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ON THE SOLUBILITY OF SILICATE CEMENTS

by

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INTRODUCTION

It is well known that one of the greatest disadvantages of silicate cement as a dental filling material is its rather high solubility in saliva. It is also well known that the durability of silicate restorations is very variable. On the other hand, the factors influencing the resistance of these restorations to dissolution, and the importance to be attached to such factors, have received less consideration. The dental practitioner has therefore had to base his manipulation of the material chiefly on the manufacturers' directions, which most often fail to account quantitatively for the instructions given, and moreover lack unbiassed control.

In the selection of commercial products the American Dental Association Specification No. 9 (see *Paffenbarger et al.* 1938) has afforded considerable help for a number of years. Still, there is some uncertainty on this point too, since clinicians have frequently claimed to obtain just as good results with silicate cements which fail to meet this specification as with those complying with all its requirements.

In order to remove, to some extent, this uncertainty a number of laboratory tests — which will be considered in detail in this work — was started in 1955 at the Department of Technology of the Royal Dental College in Copenhagen. The investigation was completed in 1961. The greater part of the routine work was done

by Mrs. *S. Kristensen,* civil engineer, while the remaining work was carried out by the author. In all series where a comparison of results was necessary for investigating a given problem, only one worker was engaged.

PREVIOUS INVESTIGATIONS

Many previous studies touch on the same or similar problems as those considered in this work, but as the general approach is different from the one used in this work, especially quantitatively, they will not be referred to here. Important exceptions are *Paffenbarger* and co-workers' abovementioned investigations, published in 1938, and those carried out by *Norman* & co-workers (1957, 1959).

In *Paffenbarger*'s work various commercial brands were tested for solubility over a 5-week period, and the values obtained for each separate week were recorded. The most remarkable results of this work are that the solubility of the individual brands differed considerably, especially after the first week, while the quantity dissolved during the following four weeks showed much less variation. A few brands showed almost the same solubility at the end of the first week, but an appreciable difference in the subsequent four weeks (thus, after the first week cements G and J had solubilities of 2.7 and 2.8 per cent, respectively, while the total values for the following four weeks were 2.0 and 1.3). This brings up the question whether the standard specification, which is based on these measurements, and classifies the brands according to solubility after the first week, should not in addition include requirements for resistance of the cements to dissolution during the following — clinically perhaps more important — period.

While the studies so far referred to are based on solubility in distilled water, *Norman* & co-workers studied silicate cement solubility in acid and alkaline solutions. In nearly all cases they were able to demonstrate a dramatic increase of the solubility in acid solutions, and a considerable difference in the solvent action of the various acids. Their investigation also shows that the difference in solubility in distilled water, which could be demonstrated between the individual brands, or which was a result

of variation in manipulative technique, was eliminated or masked, to a great extent, by the very high acid solubility. *Norman* & co-workers' study is the first systematic investigation of cement solubility in liquids with chemical properties resembling the conditions in the oral cavity.

METHODS

All measurements of silicate cement solubility were based on the method described in the American Dental Association Specification No. 9 for dental silicate cements, first revision, 1950. In some experiments the standard method was modified, and these modifications will be described in each case. The term solubility is used to express the quantity of solid substance dissolved from the test specimens under the conditions prescribed in the specification. As the test specimens did not represent substances in equilibrium, and as cement and solvent scarcely had been in equilibrium in any case, the term solubility as used here is not in accordance with the usual chemical definition. Each value given for solubility is the average of at least three measurements. A considerable number of preliminary experiments with various brands, under different conditions, showed that the greatest difference between single tests chosen at random within any one group was ± 5 per cent. This held good whether one or both workers had carried out all the tests in the group. The subsequent experimental work showed that this accuracy could be maintained in all cases.

A majority of the brands sold on the Danish market were tested. Long experimental series, however, were carried out only with certified materials which had shown fairly constant properties over a long period of observation. The lightest colour of cement powder was used. Through the 5-year period different batch numbers were employed, in each case products of the least possible manufacturing age. In the experiments for determining the influence of manipulation and test medium upon solubility the same batch number was used in each series. In these cases a great number of packages were bought and their contents of powder or acid carefully pooled before being placed in air-tight storage bottles.

The cements used in the tests are listed in Table 1.

Table 1

Brand	Manufacturer	Designation
Achatit, from 1959 Achatit Biochromatic	Etablissement Vivadent, Liechtenstein	A
Astralit	Dental Fillings Ltd., London	B
Filling Porcelain Improved, from 1959 New Filling Porcelain	The S. S. White Dental Mfg. Co., London	C
Syntrex, from 1959 Super Syntrex	De Trey Frères S. A., Zürich	D
Baker Plastic Porcelain	Baker & Co., Inc., New Jersey	E
Diafil	Messrs. Pfingst & Co., Inc., New York	F
Diasilic	Jota Dental u. Schleifmittel — GMBH, Düsseldorf	G
Certified Synthetic Enamel	Lee Smith Company, Chicago	H
F. P. 7.	Deutsche Zahn-Porzellan Ges., Berlin	I1
Terralux	Zahn-Porzellan K. G., Hamburg	I2

RESULTS

1. Solubility of the individual commercial products according to the prescriptions of the standard specification

A, B, C, and D were tested throughout the experimental period at relatively short intervals, while the other materials were tested only a single or a few times at random. The findings for the first four cements appear in Fig. 1, for the other cements, in Table 2.

Table 2

Brand	Solubility (per cent)
E	1.1 (1957)
F	0.7 (1959)
G	2.1 (1956); 2.6 (1958)
H	0.5 (1956); 0.5 (1958)
I1	4.1 (1956)
I2	4.2 (1957); 4.2 (1958)

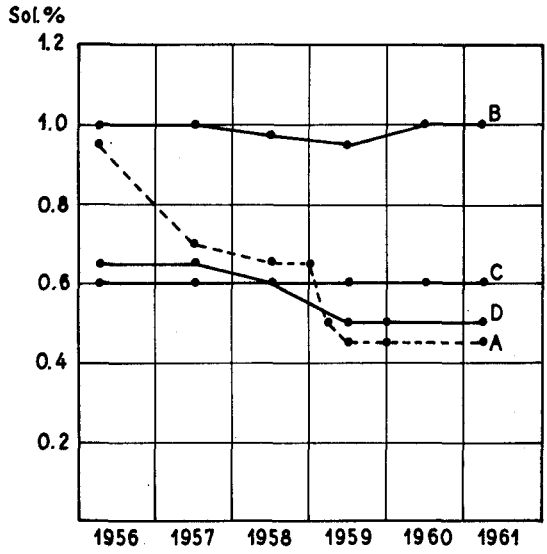

Fig. 1. Solubility of four commercial silicate cements tested during the years 1956—1961.

Fig. 1 shows that brands B and C were very constant with respect to solubility during the 5-year period. A and D had been subjected to alterations reducing their solubility in distilled water; this especially applies to A. The clinical significance of these solubility values will be discussed later.

2. Long-term solubility tests on silicate cements

The solubility of one cement, D, was tested over a longer period than the 23 hours stated in the A.D.A. specification. The test specimens were prepared according to the specification and placed in 50 ml of distilled water in weighing bottles 60 minutes after mixing was started. The bottles were kept in an incubator at 37° C., for one group of specimens until 24 hours had elapsed from start of mixing, for other groups until 48, 96, 192, or 384 hours had passed. The water was not changed during the experimental period, and the amount of dissolved cement was determined after evaporation of the solution as prescribed in the specification.

According to this method the solubility of the cement was tested at three different powder/liquid ratios, *viz.* 1.90, 1.60, and 1.40 g of powder to 0.4 ml of acid. The first proportion gives standard consistency at 12° C., the second at 22° C., while the third gives standard consistency at 28° C. At a temperature of 22° C. the first P/L ratio gives a very stiff mix, and the last a rather thin mix.

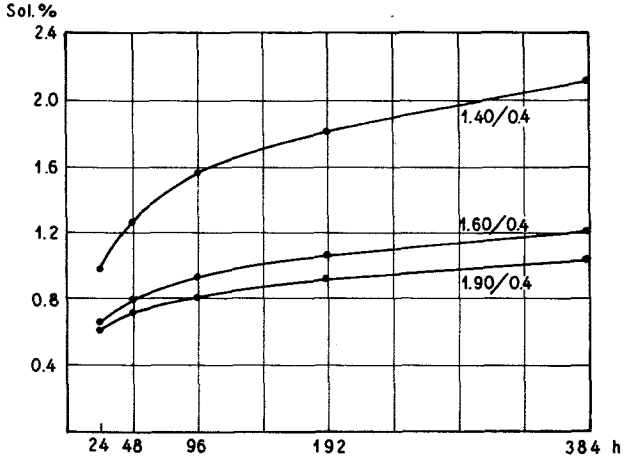

Fig. 2. Solubility in distilled water for cement D over a 16-day period (384 hours). The water was not changed during the experimental period. The different powder/liquid ratios are shown on the curves, the middle curve representing a mix of standard consistency.

The results appear in Figs. 2 and 3. Each of the points plotted represents the average of a minimum of 6 determinations.

The data show that the solubility decreased relatively much when less powder was incorporated than required for standard consistency at 22° C. On the other hand, an increase in the amount of powder caused only a moderate reduction in solubility. In the graph in Fig. 3 the logarithm of the time during which the cement was exposed to solvent action is plotted on the abscissa. The solubility curves are apparently straight-lined, which permits a fairly reliable extrapolation to the right in the diagram. If we suppose that a silicate filling will be rejected as useless when y per cent of it has been dissolved, it is possible,

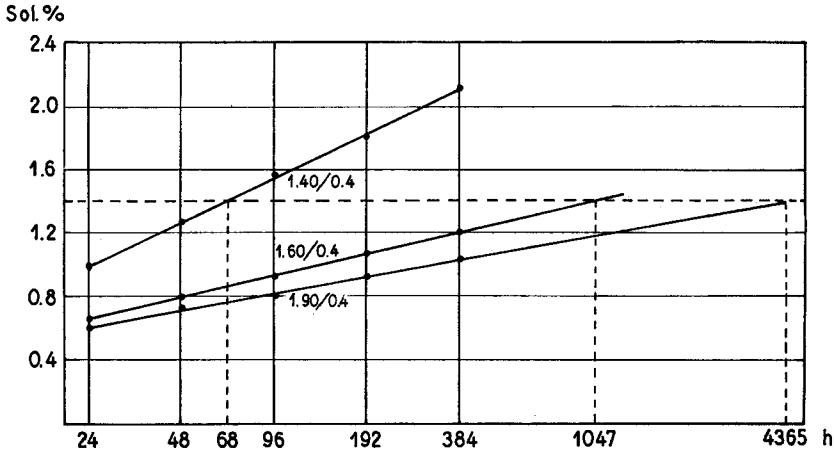

Fig. 3. Same experiment as Fig. 2, but with logarithmic abscissa. Extrapolation of the straight-lined curves makes it possible to estimate the relative durability of individual cements.

by extension of the straight curves in Fig. 3 to intersection with the horizontal line passing through the point y on the ordinate, to get an impression of the durability of restorations prepared with different P/L ratios. This procedure is illustrated, in principle, in Fig. 3 with the value 1.4 per cent as the limit of rejection. (It is pointed out that 1.4 per cent dissolution is far from rendering a clinical restoration unserviceable). This shows that relatively small differences in initial solubility may involve very large differences in the durability of silicate fillings, and that the less pronounced the slope of the semi-logarithmic curves are, the more pronounced will be the difference. Obviously, the farther the extrapolation is extended, the greater will be the risk of resulting errors, but this scarcely affects the principle of the view.

In the oral cavity the silicate cement is not surrounded by liquid at rest, but is constantly washed with saliva. It is uncertain, therefore, whether the abovementioned tests can give a true picture of the solubility of cements in distilled water. To make the conditions more like those in the mouth the experiments were repeated with the modification that the water in the weighing bottles was changed at intervals of 24 hours, after which the

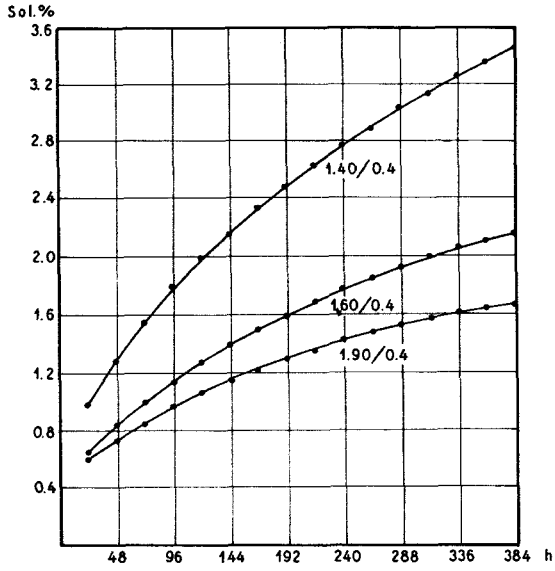

Fig. 4. Same experiment as Fig. 2, but water changed daily.

amount of dissolved cement was determined in the usual way. The results are graphed in Figs. 4 and 5.

It can be seen in Fig. 4 that the amount of cement dissolved during 24 hours decreased with the age of the cement, and that the total amount of dissolved cement after 384 hours (16 days) was somewhat greater under this set of conditions. The solubility curves in the semi-logarithmic presentation in Fig. 5 are curved at first, but gradually take on the shape of straight lines. The lower curve becomes straight-lined after about 7 days, the middle curve after about 8 days, while the upper curve remains curved throughout the experimental period. The transition from the curved to the straight-line shape can be regarded as a stabilization of the cement with respect to rate of dissolution. The diagram shows that this stabilization occurs the earlier, the larger the powder/liquid ratio. The extrapolation principle for determination of cement durability may be applied to these tests too, once the solubility curves have formed straight lines for a reasonable length of time.

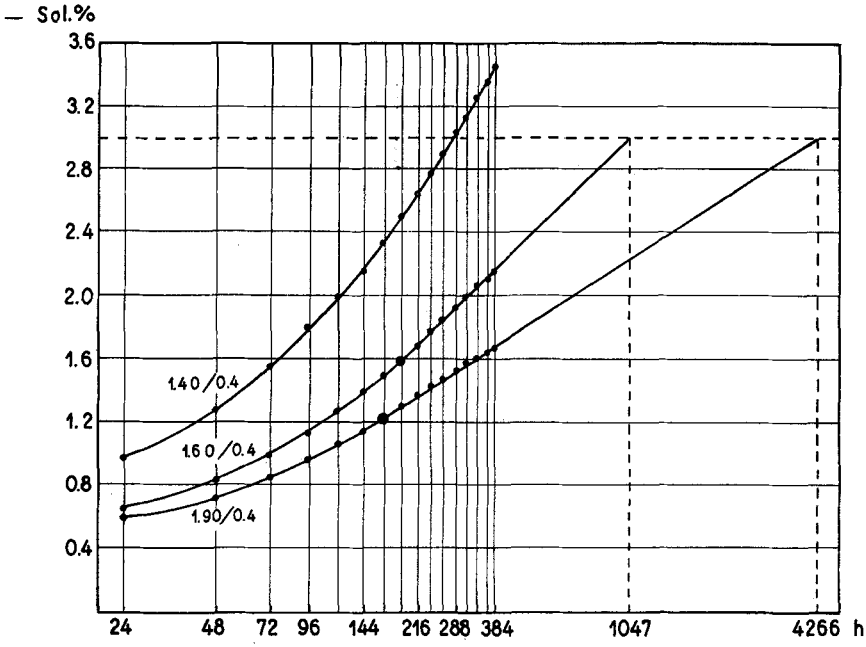

Fig. 5. Same experiment as Fig. 4, but with logarithmic abscissa. After a few days the lower curves become straight-lined, and extrapolation is therefore possible.

3. Time elapsing from mixing to contact between cement and water

The effect of this time upon the solubility of a cement (D) was investigated by modifying the technique of the A.D.A. specification. The test specimens were placed in water at different times after start of mixing, *viz.* after 5, 10, 15, 30, or 60 min. and 24 or 48 hours had elapsed. The storage period was 23 hours as prescribed in the specification. In another series, long-term experiments were run by the same method as described in section 2 for a cement immersed 15 min. after start of mix. The findings in Figs. 6 and 7, and in Table 3 are in each case the average of 6 tests.

It is apparent from the results that the solubility of the cement decreased very rapidly during the first hours after the mixing, and that only after a period of 1—2 days had it developed a fairly constant degree of resistance to dissolution. Fig. 7 shows that

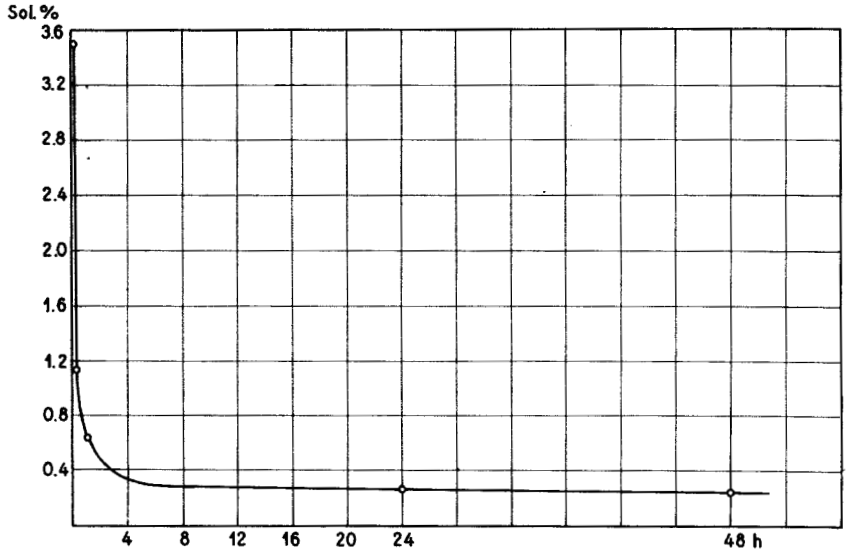

Fig. 6. Solubility of a silicate cement (D) dependent on the time elapsing from start of mixing to contact of cement with water.

Table 3

Solubility of a silicate cement in water as affected by the age of the cement.

Age of cement	% solubility
5 min.	3.09
10 „	1.14
15 „	0.94
30 „	0.83
60 „	0.63
24 hours	0.26
48 hours	0.24

the damage to which a cement is exposed by premature immersion persists (the two curves maintain the same vertical distance), but that it does not increase the tendency of the cement to dissolution during the subsequent period, when the cement has become more stabilized.

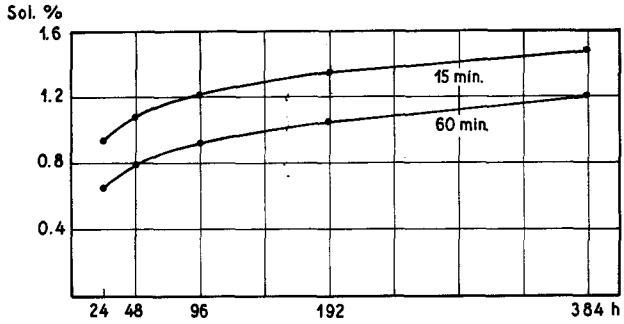

Fig. 7. Solubility of a silicate cement (D) over a 16-day period, when immersed 15 or 60 min. after start of mix. Water not changed.

4. Solubility of the cements in acid

Three brands (A, D, and G) were tested for solubility in buffered solutions of lactic acid of pH levels approximately 3, 4, or 5. The amount of dissolved cement was determined by weighing the test specimens under standardized conditions immediately before and after the dissolution test. Since various observations suggest that silicate cements absorb water until they are in equilibrium with surrounding water the following procedure was used to eliminate this source of error to a reasonable extent. Test specimens were prepared and placed in water in weighing bottles according to the standard specification. They were removed from the water 24 hours after mixing, wiped, weighed in a uniform way, and stored in the various acid solutions for a period of 24 hours. Then they were removed and weighed as previously. The difference between the two weighings was taken to represent the resistance of the cement to dissolution in the acid used. Corresponding tests were performed in distilled water. In the first series the storage medium was a 0.2 n lactic acid to which sodium hydroxide was added until the desired pH values were obtained. The pH rose somewhat during the experiment, most for low pH solutions (about one unit) and for cements with high solubility. The smallest changes were of the order of 0.1 pH unit. All experiments were made six times. The accuracy was somewhat lower than in the previously described experiments in distilled water, the greatest difference between random single tests in any one group being ± 10 per cent.

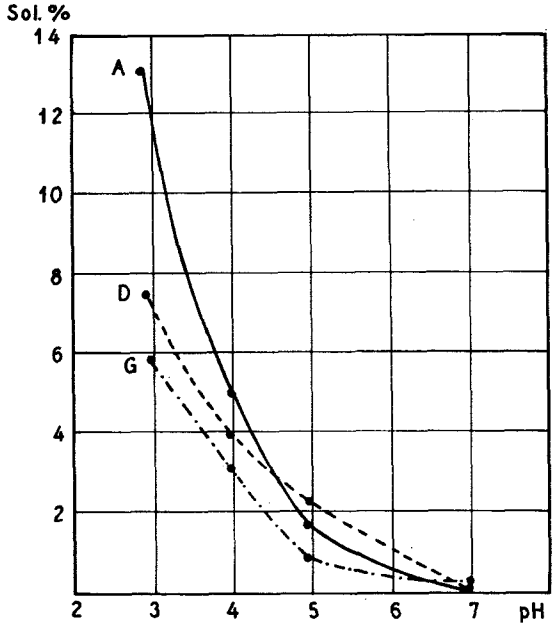

Fig. 8. Solubility of cements A, D, and G, in sodium lactate buffer, at different pH levels, the second day after mixing. G, which in distilled water has a considerably higher solubility than A and D, is less soluble in acid solutions up to pH 6.5 than either A or D.

The experimental results appear in the diagram in Fig. 8. The most remarkable finding is the very great rise in cement solubility with falling pH. It is further noticeable that cement G, which — tested according to the standard specification — showed considerably higher solubility than either A and D, was more heavily soluble than these brands at all pH levels from about 6.5 and downward. In most cases silicate cement restorations in the oral environment are exposed to pH variations between 4.5 and 6.5, while changes beyond these limits are less frequent. These observations raise the question to what extent the solubility test prescribed in the A.D.A. specification for silicate cement is clinically relevant. Undoubtedly it would be more expedient to study the dissolution tendency in environments more appropriate biologically than distilled water.

In an additional series the effect of acid concentration in the

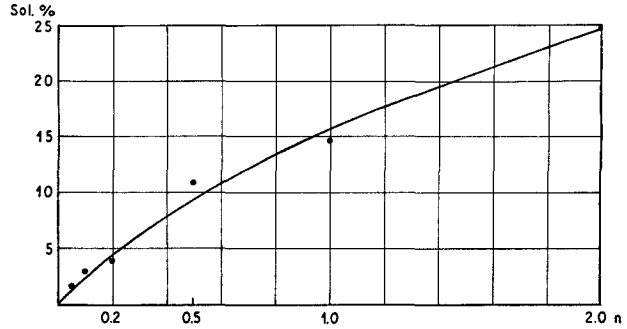

Fig. 9. Solubility of cement D in pH 4 sodium lactate buffer as affected by the acid concentration of the buffer.

sodium lactate buffer upon the solubility of a cement (D) was studied. The experimental method was the same as for the previously described acid solubility tests. The pH of the buffer was 4.0 in all the groups, while acid concentrations of n 0.05, 0.11, 0.50, 1.00, and 2.00 were used. The results are given in Fig. 9. They show a marked increase in solubility with increased acid concentration.

5. Effect of mixing time upon powder/liquid ratio

These tests were made on a cement (D) which mixed to A.D.A. standard consistency (mixing time, 1 minute) had a ratio of 1.6 g of powder to 0.4 ml of liquid. In these experiments 0.4 ml of acid and 1.6 g of powder were measured on the mixing slab, and the powder divided into eight equal portions. At predetermined intervals (first series, 9 sec.; second series, 17 sec.; and third series, 24 sec.) 0.2 g of powder was incorporated into the acid until standard consistency was obtained. The tests for standard consistency were started in the three groups 2, 3, and 4 minutes after start of mix. The proportions found for the different mixing times were 1.60, 1.54, and 1.49 g of powder per 0.4 ml of acid, *i.e.* relatively small variations considering the rather great changes in mixing time. The reduction in the amount of powder at the prolonged mixing time is doubtlessly caused by the advancing solidification of the cement. Since the cements which conform to the requirements of the specification all have about the same setting rate, it can in all probability be said about these cements in gen-

eral that their powder/liquid ratio for standard consistency depends only to a slight degree — within the limits of reasonable practice — upon mixing procedure and mixing time. With the experiments described in section 2 in mind, it may further be concluded that the abovementioned changes in mixing technique have no appreciable effect on the solubility of the cements.

6. Effect of polishing upon solubilty of cements

Test samples (cement D) were made according to the standard method, and immediately before storage in distilled water in weighing bottles they were gently polished under water with an emery cloth of the same coarseness as the strips frequently used in practice. Then the standard solubility test was made. The average of 6 measurements showed 0.59 per cent solubility, while the result obtained for unpolished control specimens was 0.65 per cent. The difference between the two groups is statistically significant.

The higher solubility found for unpolished test samples is no doubt due to the extensive amount of gel matrix which must be present in the surface of such specimens, while the polished cement surfaces consist to a higher degree of undissolved powder particles. Since all investigations on silicate cement solubility indicate that it is especially the matrix of the cements which is attacked during the dissolution process, it is reasonable to suppose that test samples with a large amount of gel matrix in the surface will be dissolved more rapidly.

In the mouth a rough, *i.e.* polished surface will probably give a poorer hygiene, and accordingly involve a greater risk of dissolution, than a smooth unpolished surface. Therefore, the laboratory tests alone do not permit any conclusions for clinical practice.

DISCUSSION AND CONCLUSIONS

An immediate evaluation of the results presented in the first section may lead to identifying low solubility in distilled water with great durability in the mouth. Yet, the findings obtained for solubility of the cements in lactic acid show that this conclusion is scarcely correct. This is especially evident when comparing

Brand G with, for example, D. Based on the standard test in distilled water G had a relatively very high solubility as opposed to D, which was among the cements showing the lowest solubility according to this test. Solubility tests carried out in lactic acid solutions at pH levels most relevant from a physiological standpoint gave the opposite result. Under these conditions G was found more resistant than D. However, the author does not feel justified in asserting, on the evidence of these laboratory tests, that G will prove more durable in the oral cavity as well. It is possible, for example, that chemical processes between storage medium and cement may affect the cement in such a way that the experimental data become misleading. Studies on this problem, preferably in connection with clinical control tests, must be made before the clinical significance of these tests can be evaluated with reasonable certainty.

Thus it is doubtful whether the American Dental Association Specification for testing the solubility of silicate cements can be used as a criterion for clinical durability. Quantitative clinical studies (*Darnutzer,* 1951) show that the durability of proximal clinical silicate restorations is least at the contact area, *i.e.* at places where the oral bacterial flora must be expected to have the best possibilities for acid production. These and other, not quantitatively expressed, observations support the view that solubility tests on a silicate cement for determination of its clinical durability must be made in acid solutions at proper pH levels and in proper concentrations.

The investigation in section 2 further shows that the resistance of a silicate cement to dissolution in water depends to a great extent on the powder/acid ratio, and that especially a thinner mix than normal consistency will result in reduced resistance. Extrapolation of the semi-logarithmic solubility curves (Fig. 5) shows that even a relatively slight initial difference in solubility may cause a considerable difference in the solubility of the cement. It is not reasonable to suppose that this will be fundamentally different for solubility tests in acid solutions.

The experimental results in section 3 showing the significance of the time of contact between cement and water must also be supposed to have general validity when the cements are tested in acids like those occurring in the oral cavity.

SUMMARY

The solubility of most silicate cements available on the Danish market (see Table 1) were studied. The tests were carried out in accordance with the American Dental Association Specification for silicate cements. The results are given in Fig. 1 and Table 2. Additional experiments on the solubility of selected cements in lactic acid (Fig. 8) show that a cement with relatively high solubility in distilled water may have a relatively low solubility in acids at the physiologically most relevant pH levels 4.5—6.5. It is therefore doubtful whether the American Dental Association Specification makes it possible to evaluate the resistance of the various cements to dissolution in the oral cavity.

The other investigations are quantitative analyses of the dependence of solubility upon powder/liquid ratio (Figs. 2—5), time of contact between cement and water (Figs. 6—7), length of mixing time, and polishing of cement surfaces. An increase in the ratio of powder to liquid seems to result in a rather considerable increase in cement durability, as does an effective protection against saliva during the first hours after mixing. A moderate prolongation of the mixing time, however, or polishing of the cement surfaces, has scarcely any great effect on the durability of the cement.

RÉSUMÉ

SUR LA SOLUBILITÉ DES CIMENTS SILICEUX

On a procédé à l'examen de la solubilité de la plupart des ciments siliceux qui se vendent sur le marché danois (voir la table 1); les examens ont été faits d'après la spécification standard américaine pour ciments siliceux; les résultats sont présentés sur la figure 1 et la table 2. Des examens supplémentaires de la solubilité des produits choisis dans de l'acide lactique (fig. 8) montrent qu'un ciment ayant une solubilité relativement très grande dans de l'eau distillée peut avoir une solubilité relativement petite dans des acides du domaine pH le plus pertinent d'un point de vue physiologique de 4,5—6,5. En conséquence, il est douteux si la spécification standard fournit le moyen d'évaluer la résistance

de divers produits cimentaires à la dissolution dans la cavité buccale.

Les autres examens sont des analyses quantitatives sur la dépendance de la solubilité à l'égard de la proportion de mélange entre la poudre et l'acide (fig. 2—5), du moment de contact entre le ciment et l'eau (fig. 6 et 7), de la durée du temps de mélange et du polissage de la surface du ciment. D'après ces expériences une augmentation de la proportion de mélange entre la poudre et l'acide semble avoir pour effet une prolongation relativement très considérable de la durabilité du ciment; une protection effective de la surface du ciment contre le contact avec la salive pendant les premières heures après le délayage du ciment a de toute évidence le même effet. Par contre, on ne peut guère attribuer une grande importance pour la durabilité du ciment à une prolongation modérée du temps de mélange ou au polissage de la surface du ciment.

ZUSAMMENFASSUNG

ÜBER DIE LÖSLICHKEIT VON SILIKATZEMENTEN

Untersucht wurde die Löslichkeit des grössten Teils derjenigen Silikatzemente, die auf dem dänischen Markt verhandelt werden (siehe Tafel 1). Die Untersuchungen wurden nach der amerikanischen Standardspezifikation für Silikatzemente vorgenommen. Die Ergebnisse sind in Abb. 1 und in Tafel 2 dargestellt. Ergänzende Untersuchungen über die Löslichkeit ausgewählter Erzeugnisse in Milchsäure (Abb. 8) ergeben, dass ein Zement, der in destilliertem Wasser eine verhältnismässig sehr grosse Löslichkeit hat, in Säuren in dem physiologisch häufigst vorkommenden pH-Bereich von 4,5 bis 6,5 eine verhältnismässig geringe Löslichkeit haben kann. Es ist deshalb zweifelhaft, ob die Standardspezifikation eine Beurteilung der Resistenz verschiedener Zementerzeugnisse gegen Auflösung in der Mundhöhle ermöglicht.

Die übrigen Untersuchungen sind quantitative Analysen über die Abhängigkeit der Lösbarkeit vom Mischungsverhältnis zwischen Pulver und Säure (Abb. 2 bis 5), vom Kontaktzeitpunkt

zwischen Zement und Wasser (Abb. 6 und 7), von der Länge der Mischdauer und vom Putzen der Zementoberfläche. Eine Erhöhung des Mischungsverhältnisses zwischen Pulver und Säure scheint demnach eine verhältnismässig sehr beträchtliche Verlängerung der Haltbarkeit des Zements zu bewirken; die gleiche Wirkung hat augenscheinlich ein wirksamer Schutz der Zementoberfläche vor Berührung mit Speichel während der ersten Stunden nach dem Ausrühren des Zements. Dagegen kann einer mässigen Verlängerung der Mischdauer oder einem Putzen der Zementoberfläche kaum grosse Bedeutung für die Haltbarkeit des Zements beigemessen werden.

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