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Progress Report

## ANALYSIS OF THE LEACH PRODUCTS OF SILICATE CEMENTS AND STUDIES TO REDUCE THEIR SOLUBILITY

by


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Abstract

The composition of the water leach of silicate cements was investigated. Sodium, phosphorus, aluminum, silicon, and calcium are the major constituents of the leach product. A number of compounds which may react with sodium or reduce water penetration into the cement were incorporated into the mix to decrease water solubility and disintegration. Small amounts of R-23 silicone additive gave the most promising results.

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## 1. INTRODUCTION

Silicate cements are the most commonly used filling material for anterior teeth and have been the subject of much research since their introduction to dentistry over 50 years ago. Most of the investigations have been concerned with the two major weaknesses of silicates: (1) their solution and disintegration in the mouth fluids, and (2) their rapid staining and discoloration. A reduction in solubility would help to prevent roughening of the filling surface and reduce staining.

The composition of a typical silicate cement powder has been reported [1] as follows: 39.9% $SiO_2$, 27.7% $Al_2O_3$, 5.9% Ca, 15.4% F, 6.6% Na, and 4.0% $P_2O_5$. The liquid contains 47.4% $PO_4^{\equiv}$,

2.3% Al, 5.6% Zn and 43.3% water.

A search of the literature failed to reveal any data regarding the composition of the soluble leach product of dental silicate restorations. A better understanding of the constituents of the leach might provide information for the reduction or elimination of solubility. Therefore, an analysis of the soluble residue of the cement was conducted and various additives were incorporated into the cement mix in an attempt to reduce solubility.

## 2. EXPERIMENTAL PROCEDURES AND RESULTS

DeTrey's cement was subjected to the water solubility and disintegration test of the American Dental Association Specification No. 9 for silicate cements [2]. The residue from this test, that is, the leach product, was subjected to a semi-quantitative spectrochemical analysis to determine the metallic constituents. A copper oxide dilution technique was employed using synthetic copper oxide standards since the weight of the leached product was on the order of only 7 to 12 mg. The result of the analysis of the leach product of this silicate cement is shown in Table I.

The silicate cement specimens were also stored in water for extended periods. The specimens were transferred to different weighing bottles after one week and one month. Analyses of the residues obtained on evaporation of the water solution in which the specimens were kept from one month to three months

are also shown in Table I.

Sodium is by far the major constituent of the 24-hour leach product, between 10 and 20% of the leach is made up of phosphorus; the leach also contains 5-6% aluminum, 4-5% silicon, 1-2% calcium, 0.02% magnesium and a number of trace elements. On extended storage in water the composition of the leach is changed somewhat as indicated by the higher percentage of aluminum, silicon and magnesium in the one to three months' leach.

Since sodium was the major constituent of the 24-hour leach, various chemicals (D,L-methoxyphenylacetic acid, silanes[a] and R-23 silicone[a]) were added to the cement mix. It was anticipated that some of these compounds might react with the soluble sodium constituents with the formation of less soluble products.

Silanes and silicones were investigated as possible additives because of their water repulsion, resistance to oxidation and the ability of some of the intermediates to polymerize or crosslink. The silicones might also react with some ions to form more insoluble compounds and to reduce the penetration of water into the silicate restoration.

a. Silanes and R-23 were obtained through the courtesy of the Union Carbide and Chemicals Co., New York, N. Y.

The silicate mix was prepared as follows:

The silicate liquid was placed on a glass slab, using a calibrated 1 ml pipette. The desired amount of additive was mixed in carefully by spatulation with the silicate liquid. This solution was then mixed with the powder according to the American Dental Association Specification No. 9 [2]. The procedure for solubility and disintegration outlined in this specification was then followed. Requirements for standard consistency were followed for each mix.

DeTrey's synthetic porcelain was used for all specimens. This cement is widely used and has a low solubility. Hence, it was thought that any reduction of the solubility and disintegration of this cement would be likely to produce a proportionate reduction for other brands.

D,L-methoxyphenylacetic acid when added in about 5% concentration to the mix increased the solubility of the product by 28%.

β-carbethoxypropylmethyldiethoxy silane and β-carbethoxyethyltriethoxy silane when added in 0.05 ml amounts to the standard mix resulted in products having greatly increased water solubility and disintegration. Ethyltriethoxy silane and amyltriethoxy silane, when incorporated into the silicate cement in the amounts of 0.025 ml or 0.05 ml reduced the solubility and disintegration by 25 to 32%. Both, however, appeared to volatilize and are listed as being slightly toxic, so work with these compounds was discontinued.

R-23 silicone, on the other hand, is listed by the manufacturer as being non-toxic. It is of thick, molasses-like consistency. Incorporation of 0.025 ml or 0.05 ml of R-23 into a standard silicate mix reduced the 24-hour solubility and disintegration by 20 to 40% (Table II).

The effect of the shade of cement on solubility and disintegration was determined using 8 specimens each for 4 shades of DeTrey's synthetic porcelain. As can be seen from Table II there is no significant effect of shade on solubility and disintegration. The addition of the R-23 silicone reduced the solubility in the 24-hour test regardless of shade.

Tests were also undertaken to evaluate water solubility and disintegration of this cement over longer periods of time. In these tests four or more specimens were used for each composition.

On prolonged water exposure the solubility and disintegration increased and reached values for the three months' exposure of 1.4% and 1.5% for the R-23 treated and standard mixes, respectively. A constant reduction of 0.1% on incorporation of the silicone was observed for the one week and one and three months' specimens, however, the percentage reduction decreased with time.

Samples of the leach product of silicate cements containing the R-23 silicone were subjected to spectrochemical analysis. The results and the analyses are shown in Table I.

In the 24-hour leach the percentage of sodium, phosphorus and calcium remained approximately the same. Due to the small amount of sample available for analysis, accurate quantitative estimation for sodium and phosphorus was not possible. Small differences in composition were noted for aluminum and magnesium. The greatest difference was noted in the amount of silicone in the leach products with a percentage reduction from 5% in the standard, to 1% in the leach from the R-23 additive containing cement. This may suggest that the R-23 silicone reacts with silicon to form a less soluble compound.

The composition of the one to three months' leach did not change appreciably on incorporation of the R-23 into the mix. A slight reduction in the percentage of magnesium occurred.

The nearly identical composition of the leach and the constancy in the reduction of the solubility and disintegration after prolonged water exposure appears to be further evidence that the R-23 silicone reacts initially with some of the silicon in the cement to form an insoluble compound. It can be seen from Table I that the incorporation of the R-23 reduces the silicon content in the 24-hour leach by 3 to 4%. This should account for an equal; that is, a 4% reduction in the solubility and disintegration. However, the much larger 20% decrease in the 24-hour solubility and disintegration, coupled with the fact that elementary composition of the leach product remains almost identical (with the exception of the silicon reduction) in the R-23 silicone-treated cement may suggest that the silicone also reduces somewhat the water permeability of the cement.

The reduced diffusion of water into the cement will reduce the initial solubility and disintegration.

The effect of the R-23 silicone additive on the setting time and compressive strength of the silicates is shown in Table III. The setting time of the cements was not affected by the additive. In all but one case, however, the compressive strength of the material was slightly reduced.

Recently Cdr. A. E. Gustavson of the U. S. Naval Dental School, Bethesda, Md., investigated the penetration of methylene blue dye into silicate cement mixes containing 0.05 ml and 0.1 ml R-23 silicone [3]. No significant reduction in dye penetration was obtained for DeTrey cement. However, incorporation of R-23 into S. S. White and Lee Smith cements lowered the dye penetration by as much as one-half. This reduction is probably due to the slower water diffusion into the silicone-treated cements.

## 3. SUMMARY

Analysis of the leach product of silicate cements shows that sodium is the major constituent. Phosphorus, aluminum, silicon, calcium, and magnesium are present in larger than trace amounts. On prolonged water exposure the percentage of aluminum, silicon and magnesium in the leach increases. An effort was made to reduce the solubility and disintegration of silicate cements by incorporating various compounds into the mix. Small amounts of R-23 silicone in the mix give the

most promising results of the compounds investigated. Spectrochemical analysis indicates a reduction of silicon in the 24-hour leach product of R-23 treated cements. Twenty-four hour solubility and disintegration is reduced from 0.5% to 0.4%. This 0.1% reduction in the solubility and disintegration values remains constant in magnitude on prolonged water exposure. The initial decrease in the solubility and disintegration appears to be due to the formation of an insoluble silicon compound as well as reduced water diffusion into the R-23 treated cement.

BIBLIOGRAPHY

1. Paffenbarger, G. C.; Schoonover, I. C.; and Souder, W. Dental silicate cements: physical and chemical properties and a specification. J.A.D.A. 25:32 Jan. 1938.

2. American Dental Association specifications for dental materials. Specification No. 9 for dental silicate cements. American Dental Association, Chicago 11, Illinois. Page 36. 1958.

3. Gustavson, Cdr. A. E. Private communication.

Table I

COMPOSITION OF LEACH PRODUCTS[1]

| Element | Leach Product | | | | |
|---|---|---|---|---|---|
| | 24-hour | | 1 to 3 months | | |
| | additive | | additive | | |
| | none | 0.05 ml R-23 | none | 0.025 ml R-23 | 0.05 ml R-23 |
| | % | % | % | % | % |
| Na | > 20 | > 20 | >10 | >10 | >10 |
| P | 10-20 | 10-20 | >10 | >10 | >10 |
| Al | 5-6 | 4-5 | >10 | >10 | >10 |
| Si | 4-5 | 0.5-1 | >10 | >10 | >10 |
| Ca | 1-2 | 1-2 | 1-10 | 1-10 | 1-10 |
| Mg | 0.02 | 0.1-0.5 | 0.1-1 | 0.01-0.1 | 0.01-0.1 |

1 Spectrochemical analyses by Mrs. Martha Darr of the Spectrochemistry Section.

Table II

SOLUBILITY AND DISINTEGRATION

| Sample | 1 day | 1 week | 1 month | 3 months |
|---|---|---|---|---|
| | % | % | % | % |
| **Shade 20** | | | | |
| Standard | 0.5 | 0.7 | 1.1 | 1.5 |
| 0.025 ml R-23 | - | 0.6 | 1.1 | 1.4 |
| 0.05 ml R-23 | 0.4 | 0.6 | 1.0 | 1.4 |
| **Shade 21** | | | | |
| Standard | 0.5 | - | - | - |
| 0.025 ml R-23 | 0.3 | - | - | - |
| 0.05 ml R-23 | 0.4 | - | - | - |
| **Shade 36** | | | | |
| Standard | 0.5 | - | - | - |
| 0.025 ml R-23 | 0.4 | - | - | - |
| 0.05 ml R-23 | 0.4 | - | - | - |
| **Shade 46** | | | | |
| Standard | 0.5 | - | - | - |
| 0.025 ml R-23 | 0.4 | - | - | - |
| 0.05 ml R-23 | 0.4 | - | - | - |

Table III

PHYSICAL PROPERTIES

| | Additive | | |
|---|---|---|---|
| | None | 0.025 ml R-23 | 0.05 ml R-23 |
| Shade No. 20 | | | |
| Setting Time (min.) | 4 | - | 4 |
| Compressive Strength (psi) | 24,000 | 26,000 | 18,000 |
| Shade No. 46 | | | |
| Setting Time (min.) | 4 | 4 | 4 |
| Compressive Strength (psi) | 24,000 | 21,000 | 19,500 |