopy (EDAX) analyses made in percentage by weight. Within parentheses the abbrevations used in the study

Metal	Dentallium* (D)	Biocast† (B)	Wirobond‡ (W)	Ceramalloy§ (C)	Ceramalloy II§ (CII)
Cobalt	68	63	63		
Chromium	19	30	29	17	18
Nickel				72	69
Molybdenum	7	3	7	5	6
Silicon	6	4	1	6	6

* Svedia, Enköping, Sweden.
† Jeneric Gold Co., Wallingford, Conn., USA.
‡ BEGO, Bremer Goldschlägerei Wilhelm Herbst, Bremen, FRG.
§ Ceramco Inc., East Windsor, N.J., USA.

Table 3. 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.

carbon, and metals present in concentrations less than 1% by weight were not detected by this method.

The alloys were cast in the shape of 10 mm × 30 mm plates, 1 mm thick; the plates had three holes 5 mm in diameter. The total surface area was 6 cm^2. In addition, plates of the same type were made of acrylic resin. All the plates were mounted in acrylic holders (Fig. 1).

Sjödings C gold was invested in Kerr Cristobalite Investment for inlays (Sybron Italia, Scafati, Italy) and the other gold alloys in Jelenko Complete Investment (J. F. Jelenko & Co., USA). Burnout and preheating were carried out in an electric furnace at 250°C for 2 h and 750° for 1 h (Sjödings C 650°C). To mimic the method generally used in a dental laboratory, the gold alloy proportions used were approximately 70% new metal and 30% metal that had been melted earlier and then cleaned in concentrated hydrochloric acid. Melting and casting took place in a vacuum casting machine (Combilabor Cl-G, Heraeus, Hanau, FRG) with a crucible made of carbon. The casting was bench-cooled at room temperature for 3 min before being quenched in water. The castings were sandblasted (EKO, P. Ehrlander & Co. AB, Gothenburg, Sweden) and then kept in concentrated hydrochloric acid for 5 min.

The Co–Cr and Ni–Cr alloys were invested in BEGO Wirovest Special Investment (BEGO, Bremen, FRG). Burnout was carried out in an electric furnace, at 250°C for 2 h, and pre-heating was at 1000°C for Co–Cr alloys, at 820°C for Ceramalloy and at 740°C for Ceramalloy II, all for 45 min.

Melting and casting took place in a high-frequency induction casting machine (type 026, OBEL-P-Products, Copenhagen, Denmark) with a detachable ceramic crucible. Only new metal was used. The casting procedure began 10 sec after the casting temperature was reached. The casting ring was allowed to cool for 30 min at room temperature before being quenched in water. The castings were again sand-blasted.

All casting specimens were polished to 600 grit with silicon-carbide paper (3M, St. Paul, Minn., USA).

Plugs of amalgam, 4 mm long and 5 mm in diameter, were made in steel molds, and

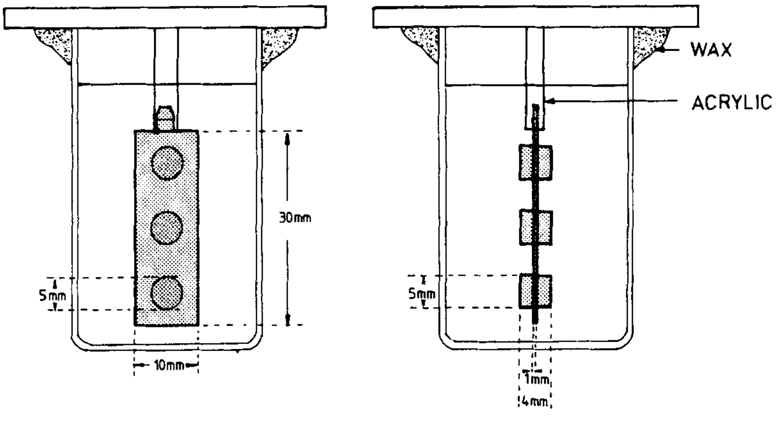

Fig. 1. A plate with three plugs in phosphate-buffered saline solution.

the condensation was done by hand for 60 sec, starting 30 sec after trituration (21). The condensation was done with an amalgam condenser with a tip diameter of 1.5 mm. On the condenser a strain gauge (FFA H117, Flygtekniska Försöksanstalten, Stockholm, Sweden) was mounted, which registered the applied pressure on a pen recorder (Omniscribe, Houston Instruments, Houston, Tex., USA). The mean pressure applied was 10 N/mm^2, and the thrusts were given with a frequency of 1/sec. Excess amalgam was brushed away 120 sec after the end of trituration, and the specimens were separated from the mold. The amalgam specimens were polished with a silicon-carbide wheel with intermittent soaking in water 24 h after condensation.

The plugs were then placed in the holes of the plates, and because of some conicity the plugs were stuck to the plates by friction. Five specimens of each combination were made. As controls, five plates of each casting alloy (with the exception of 24K and Jeĭ 'O') were made without amalgam plugs.

The experiments

The specimens were washed in alcohol (95%) and dried in air before being placed in glass beakers (25 ml) with 23 ml sterile 0.9% NaCl solution (made of deionized double-distilled water) buffered to pH 6.0 with phosphate buffer (NaH_2PO_4, 8.8 mM, and Na_2HPO_4, 1.2 mM). The beakers were stored at 37°C and shaken once a day for a few seconds. The experiment was in progress for 35 weeks. Every 7 weeks the solutions were renewed. The corrosion products that precipitated on the surface of the specimens were removed by light brushing with a soft toothbrush in the solution. No bacterial growth was found in any of the solutions throughout the experiment.

Precipitated corrosion products were dissolved by adding 3 ml 12 M HCl (Salzsäure rauchend 37%, pro analysi, E. Merck, Darmstadt, FRG). The solutions were stored in glass bottles (4°C) and analyzed when all the precipitations were dissolved (that is, when a clear solution was obtained). When Ag was measured in the solutions, diluted ammonia was added.

The solutions were analyzed with an atomic absorption spectrophotometer (AAS) (Pye Unicam SP 190, Pye Unicam Ltd, Cambridge, UK) with regard to Cu, Zn, Ag, Co, Cr, Ni, Mo (air/acetylene flame), Sn (nitrous oxide/acetylene flame), and Hg (cold vapor). The analytical techniques described by Price (22) were used, and the standard solutions were diluted from stock solutions of analytical reagent grade (BDH laboratory reagents, BDH Chemicals Ltd, Poole, UK). Deionized and double-distilled water was used. Correction for background, corresponding to the concentrations obtained in blank solutions, was subtracted from the concentrations measured in the test solutions.

To evaluate the effect of changing the solutions and the effect of oxygen saturation in the solution, two experiments were performed. In the first, the solution was changed once a week, and in the other a solution volume of 300 ml was saturated with oxygen once a day. If pH 6.1 was reached, fresh solution was added.

In one experiment a solution buffered to pH 4.0 (Na_2HPO_4, 7.7 mM, and citric acid, 6.1 mM) was used.

The gold alloys were, after the 35 weeks in the saline solution, etched in aqua regia for 60 sec. The aqua regia was then analyzed for the amounts of Cu, Zn, Sn, Hg, and Ag.

Statistical analysis

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

Results

Effects on the amalgams

When the amalgams in contact with the type III gold alloy and the acrylic plates were compared, large differences in the amounts of elements released during the initial 7-

week period were observed (Figs. 2a–c). The release of Cu from Dispersalloy and ANA 2000 in contact with the gold alloys was especially pronounced. The amounts of elements released in the first 7 weeks from the amalgams in contact with the Co–Cr alloys were the same as when they were in contact with the acrylic plates. In contact with the Ni–Cr alloys, larger amounts of Cu, Zn, Hg, and Ag were released from ANA 68, and with one of the Ni–Cr alloys, CII, more Cu was released from ANA 2000 during the initial 7-week period. No such influence was observed for Dispersalloy. The release of elements during the following 7-week periods progressed towards a steady state, independently of casting alloy in contact, and the initial differences observed were reduced. However, one exception was found; ANA 68 and ANA 2000 in contact with Ceramalloy progressed towards a lower level during the 35 weeks than when in contact with the other casting alloys.

No Co (<0.03 µg/ml), Cr (<0.13 µg/ml), or Ni (<0.03 µg/ml) was released from the amalgams.

In general, more corrosion products appeared in the solutions over the 35 weeks when the amalgams were in contact with pure gold or gold alloys than when in contact with Co–Cr or Ni–Cr alloys or placed in acrylic plates (Table 4). No differences were found between the various dental gold alloys in their long-term effect on the amalgams. However, during the first 7 weeks, when pure gold (JS 24) was in contact with ANA 68, the release of Cu, Sn, Hg, and Ag was larger than when ANA 68 was in contact with the other gold alloys. The opposite effect was observed for ANA 2000.

The Co–Cr alloys had a slightly increasing effect on the release of elements over the 35 weeks, particularly Cu from Dispersalloy and ANA 2000. With ANA 68 this increase was recorded only for Sn, and the other elements decreased in the solutions. No dif-

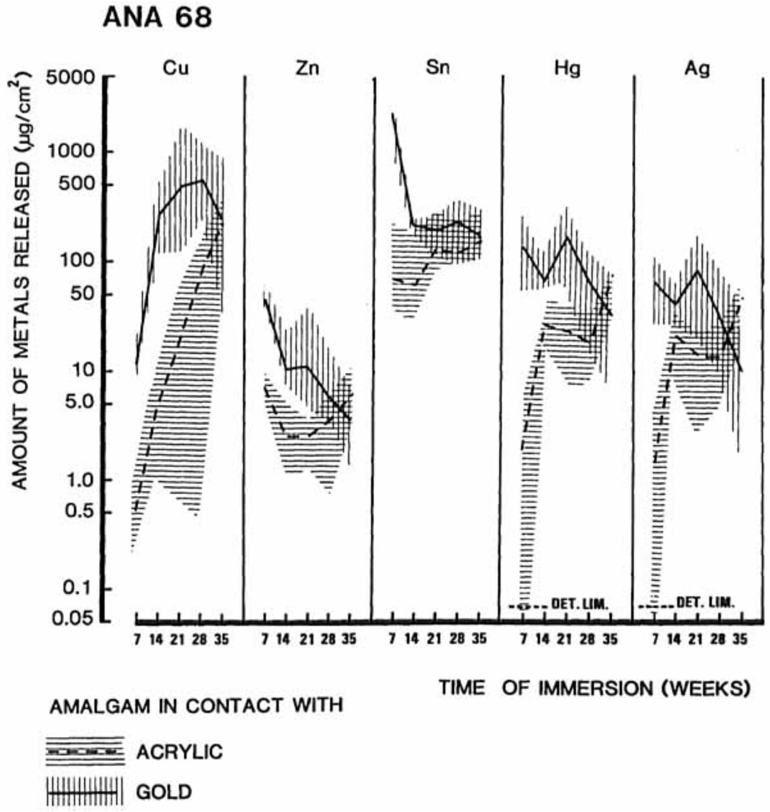

Fig. 2a. Amount of metals released from ANA 68 into the saline solutions after 7, 14, 21, 28, and 35 weeks in contact with acrylic and a type III gold alloy. The lines and shadows represent mean value and range of five specimens in each group. DET.LIM. = detection limit.

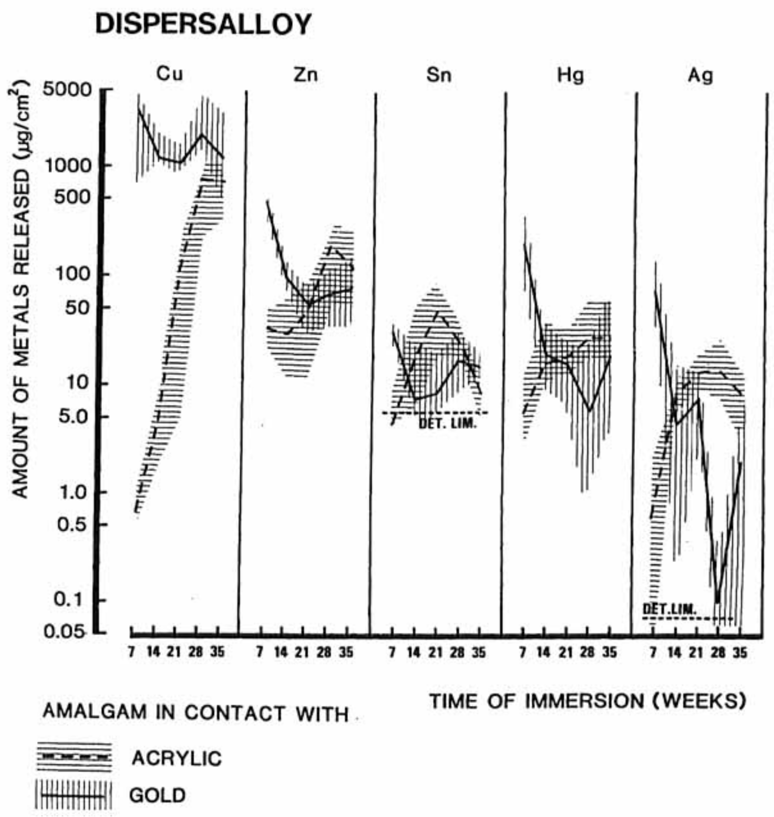

Fig. 2b. Amount of metals released from Dispersalloy into the saline solutions after 7, 14, 21, 28, and 35 weeks in contact with acrylic and a type III gold alloy. The lines and shadows represent mean value and range of five specimens in each group. DET.LIM. = detection limit.

ference was found between the Co–Cr alloys with regard to their influence on the total release of elements during the 35 weeks.

Smaller amounts of elements were released from the amalgams during the 35 weeks when they were in contact with Ceramalloy than with Ceramalloy II and when placed in acrylic. Therefore Ceramalloy was not included in the group of Ni–Cr alloys in Table 4.

The release of elements during the 35 weeks was larger from Dispersalloy and ANA 2000 than from ANA 68. The amounts of Hg and Ag released from the amalgams were closely related. When the amalgams were in contact with acrylic plates, the relation Hg/Ag was 1.9 : 1.0. In contact with gold this relation was larger, 2.8 : 1.0.

Some of the alloy combinations showed pronounced formation of corrosion products on the surface of the amalgam and on the bottom of the beakers. This was particularly true when the high-copper amalgams were in contact with the gold alloys; large amounts of blue or blue-green precipitations were observed during the entire experimental period. When in contact with acrylic plates and Co–Cr and Ni–Cr alloys, precipitations were observed after 14 or 21 weeks. Although the corrosion products on the surface of the plugs were more pronounced with the high-copper amalgams than with ANA 68, they were easy to brush off, leaving a relatively clean light-grey surface with small red areas. The surface of ANA 68 amalgam was, after some time, partly covered with a dark grey and blue-grey layer.

The pH of the solutions often increased, sometimes to as high as 9–10, during the 7-week periods.

Effects on the gold alloys

Cu, 4.9 μg/cm² (range, 4.0–6.8; 35 weeks),

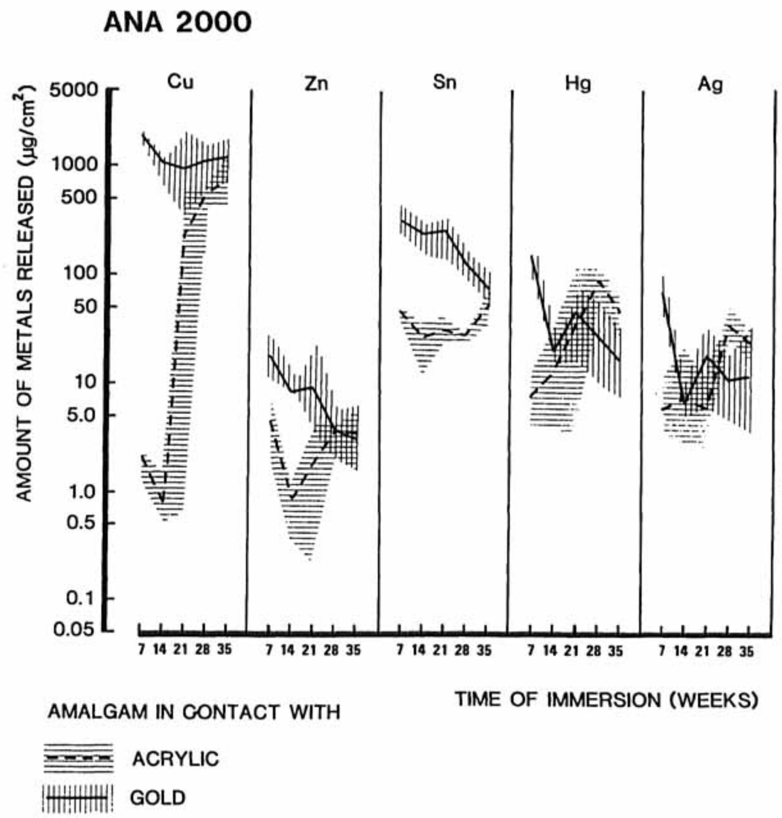

Fig. 2c. Amount of metals released from ANA 2000 into the saline solutions after 7, 14, 28, and 35 weeks in contact with acrylic and a type III gold alloy. The lines and shadows represent mean value and range of five specimens in each group.

and Zn, 1.1 μg/cm² (0.3–1.5), were released from the type III gold alloy plates without amalgam plugs in contact. Only Zn, 1.4 μg/cm² (0.9–4.3), was released from the metallo-ceramic gold alloys.

Tarnish—that is, a brownish-red dull appearance of the gold plates—was seen starting 1–2 mm from amalgam plugs in contact. Pure gold was more tarnished than the other gold alloys. When etched in aqua regia, Cu was found in higher amounts on gold alloys that had been in contact with the high-copper amalgams, whereas Sn was found in larger amounts after contact with the conventional amalgam. No such difference was found with Zn, Ag, or Hg (68 ± 66 μg Hg/cm² (mean ± SD); $n = 90$).

Effects on the Co–Cr and Ni–Cr alloys

The Co–Cr alloys released less Co or Cr in contact with the amalgams than when they were immersed separately (Table 5). No difference was observed between the amalgams, with regard to their influence on the Co–Cr alloys.

The release of elements from Ceramalloy and Ceramalloy II was not influenced by the amalgams in contact. When immersed separately, Ceramalloy released a mean of 625 μg Ni/cm² (range, 333–1069) and in contact with the amalgams 703 μg Ni/cm² (138–1456). The release of Cr was 10.8 (7.8–17.8) and 29 (3.0–66), respectively. The corresponding values for Ceramalloy II were Ni, 242 (50–974) and 128 (6.5–763), and Cr, 8.2 (3.0–38) and 11.1 (3.0–92). All Ceramalloy plates and 4 out of 20 Ceramalloy II plates showed crevice corrosion.

Effects of changing the solution

The amount of Cu and Sn released from ANA 68 was larger when the solutions were

Table 4. The amounts of metals released from ANA 68, Dispersalloy, and ANA 2000 in contact with the acrylic and the casting alloys in the saline solution for 35 weeks (accumulated values from measurements every 7 weeks)

	Amounts of metals released (μg/cm²)									
	Cu		Zn		Sn		Hg		Ag	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
ANA 68										
Acrylic ($n = 5$)	320	(78.3–563)	22.1	(16.9–22.4)	555	(389–777)	148	(57.1–193)	94	(36.4–134)
Gold alloys ($n = 30$)	2641	(875–4411)	79	(49.6–170)	2701	(1404–3970)	1650	(218–4281)	581	(150–1880)
Co-Cr alloys ($n = 15$)	93	(4.2–382)	10.0	(5.8–19.5)	1004	(841–1404)	62	(2.4–222)	25.3	(1.0–92.7)
Ni-Cr alloys† ($n = 5$)	97	(8.4–246)	28.3	(18.8–33.9)	781	(452–1289)	201	(44.2–435)	104	(36–222)
Dispersalloy										
Acrylic ($n = 5$)	1604	(1291–2166)	419	(346–515)	97	(52.0–126)	94	(79.7–136)	45.8	(35.6–64.5)
Gold alloys ($n = 30$)	10624	(4229–19760)	793	(486–1620)	101	(49.0–289)	160	(69.5–486)	53	(20.4–143)
Co-Cr alloys ($n = 15$)	4119	(2271–8753)	1679	(465–4429)	95	(58.1–154)	118	(95.2–121)	41.5	(35.5–56.3)
Ni-Cr alloys† ($n = 5$)	5323	(3181–6968)	514	(468–585)	107	(93.4–127)	166	(121–239)	94	(83.2–103)
ANA 2000										
Acrylic ($n = 5$)	1495	(887–2526)	14.4	(9.4–22.4)	177	(147–208)	179	(136–277)	80	(63.2–120)
Gold alloys ($n = 30$)	5627	(2470–17212)	94	(17.9–289)	921	(423–3154)	291	(147–404)	115	(60.4–214)
Co-Cr alloys ($n = 15$)	2680	(1803–4637)	38.2	(23.3–62.7)	403	(208–702)	334	(210–578)	131	(83.6–218)
Ni-Cr alloys† ($n = 5$)	2943	(1577–5200)	34.2	(23.1–55.0)	298	(225–384)	336	(261–408)	184	(114–308)

* Indicates significant difference, $P < 0.01$, between the two values.

† Ceramalloy II.

Table 5. The amounts of Co and Cr released from the Co–Cr alloys immersed separately ($n = 5$ of each type) in the saline solution and in contact with amalgams ($n = 15$ of each type) for 35 weeks (accumulated values from measurements every 7 weeks)

	Amounts of metals released (μg/cm^2)						
	Co				Cr		
	Separately		In contact		Separately		In contact
Co–Cr alloy	Mean	Range	Mean	Range	Mean	Range	Mean
Dentallium	5.0	(ND–12.2)‡	3.2	(1.8–8.8)	3.9	(<3.0–5.6)	<3.0*†
Biocast	3.1	(1.4–8.3)	0.8*	(0.5–2.2)	<3.0		<3.0
Wirobond	7.3	(2.9–13.9)	2.5*	(1.2–5.6)	<3.0		<3.0

* Indicates significant difference ($P < 0.01$) between the alloy immersed 'separately' and 'in contact'.
† Cr detected in the solutions for 4 out of 15 specimens.
‡ ND = not detectable.

renewed once a week compared with every 7 weeks (Table 6). However, less Hg and Ag were released. With Dispersalloy, the release of Hg and Ag was initially low when the solutions were changed once a week, but in contrast to ANA 68, the release of Hg and Ag increased with time.

The release of Ni and Cr from Ceramalloy decreased in contact with ANA 68 when the solutions were renewed more frequently.

Effects of oxygen saturation

Saturating the saline solution with oxygen increased the release of Cu, Zn, and Sn from Dispersalloy in contact with type III gold alloy (Table 7); the release of Hg and, to some extent, also that of Ag was decreased. The differences in the release of elements increased with time during the 35 weeks when oxygen-saturated solutions were compared with non-oxygen-saturated solutions.

Effects of pH

The release of all elements from the amalgams increased in the pH 4 saline solution compared with the pH 6 saline solution (Fig. 3). The liberation of Cu was apparent from all three amalgams, and amounts released were relatively steady during the 35 weeks in the pH 4 solution. However, all other elements decreased with time at this pH. No difference in the amounts of Ni and Cr released into the solutions from the Ni–Cr plates (C) was found. However, precipitations due to crevice corrosion of the plates were not formed in the pH 4 solution, whereas large amounts of corrosion products accumulated in the opening of the crevice at the holder of the plate in the pH 6 solution.

Discussion

The results obtained the first 7 weeks were different from those obtained during the rest of the experiment. During the first 7 weeks there was a large release of elements from the amalgams that were in contact with the gold alloys. Amalgams immersed separately and those in contact with other casting alloys released smaller amounts of elements. The Ni–Cr alloys caused a relatively high release of some elements from ANA 68, and one of the Ni–Cr alloys, CII, also from ANA 2000, but this release was not as large as when in contact with the gold alloys. Dispersalloy was not influenced by contact with the Ni–Cr alloys, nor were any of the amalgams influenced by contact with the Co–Cr alloys.

During the rest of the experiment the release of elements from the amalgams tended towards the same level, independent of the casting alloy in contact, with the exception of ANA 68 and ANA 2000 in contact with Ceramalloy, which progressed towards a lower level. The accumulated amounts of elements released during the experiment showed that the amalgams in contact with

Table 6. The amounts of metals released when ANA 68 and Dispersalloy were in contact with Ceramalloy and immersed in the saline solution for 35 weeks. The solutions were changed to fresh solutions once a week or once every 7 weeks (accumulated values from once a week and every 7 weeks respectively)

	Amounts of metals released (μg/cm²)													
	Cu		Zn		Sn		Hg		Ag		Ni		Cr	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
ANA 68														
Once a week	10.3*	(9.2–11.5)	17.0	(15.3–19.8)	623*	(579–735)	3.1*	(0.7–6.8)	1.8*	(0.4–5.3)	75*	(53.5–108)	2.4*	(0.5–4.3)
Once every 7th week	5.4	(4.3–6.7)	22.7	(15.7–27.1)	70.2	(47.7–97.1)	35.0	(29.6–43.6)	18.0	(14.1–23.6)	784	(247–1456)	22.5	(10.0–29.0)
Dispersalloy														
Once a week	3324	(13.9–6314)	477	(203–783)	189	(133–259)	58	(10.2–125)	20.3	(1.8–47.0)	460	(198–944)	22	(7.6–122)
Once every 7th week	243	(3.6–659)	201	(76–257)	83	(7.8–173)	27.0	(13.8–52.3)	10.4	(2.3–21.8)	511	(138–958)	15.6	(6.1–32.5)

* Indicates significant difference ($P < 0.01$) between the two groups.

Table 7. The amounts of metals released from Dispersalloy in contact with the type III gold alloy immersed in the saline solution, saturated with oxygen (n = 5; pH adjusted to 6.0) and not saturated with oxygen (n = 5; pH allowed to increase), during 35 weeks (accumulated values from measurements every 7 weeks)

	Amounts of metals released (μg/cm²)									
	Cu		Zn		Sn		Hg		Ag	
Method	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Oxygen-saturated	29,553*	(27,057–31,642)	2040*	(1872–2140)	663*	(508–936)	103*	(73–146)	63	(49–87)
Not oxygen-saturated	8467	(4229–11,189)	753	(653–853)	80	(53–120)	253	(167–486)	87	(67–143)

* Indicates significant difference ($P < 0.01$) between the two groups.

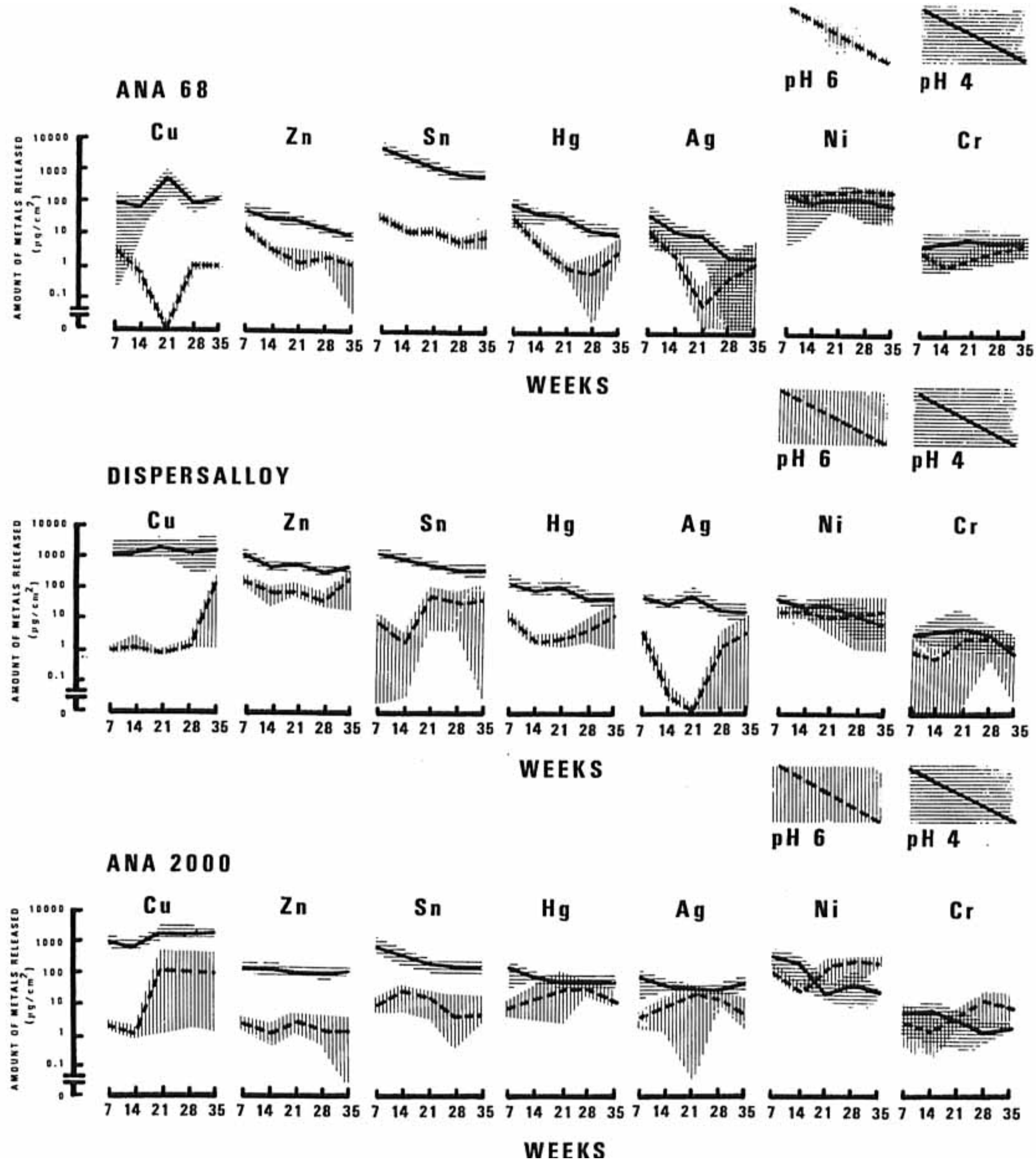

Fig. 3. Amounts of metals released from ANA 68, Dispersalloy, and ANA 2000 into the saline solutions, pH 4.0 and pH 6.0, when placed in contact with Ceramalloy. The release of Ni and Cr from Ceramalloy is also given. The lines and shadows represent mean value and range of five specimens in each group.

the gold alloys still liberated larger amounts of elements than the other alloy combinations. Dispersalloy and ANA 2000, when they were in contact with the Co–Cr alloys and Ceramalloy II, both showed slightly higher release of elements than when placed in acrylic plates, whereas ANA 68 was not influenced with regard to the total amount released. One of the Ni–Cr alloys, Ceramalloy, decreased the amount of metals liberated from the amalgams.

The release of elements from the Co–Cr

and Ni–Cr alloys immersed separately—that is, without amalgam plugs in contact—has been presented earlier (23) and compared with the release of elements when they were in contact with a type III gold alloy. The Co–Cr alloys were probably cathodically protected in contact with the amalgams, whereas the Ni–Cr alloys were not.

To reduce the number of factors that could influence the corrosion process and to make comparisons with previously published data possible, a 0.9% NaCl solution was used. Von Fraunhofer & Staheli (11), using a 1% KCl solution, showed that the current created when gold and amalgam were placed in contact decreased with time, and after a few hours the current could no longer be recorded. This decrease of current indicated formation of a corrosion product layer that passivated the amalgam surface. However, the present study showed that this passivation did not prevent elements from being continuously released from the amalgam surface. Holland (13) reported fluctuations in the current during the first hour when gold and conventional amalgam were in contact. These fluctuations imply that the corrosion product layer formed did not give complete passivation. It should also be emphasized that the currents registered in polarization experiments do not reflect the amount of corrosion products released from the amalgam surface.

Although the specimens were prepared in a standardized manner, the differences in corrosion behavior between identical specimens were pronounced. This is a common observation (24). The explanation for the variations in the amounts of metals released is probably to be found in the complex nature of the corrosion of the amalgams. It should also be noted that the measurements were obtained from amalgam specimens with a relatively large surface area, 3 cm^2 in each solution. This probably had an equalizing effect on the amount of elements released. Whereas some of the corrosion products formed on the amalgam surface are released into the electrolyte, others will be deposited on the amalgam surface (25). These deposits could be partly quantified if dissolved in acid after the experiment (16). In the present investigation, precipitations on the amalgam surface were lightly brushed off with a soft toothbrush. The Hg/Ag ratio in the solutions was relatively constant, independent of the type of amalgam, throughout the 35 weeks, implying that Hg may not disappear as vapor from the solutions during the experimental period.

The conventional amalgam released larger amounts of Sn into the solutions than the amalgams containing more Cu. Tin-hydroxychlorides have been reported, both in vivo and in vitro, to be the main products on the surface of corroded conventional silver-tin amalgams (26). These compounds have low solubility in water. In the present study the light abrasion of the surface could have removed the outer part of this layer.

The release of Cu into the solutions was not related to the amount of Cu present in the various amalgams. Dispersalloy showed, in relation to its copper content, a high tendency to liberate Cu. These findings are in agreement with those earlier reported by Espevik (16).

During the first 7 weeks of the experiment, Zn was released in larger amounts than Cu from all the amalgams. Short-term studies have shown that Zn is liberated early from the amalgams (24, 27, 28), whereas the present study also showed that the release of Zn remained unaltered during the 35 weeks.

In the early stages of the experiment—that is, the first 7 weeks—the high-copper amalgams, when not in contact with casting alloys, lost slightly larger amounts of Hg than the conventional ones, which confirms results published by others (29, 30). Changing the saline solution more often (Table 6) or increasing the solution volume and including oxygen saturation (Table 7) altered the corrosion of the amalgams. Cu, Zn, and Sn showed tendencies to increase, whereas Hg and Ag from ANA 68 decreased in the solutions. However, Hg and Ag from Dispersalloy increased with time, when the solutions were renewed once a week, to levels higher than those released when the solutions were changed every 7 weeks. The amounts of Hg and Ag released seem to be dependent on the concentration of Cl^- in the electrolyte (24, 29, 31, 32). Hg and Ag have also been shown to be present in the removable layer of conventional amalgams after corrosion in NaCl solutions (33). Different experimental conditions in studies on amalgam corrosion, such as composition of the solution, oxygen saturation, time of immersion, and analyzing procedures, could explain divergent results obtained with regard to elements liberated from the amalgam surface. The constant flow of saliva in the oral cavity might account for the relatively small amounts of Hg and Ag released from parts of the amalgams that are exposed to saliva.

When the amalgams were immersed in the pH 4 saline solution, the amounts of all the elements released increased compared with the pH 6 solution. The release of Cu was relatively high and steady throughout the entire 35-week period, whereas the other elements tended to decrease with time. Dérand & Johansson (30) have earlier reported increased amounts of Cu and Hg in the solution when the pH was changed from 7 to 4.

The rise in pH of the solutions during the 7-week periods was probably due to reduction of O_2 and formation of hydroxides, which consumed the phosphate buffer. A blue-green precipitate, probably $Cu_4(OH)_6Cl_2$ (25), was formed in large amounts on the surface. This layer was easily abraded, and the more abrasion-resistant CuO layer was present underneath. After 7–14 weeks the amounts of elements, especially Cu, released into the solutions increased sharply. The release of Hg and Ag from ANA 68 also showed pronounced tendencies to increase. This increase with time has earlier been reported by Kozono et al. (29), using a 0.5% NaCl solution. After 4 months in the solution the dissolution of the elements Cu, Zn, and Hg started to increase from some of the amalgams tested, whereas the dissolution from amalgams immersed in distilled water gradually decreased during the 6 months of the experiment. Lin et al. (34) found that diluted Ringer's solution, compared with ordinary Ringer's solution, slowed down the formation of Cu_2O and $CuCl_2 \times Cu(OH)_2$ on the surface. This increase in elements released could be due to corrosion occurring in the amalgams' subsurface (35). The mechanism of the subsurface corrosion of amalgams shows similarities to that of pitting corrosion of casting alloys (36). In the present study the activating chloride ion and an inadequate buffering capacity to prevent lowering of pH inside the amalgam could make the corrosion self-propagating.

During the first 21 weeks there were pronounced differences, between the gold–amalgam combinations and the other casting alloy–amalgam combinations, in the amount of corrosion products released. However, with time, probably due to subsurface corrosion, the amalgams were less influenced by the casting alloys in contact. Over the entire 35-week period amalgams with a high copper content released much larger amounts of Cu in contact with the gold alloys than when not in contact with casting alloys. Conventional amalgams, however, considerably increased the amounts of Hg liberated into the solutions.

The contamination of the gold alloy surfaces due to the amalgam corrosion could cause changes in the physical properties of the gold alloys. The release of elements from the gold alloys will be discussed elsewhere (23).

A high susceptibility of the Ni–Cr alloys to crevice corrosion was found. The crevice corrosion of Ceramalloy was so heavy that it cathodically protected the amalgams in contact. When the solutions were changed every week, oxygen probably formed a more corrosion-resistant film with Cr than when the solutions were changed every 7 weeks only. The release of Ni and Cr from Ceramalloy measured in the pH 4 and pH 6 solutions was similar. However, the total amount of corrosion products formed was larger in the pH 6 solution because of large amounts of precipitations. Perhaps the amalgams in contact offered more protection in the pH 4 solution.

In this study the cathode to anode ratio was 2 : 1; with other area ratios the corrosion may be different. The effect of galvanic activity on the corrosion of amalgams and casting alloys in the oral cavity will depend on the relationships between aggressive and inhibitory factors acting on the surfaces. Stresses, abrasion, certain foods, aeration, chlorides, a low salivary flow, some microorganisms, and subsurface corrosion of the amalgams may increase the corrosion. Buffering systems and particular constituents in the saliva, such as phosphates, carbonates, and organic compounds (37, 38), could inhibit the corrosion process, but critical situations may occur when inhibitory factors are reduced, such as low secretion rate of saliva and impaired buffering capacity, and/or when corrosive factors are increased, such as poor oral hygiene. It should be noted that an excess of aggressive factors in patients often coincides with a deficiency of inhibitory factors.

The susceptibility of Cu to be liberated from high-copper amalgams should be emphasized. This is specific at a low pH, when there is lack of inhibitory agents, and when the corrosion has proceeded to the subsurface area of the amalgam. It should also be noted that copper is relatively easily dissolvable in aqueous solutions. In a permanent situation, close to the oral mucosa, this could be a potential risk for developing biological effects.

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