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Water uptake and loss in silicate cements

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The water absorption of a dental silicate cement was measured both in de-ionized water and in pH controlled phosphate buffers of several ionic strengths. Uptake is found to be related to ionic strength. Water loss was studied using thermogravimetry. Water loss is seen to be a continuous process from ambient temperatures to in excess of 500° C. The implications of the findings are considered not only from a clinical viewpoint but also in relation to past reports of solubility of this material which were uncorrected for water uptake. The usefulness of the concepts of "evaporable" and "non-evaporable" water are considered and the results are examined to assess the importance of drying temperature in carrying out solubility measurements.

1. Introduction

It is well known that many biomaterials take up water in service. Such water uptake can lead to change in properties and also to changes of dimension. It is thus desirable to have some knowledge of the phenomenon for all materials.

The present paper relates to water uptake and loss as it occurs in the still widely used dental silicate cements. In spite of the fact that these materials have been the subject of research for some 45 years, this aspect of their behaviour has hardly been studied. That water uptake can be a problem with the silicate cements is elegantly shown by a photograph due to Wilson and Batchelor [1] in which a cylinder of the material is shown spilt open by pressures due to water absorption.

The problem appears to have been studied by only two authors, and both adopted rather specialized conditions of study.

Wilson *et al.* [2] measured weight gains of disks suspended in a 100% r.h. atmosphere: water was taken up. However, it seems probable that such water uptake was related to the hygroscopic nature of the phosphate acid itself, the reaction of which (as Wilson has so elegantly shown) takes many weeks to reach completion. By adopting this methodology these authors chose to eliminate water uptake processes due to exchange, in which ionic components diffuse out, to be replaced by water. Their conditions were thus far removed from those prevailing *in vivio.*

Eichner [3] plots water uptake against time. His data was obtained by weighing disks of cement after exposure to water and then again after two weeks in a desiccator (at unspecified temperature). Such results would only be valid if something was known regarding water loss from silicates and its relationship to temperature. Eichner says nothing on this point. Wilson *et al.* [2] have obviously given thought to this, and shown water loss at 105° C over 72 h. The same author has returned to the problem (Wilson *et al.* [4]) where water content in a range of dental cements is divided into "evaporable" and "non-evaporable". Silicate cements are there stated to contain the smallest proportion (50%) of "evaporable" water. However, in the present study we have sought to examine water absorption and to consider the effect of the medium (and its ionic strength)

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on this. Secondly, the whole question of water loss seemed to be an appropriate subject for the application of thermogravimetry (TG). The data from this work, which is shown below, has further importance. The measurement of cement solubility, according to the procedure laid down in ADA Specification No. 9, is widely used. But, bearing in mind that the dissolved materials, which are then evaporated to dryness, are chemically related to the original cement, how critical is the drying temperature? To our knowledge this has not been considered.

The question of water uptake and loss is also important in that a knowledge of this is needed for critical evaluation of those (such as Eriksson [5] or Eriksson and Stralfors [6]) who chose to follow the rate of cement dissolution by weighing the disks themselves before and after exposure, rather than the evaporated eluate. Several authors have criticized this procedure precisely because of errors of drying temperature.

It is now widely accepted that all phenomena such as solubility of silicate cements and fluoride release are strongly dependent on whether the liquid is changed or not and such behaviour presumably reflect the changing composition of the liquid, both in terms of ionic strength and pH as products from the cements are released into it. Such efforts are demonstrated by the graphs of Jorgenson [8] who compared dissolution into distilled water (unchanged) with similar data for water changed daily. Profound differences were seen and there are many other confirmations of this finding which will not be quoted here.

One aspect of the present work was therefore to measure water uptake by the silicate cements, firstly in water changed daily and secondly into a series of solutions of different ionic strength (phosphate buffered) but with a pH (7.0) which, being buffered, did not change over the period of the measurements. As will be shown below, substantial differences were found between our own results and those of Eichner.

In this work, a proprietary silicate cement, made up as disks was immersed both in distilled water and in a series of buffer solutions, and its weight change was recorded over a period of time together with loss of material due to dissolution, the latter being determined by evaporation of eluate, according to the procedure laid down in ADA Specification No. 9.

The second part of this study was therefore based on a thermogravimetric investigation of silicate samples of various ages and histories.

2. Experimental procedure

All results are based on a single material (Bio-Trey, Messrs Amalgamated Dental Co.). Batch numbers UM4 WL and YF 10ZA (liquid) and UH9, UJ; UH9 TK and WC32WE (powder). This was made up into disks contained in split rings. Disk thickness was 1.5 mm, diameter 20 mm. Mixing time was 1 min at room temperature (23° ± 3° C) and relative humidity 52 ± 2%. Powder to liquid ratio was 1.2:0.5, expressed as $g\,g^{-1}$. This corresponds to manufacturers recommended ratios, though these are expressed in $g\,ml^{-1}$. Curing time was 1 h at 37° C. These disks were then immersed, using a floss thread previously inserted into the setting cement, in de-ionized water or phosphate buffer. Fifty millilitre aliquots of these were used in 100 ml pyrex beakers, which were kept in a constant temperature enclosure at 37° C for the period of the experiment. A range of phosphate buffers was used, all of which held the same pH (7.0) but were based on different ionic strengths. Compositions were (a) 0,98 $g\,l^{-1}$ PO_4^{2-} (based on Na_2HPO_4); this was made up from 1.14 g Analar Na_2HPO_4 and 0.301 g Analar KH_2PO_4 per litre); (b) 0.25 g PO_4^{2-} per litre; and (c) 1.72 g PO_4^{1-} per litre, using the same salts but adjusting the ratios to maintain the pH of 7.0.

Water absorption was determined by weighing the disks and correcting weight loss or gain for the known weight (determined by evaporation of eluate) of material lost by dissolution. Disks were lightly brushed after removal from solution, then blotted dry and weighed.

Thermogravimetric data was obtained using a Stanton Redcroft TD 70 thermogravimetric balance. Disks were treated as above, then broken into small pieces and ground up using an agate pestle and mortar, after which they were inserted into the pan of the TG apparatus.

3. Results

3.1. Water uptake

This is shown in Fig. 1. As can be seen, there is a very considerable difference between the daily changed and unchanged conditions.

3.2. Thermogravimetric studies

These are shown in Figs. 2 and 3.

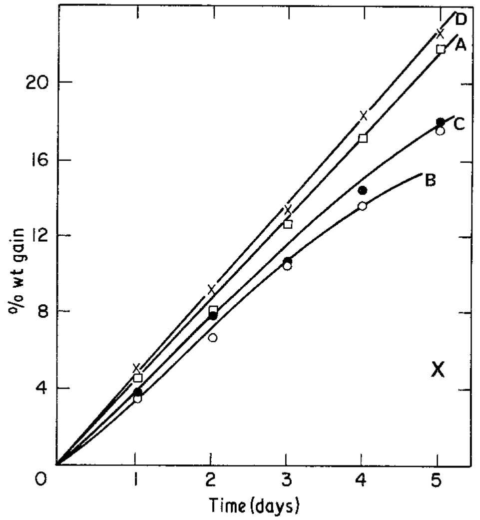


Figure 1 Cumulative water absorption by silicate cement disks, expressed as % weight gained. (A) de-ionized water, pH approximately 6. (B, C, D) phosphate buffers, all at pH = 7, with phosphate concentrations (as $PO_4^{=}$) 0.98 (B), 1.72 (C) and 0.25 (D) g l^{-1}. Time in days. All points are mean of five separate samples, with solutions changed daily. Point X is the mean of five samples in de-ionized water unchanged over the period of the experiment.

4. Discussion

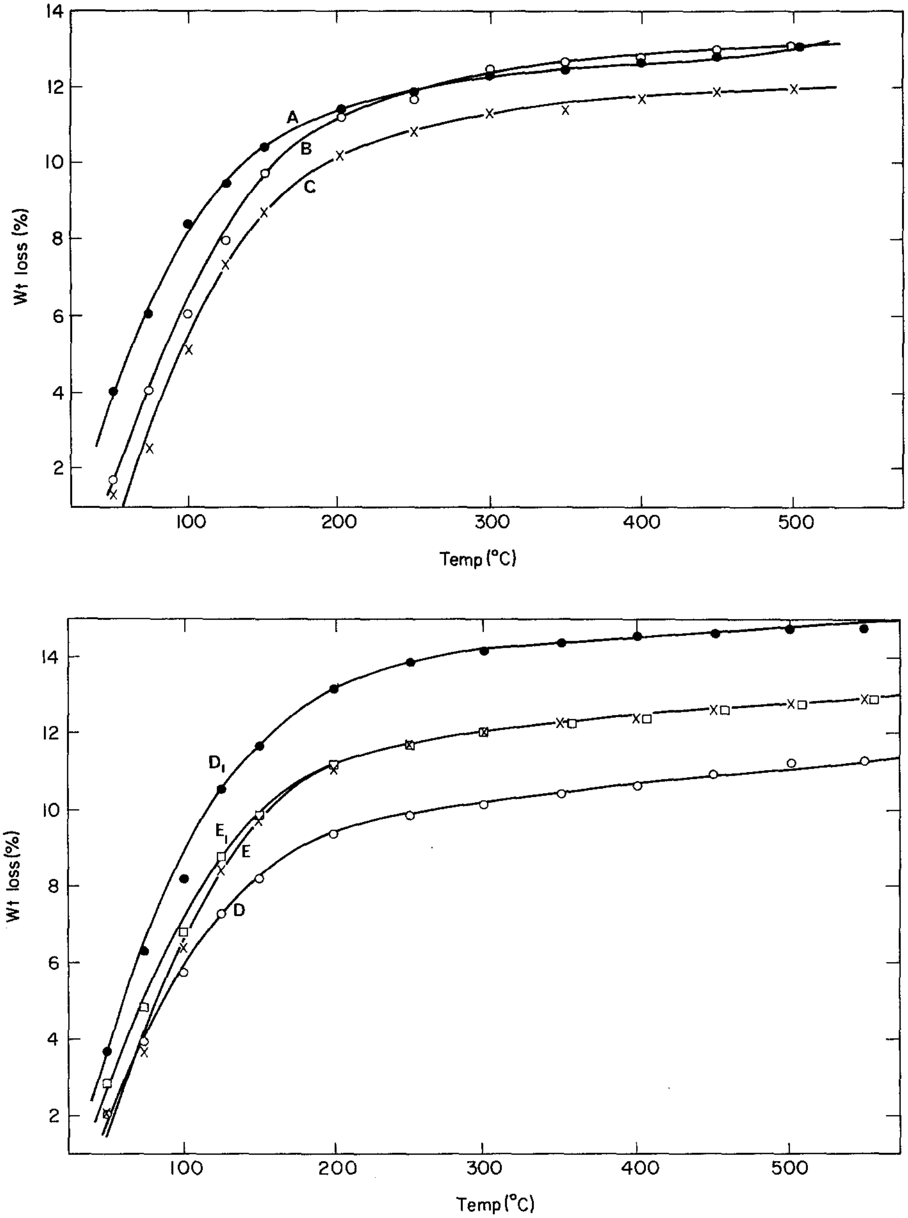
4.1. Water uptake

As can be seen from Fig. 1, water uptake is broadly a function of ionic strength in solution, with the lowest ionic strength solution (D) and de-ionized water (which of course itself acquires an ionic content due to uptake of dissolved salts) showing the greatest water absorption. The ranking of solutions C and D is not as one might expect, and this may be explained in terms of the understanding, only recently appreciated, that there is bidirectional mobility of species from cement into solution and in the reverse direction. This has been reported by Winter *et al.* [10] in respect of phosphate uptake and release from solution while Lesan [11] has shown a similar phenomenon in respect of fluoride ions. The manner in which solutions containing both species behaves will obviously be complex. All points on Fig. 1 represent the mean of five samples. Our data can only be compared with that of Eichner in respect of curve A (de-ionized water). His results indicate that approximately twice as much water was absorbed in the first 24 hours as was found by us. Whether this reflects a difference in P:L ratio (which Eichner does not specify) one cannot say. After 24 hours, the difference in experimental conditions make further comparison difficult. However, inspection of Fig. 1 shows that with water changed daily uptake of moisture continues more or less linearly, presenting a very different picture to the asymptotic approach to constant moisture shown by Eichner, with a value in his case of 8 to 10% in contrast to the 20% water content seen in the present study (Fig. 1, curve A)), this figure showing no sign of reaching a limit. Once again, treated on a cumulative basis, it is clear that these findings have clinical implications, since cements placed orally are subject to continuous irrigation with fresh saliva. Then too, that saliva is a liquid with ionic strength far removed from de-ionized water, having a range of phosphate concentrations from 61 to 710 mg l^{-1} [7]. On the basis of these findings, we do not believe that solubility measurements of this type conducted in de-ionized water are at all appropriate.

4.2. Water loss

Examination of Figs. 2 and 3 shows that water is lost from the silicate cements on heating, and that this loss continues even above a drying temperature of 400° C. It is seen that at 110° C, the drying temperature selected by Eriksson, water loss is in full swing. Of course it may be argued (and the facts are not presently available) that drying for extended times, even at a lower temperature, may achieve the same effect. On the evidence, as it relates to SiO_2 [9] water is absorbed with a range of varying bond strengths such that no time of heating will remove water below its characteristic binding temperature and the implications for the "weight loss" method of determining solubilities as used by Eriksson is clear.

The thermogravimetric data can also be used to give an insight into the binding of water in the silicate cements. Curves (B) and (C) in Fig. 2 relate to samples which had been immersed in water for 1 month and 2 months respectively, while (A) was a freshly prepared disk (no immersion). It is seen that, at any given temperature most water is lost from the fresh Sample A, followed by B then C, thus showing that during the storage time, the water had become more firmly bonded – that is to say required a higher temperature for its removal. Similar effects can be seen in Fig. 3. Curve (D) shows data for a freshly prepared disk, desiccated over silica gel for 43 days. Curve (D_1) was the same as (D), but with immersion in de-ionized water for 16 hours following the desiccation. Curve (E) was for a freshly prepared sample, immersed in



Figures 2 and 3 Thermogravimetric scan of crushed silicate disks. Points as follows: (A), disk mixed according to standard procedure then cured at 37° C for 1 h; (B) and (C), as in (A) but immersed in de-ionized water at 37° C for 1 week and stored at room temperature for 1 month and 2 months respectively. (D), as in (A) but desiccated over silica gel for 43 days. (E), as (A) but immersed in de-ionized water at 37° C for 1 week, then desiccated over silica gel for 36 days. (D_1) and (E_1), as (D) and (E) respectively but immersed in de-ionized water at 37° C for 16 h, then dried at room temperature for 2 h before testing.

water for 1 week, then desiccated for 36 days. Finally, (E_1) but as for (E) but re-immersed in water for 16 hours following the desiccation.

From all of these data, it is clear that TG results depend critically on the history of the sample and that the technique can only be used if such history is known and controlled. [N.B. Any attempt to correlate water uptake (e.g. from Fig. 1) with loss (from Figs. 2 and 3) should be made bearing in mind that the former weight gains are percentage gains on "dry" weight while the latter are percentage losses on the "wet", i.e., larger figure. We are somewhat uncertain regarding the use of terms "evaporable" and "non-evaporable" water since it would seem (Figs. 2 and 3) that the relative amounts depend purely on an arbitrarily chosen drying temperature. The suggested picture is that of a continuum. While various factors including those studied here, and the "modifiers" studied by Wilson [2] can alter water bonding energies, there is no evidence for a "threshold" effect as the terms above suggest.]

5. Conclusions

As has so often been found, it would appear that earlier *in vitro* tests have been too far removed from *in vivo* conditions, and the material considered here shows very considerable differences in its water uptake with variation of test conditions. It would appear that far greater amounts of water can be taken up than the literature suggests and the implications of this must be considered both in planning further research, and in the evaluation of previously published data.

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