Liberation of copper, zinc, and cadmium from different amalgams

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Release of copper, zinc, and cadmium from six different amalgams in 0.9% NaCl solution has been registered during a 4-week period. The products showed widely different corrosion behavior. A dispersion-type amalgam released the smallest amounts of copper but the largest amounts of zinc. A product containing indium had a high rate of copper dissolution. Cadmium was liberated to a great extent from a copper amalgam. The rate of corrosion varied greatly for the different products during the time of the experiment. The liberation of copper and zinc was inversely correlated. □ *Corrosion; filling materials; metals*

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Corrosion behavior of dental amalgam has been extensively studied by electrochemical methods. These procedures include interpretation of potential-current curves (2, 7, 14) and potential-time behavior (10). Corrosion rates have also been assessed by light reflectance of polished amalgam surfaces (3). The solid corrosion products formed under both in vitro and in vivo conditions have been characterized (11,13). Tin was found to be the main constituent of the deposits.

Few investigations have considered the release of specific elements from dental amalgams. However, Espevik (5) measured the liberation of copper from amalgams with different copper content. It was found that a dispersion-type amalgam released more than a single phase and a conventional product. A copper amalgam liberated considerably higher amounts than any of the other materials.

Analyses of cell culture media for several elements after 1 day and 3 days of exposure of various amalgams showed that a conventional amalgam released zinc (8). A copper amalgam liberated large amounts of copper and also cadmium in considerable amounts (8). Brune (1), using nuclear tracer techniques, measured the release of zinc, copper, and mercury from a single phase, a dispersed phase, and a conventional amalgam. The single-phase product gave off the largest amounts of copper and mercury.

The aim of the present investigation was to measure liberation of the commonest auxiliary elements of dental amalgam—copper and zinc—from different commercial products. Cadmium release from a copper amalgam was also assessed. Furthermore, the changes in rates of corrosion during the time of the experiments were evaluated.

Materials and methods

The products tested are listed in Table 1. Amalgam specimens were produced according to ADA Specification no. 1. They were stored at 37°C in dry air for at least 1 week before testing.

The specimens were placed in test tubes containing 30 ml 0.9% NaCl solution at 37°C, one specimen in each tube. At least three specimens of each brand were tested. At intervals of 1 week the amalgams were transferred to another set of tubes containing fresh NaCl solution. The experiment lasted for 4 weeks.

After the amalgams had been removed, hydrochloric acid was added to the solution to dissolve solid corrosion products. Copper, zinc, and cadmium were analyzed by flame

Table 1. Products included in the investigation

Code	Product	Manufacturer/distributor	Batch no.	Ag	Sn	Cu	Zn	Other	
ABE	Abedent	AB Baaths Dentalindustri, Märsta, Sweden	1709.80	44*	Bal?	26*	0.3*		Capsulated
DISP	Dispersalloy	Johnson & Johnson Dental Products Co., N.J., USA	7F312	69.6†	17.7†	11.8†	0.7†		
IND	Indiloy	Shofu Dental Corp., Calif., USA	437701	59.1†	23.9†	12.6†	0.1†	In:4.3†	
NEO	Neo Silbrin‡	Siccu-Gesellschaft, München, GFR	—	0.5	—	31.3	<0.1	Cd:1.5	Premixed tablets
NTD	New True Dentalloy	S.S. White Ltd., Harrow, UK	11754E	71.2†	25.5†	3†	0.9†		
SYB	Sybraloy	Sybron/Kerr, Scafati, Italy	1204782226	39.9†	30.2†	29.9†	nd†		Capsulated

Bal = balance to 100%; nd = not detected.
* Information from the manufacturer.
† From de Freitas (6).
‡ Analyses of Neo Silbrin performed by E. S. Erichsen, University of Bergen.

atomic absorption spectrophotometry (Perkin–Elmer Model 372 Atomic Absorption Spectrophotometer). The specimens were visually inspected.

The values obtained during the successive 4 weeks were cumulated and corrected for the geometric surface area of the specimens. Spearman rank correlation coefficients (r_s) were calculated for different variables.

At the end of the experiment, Indiloy and Dispersalloy cylinders were cut longitudinally, embedded in epoxy resin, polished, and coated with carbon for scanning electron microscopy. A backscattered electron detector was used to reveal the metallographical structure of the specimens (Jeol JSM-35 Scanning Microscope with Kevex μX System 7000 X-ray analyzer).

Results

The amounts of copper, zinc, and cadmium released are shown in Figs. 1, 2, and 3.

After 4 weeks, copper from Indiloy showed the highest values, while Dispersalloy liberated the least. For zinc the relationship was reversed.

Rates of liberation of metals during the first and last week of the experiment are presented in Table 2. For zinc the rate decreased for all products. For copper only Dispersalloy and New True Dentalloy exhibited lower corrosion rates at the end of the experiment than at the beginning.

The correlation coefficient between amounts of copper released after 4 weeks and copper content of the products was not statistically significant ($r_s = 0.60$, $p > 0.1$), whereas the corresponding value for zinc was significant ($r_s = 0.84$, $p < 0.05$). A negative

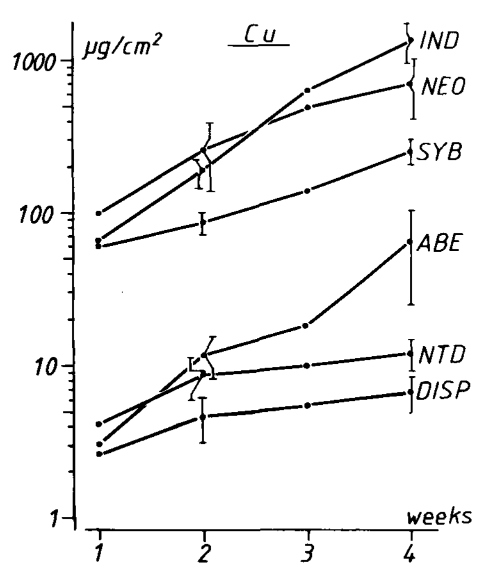

Fig. 1. Cumulative release of copper from six different amalgams. Vertical lines on the curves represent standard deviations. Product code is given in Table 1.

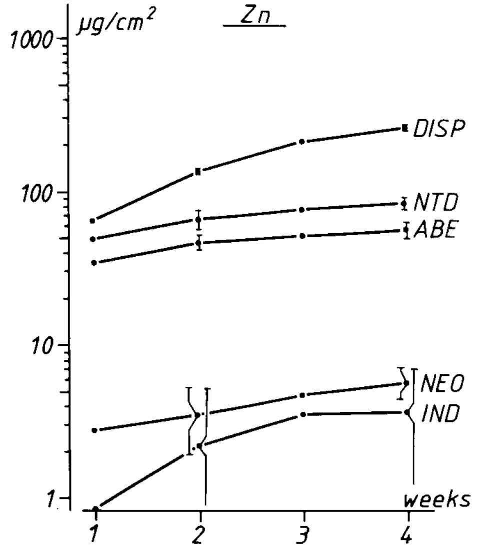

Fig. 2. Cumulative release of zinc from different amalgams. The product Sybraloy had values below the detection limit of the analyzing method. Product code is given in Table 1.

correlation existed between amounts of copper and amounts of zinc after 4 weeks ($r_s = 0.83$, $p = 0.05$) The high-copper amalgams, especially the pure copper amalgam,

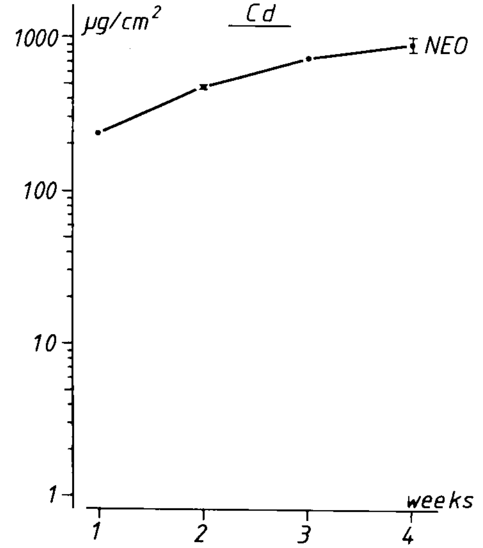

Fig. 3. Cumulative release of cadmium from the copper amalgam Neo Silbrin. Product code is given in Table 1.

Table 2. Release of zinc and copper during the 1st and 2nd week of immersion in 0.9% NaCl solution. The values are in µg/cm². Product code is given in Table 1

		Product					
Element	Week	ABE	DISP	IND	NEO	NTD	SYB
Zn	1	34	66	1	3	49	0
	4	4	51	0	1	9	0
Cu	1	3	3	64	94	4	58
	4	46	1	1570	200	2	114

attained greenish deposits after a few days of immersion.

Except for Indiloy, the backscattered electron micrographs demonstrated only small changes due to the corrosion (Fig. 4). The Indiloy specimen had a deteriorated zone extending up to 200 µm into the amalgam, most pronounced at the edges of the specimen. The η-phase seemed to be the part most severely attacked.

Discussion

The present investigation indicates that there are large differences in both rate and mode of corrosion among different amalgams. Furthermore, the rate of corrosion changes considerably during the course of the experiment and differently for the various products. It should be noted, however, that the electrolyte used here may not replicate clinical conditions (4).

The inverse correlation between release of copper and release of zinc may be explained by cathodic protection from the zinc, this element being one of the most electrochemically active components of amalgams (12).

Copper release is not well correlated with the copper content of the products. The present results for copper are in conflict with those of Espevik (5), who found that Dispersalloy corroded more than Sybraloy. However, he used a different electrolyte, and adherent corrosion products were removed from the surface of the specimens. On the other hand, Brune (1) found the same ranking between Sybraloy and Dispersalloy as in the present study.

An explanation of the high degree of cop-

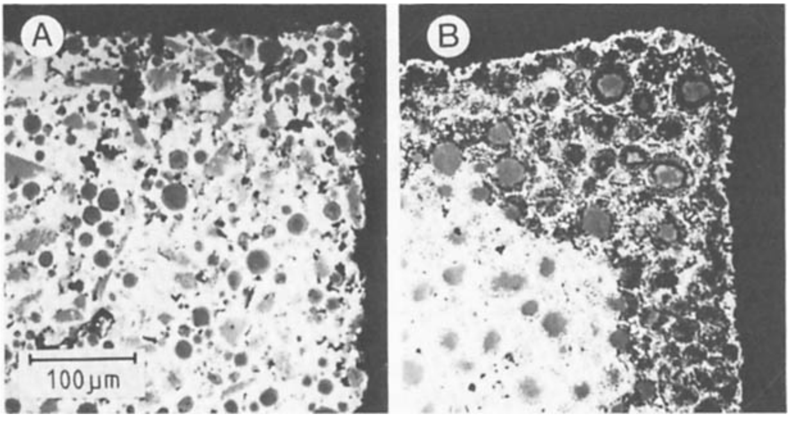

Fig. 4. Backscattered electron micrographs of amalgams corroded for 4 weeks in 0.9% NaCl. (A) Dispersalloy; (B) Indiloy.

per dissolution from the product Indiloy was not found. It has, however, been demonstrated that the corrosion of the copper-rich η-phase is dependent on the surrounding phases in the amalgam (9).

Cadmium present in the copper amalgam is released to a great extent. Because of the toxic properties of cadmium, such materials should be avoided in clinical use.

Since this study demonstrates that different amalgams exhibit corrosion rates that change considerably during the time of the experiment, it is indicated that prediction of the corrosion behavior of dental amalgam should not be based on short-time electrochemical tests only.

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