THE

STRENGTH AND SOLUBILITY

OF

SILICATE CEMENT

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William James Jackson B.D.S.
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PREFACE

Silicate cement was introduced at the turn of the century. Almost from the outset, dentists recognised the shortcomings of the material, but because silicate cement was the only tooth-coloured, easily manipulated restorative material available, it was widely employed.

Paffenbarger and his co-workers at the National Bureau of Standards, Washington, produced a specification for silicate cement in 1938 and stressed the manipulative variables which they believed had the greatest effect on the physical properties of the fully hardened material.

In 1939, these workers assumed that the hardening reaction of silicate cement was similar to that of silicic acid gels as described by Hurd (1938). On the basis of this assumption, certain concepts regarding the manipulation of the material evolved. However, the clinical performance of silicate restorations remained extremely variable and dentists sought a stronger, less soluble material. Other tooth-coloured restoratives were introduced but none proved more satisfactory and attempts to improve the physical properties of silicate cement by chemical modification met with little success.

In more recent times, Wilson and his associates, in the laboratories of the Government chemist in London, have shown conclusively that silicate cement is a phosphate-bonded material and "dissolution in acidic and citrate media must be regarded as an inherent defect which stems from the fundamental chemistry of the system."

Within the last five years, newer organic composites have been introduced and many dentists have discarded silicate cement. It seems

ironic that the material is being rejected at a time when the chemistry and the significant factors affecting clinical durability are being definitely established. Because silicate cement possesses a unique anticariogenic property it is well suited to the restoration of minimal lesions, particularly when oral hygiene is good. Thus the use of composite resins and silicates should not be mutually exclusive.

In accordance with this opinion, the aims of this thesis were to consider the dental implications of the recent studies by Wilson et al, to test the validity of the "traditional concepts" regarding the effects of manipulative variables (particularly with regard to newer materials and manipulative techniques) on the physical properties of silicate cement and to attempt to clarify the clinical significance of these variables.

REVIEW OF THE LITERATURE

PART A : CHEMISTRY OF SILICATE CEMENT

CHAPTER I : DEVELOPMENT OF SILICATE CEMENT

G.V. Black's properties for the "ideal" restorative material are not totally possessed by any one of the materials currently available to the dentist. Black lists the most desirable properties of a permanent restorative material as :

1. indestructibility in oral fluids
2. adaptability to the cavity walls
3. freedom from volume change after placement in the cavity.
4. resistance to attrition and ability to withstand the force of mastication.

"The qualities of secondary importance are color, or appearance, non-conductivity of thermal impressions, and convenience of manipulation." (Black, G.V. 1908, p. 224).

When applying these requirements to anterior restorative materials, the increased demands made by patient and dentist over the years have given more weight to the "secondary" factors of colour and ease of manipulation. This fact is borne out by the continuing search for a tooth coloured restorative material which is relatively simple to manipulate.

The porcelain inlay, introduced in the latter part of the nineteenth century, provided an excellent aesthetic restoration. However, because of its tedious fabrication and questionable fit, it has now been virtually discarded.

The use of cements as tooth coloured restorative materials has had a short but controversial history. In the mid 1950's zinc and magnesium oxychloride and zinc oxysulphate cements were introduced. Despite support by such an eminent member of the profession as Charles Tomes, these cements fell into disfavour during the next twenty years. Peyton (1968, p. 417) suggested that all proved unsatisfactory as they were highly irritating to the pulp, markedly soluble in the oral environment and though tooth coloured, lacked the characteristic translucence of teeth.

After many unsuccessful attempts to produce an aesthetic cement with desirable physical characteristics, silicate cement was introduced in 1871 by an Englishman, Thomas Fletcher. In his opinion both zinc and magnesium oxychloride were "worthless and untrustworthy", as were Hubbock's oxide and Vielle Montaigne oxide (Fletcher, 1871). The manufacture of the components of these dental cements was not strictly controlled and hence their physical properties varied greatly from batch to batch.

Fletcher's first experimental "cements" were powdered silica mixed with different gum bases to form a filling material, putty-like when heated but rigid at mouth temperatures. By 1871 he was forced to admit that one such proposed material was unsatisfactory. "The filling composed of powdered silica and gum-copal which I proposed some time ago has proved as great a failure as the other white fillings which have been from time to time introduced, although I had tested it for some months before mentioning it, with perfect success.

I am at present testing carefully a compound which appears to have every desired property, but after having made one decided failure, I shall certainly test this for a much longer time before saying anything about it.

The mode of preparation is as follows : To a boiling solution of gelatine a solution of tungstate of soda is added and the mixture well stirred. From this solution an insoluble tungstate of gelatine is precipitated by the addition of hydrochloric acid, and the precipitate is washed in hot water. The substance obtained is a mass flexible and soft as gutta percha whilst hot, and very hard when cold; it will admit of the incorporation of a large proportion of powdered silica or other material without impairing its strength, and in most points appears to be a very permanent and suitable compound for the purpose required." (Fletcher, 1871).

This formulation proved as unsatisfactory as previous "cements". However, in 1878 Fletcher introduced yet another material which was remarkably similar to silicate cements in use today. The powder was a combination of fused silica (SiO_2), alumina (Al_2O_3), and lime (CaO) and was mixed with an orthophosphoric acid liquid to produce a cement. Dentists, aware of the earlier failures of Fletcher and others, were sceptical about this new material and the use of silicate cement was virtually abandoned for the next twenty-five years.

It was left to two Germans, Steenbock (a chemist) and Ascher (a dentist), to reintroduce a silicate cement in 1904. It was marketed as "Ascher's Artificial Enamel" and was not unlike Fletcher's 1878 material.

Several other cements soon appeared and "this was the beginning of the widespread use of silicate cement as a restorative material." (Peyton, 1968, p. 431).

The use of silicate cement increased rapidly as it seemed to be aesthetic and easily manipulated. Voelker, a strong proponent, concluded that silicate cements "have largely taken the place of gold fillings and of porcelain inlays in simple approximal, buccal, labial and lingual cavities, especially in the anterior teeth.....The ease of preparation of the cavity and insertion of the filling, the avoidance of pain and loss of sound tooth structure so often associated with the use of porcelain inlays, as well as the uncertainty as to the permanence of the latter, and the greater esthetic effect of the silicate fillings over gold, combined with a much slighter strain on the purse-strings particularly appealing to those in moderate circumstances, have proved decisive factors in popularizing this class of fillings with the intelligent laity - even though such fillings cannot yet be called permanent in the loose sense in which that term is applied to gold and porcelain, and in spite of the fact that silicate fillings fail at times and have to be replaced like other filling materials. We can only approximate the ideal as yet." (Voelker, 1916).

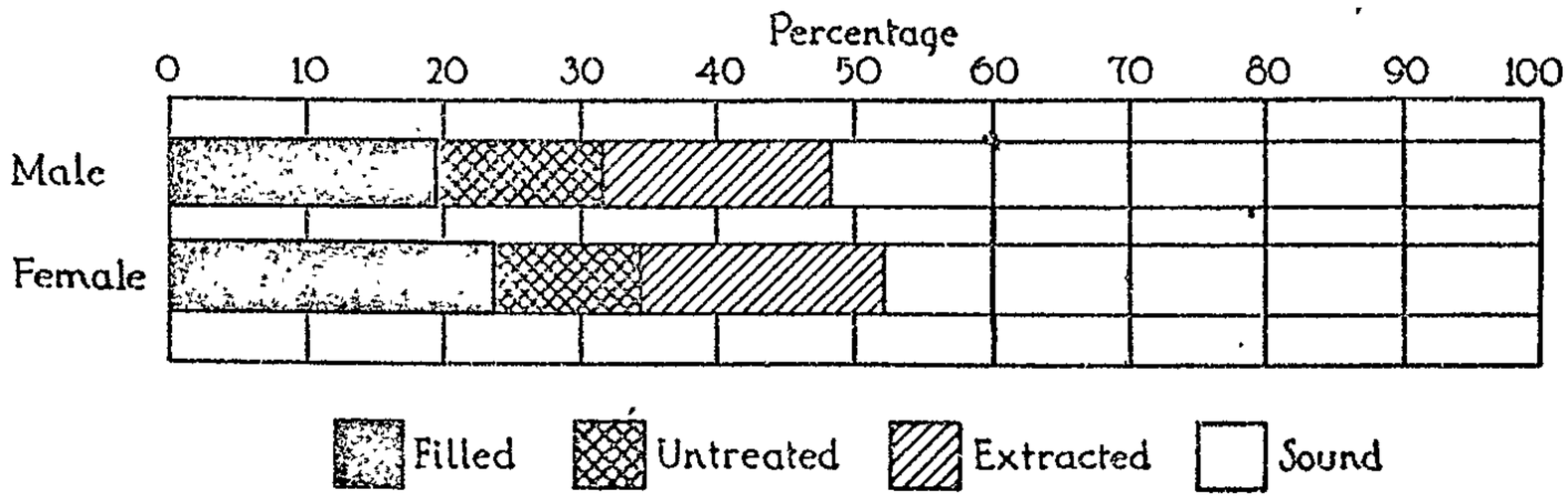
However, Voelker's enthusiasm was not shared by all of his contemporaries, notably Huff (1928) who suggested that "many dentists are digging their professional graves with a glass slab and an agate spatula" and A.D. Black (1928) who maintained that "this material meets in no reasonable measure any of the qualities most desired.....The extensive use of this material in recent years is a distinct backward step in the field of Operative Dentistry." It was noticed that the life of silicate restorations varied considerably. Dissolution and disintegration of the fillings was clinically obvious after only a few months in some mouths.

Original aesthetics also suffered, the restoration tended to stain particularly along the margins. Much worse was the observation that silicate cement seemed irritating to the pulp and in many cases caused pulp death. The material fell into disfavour with eminent American dentists. (Black A.D., 1928).

The manufacturers began to control the composition of powder and liquid more rigidly. The arsenic content of the powder was minimized and steps were taken to reduce the effects of the prolonged acidity of the cement on the pulp. These factors were thought to contribute directly to pulp damage. (Peyton, 1968, p. 431). Investigators modified silicate powders by the addition of small quantities of dielectrics, e.g. white petroleum jelly and soap, in an attempt to reduce the acidity. (Eberly, 1934). Methods, including the placement of nitrocellulose cavity varnishes and alkaline bases prior to cement insertion, were employed by dentists to protect the pulp. (Mamlet, 1936).

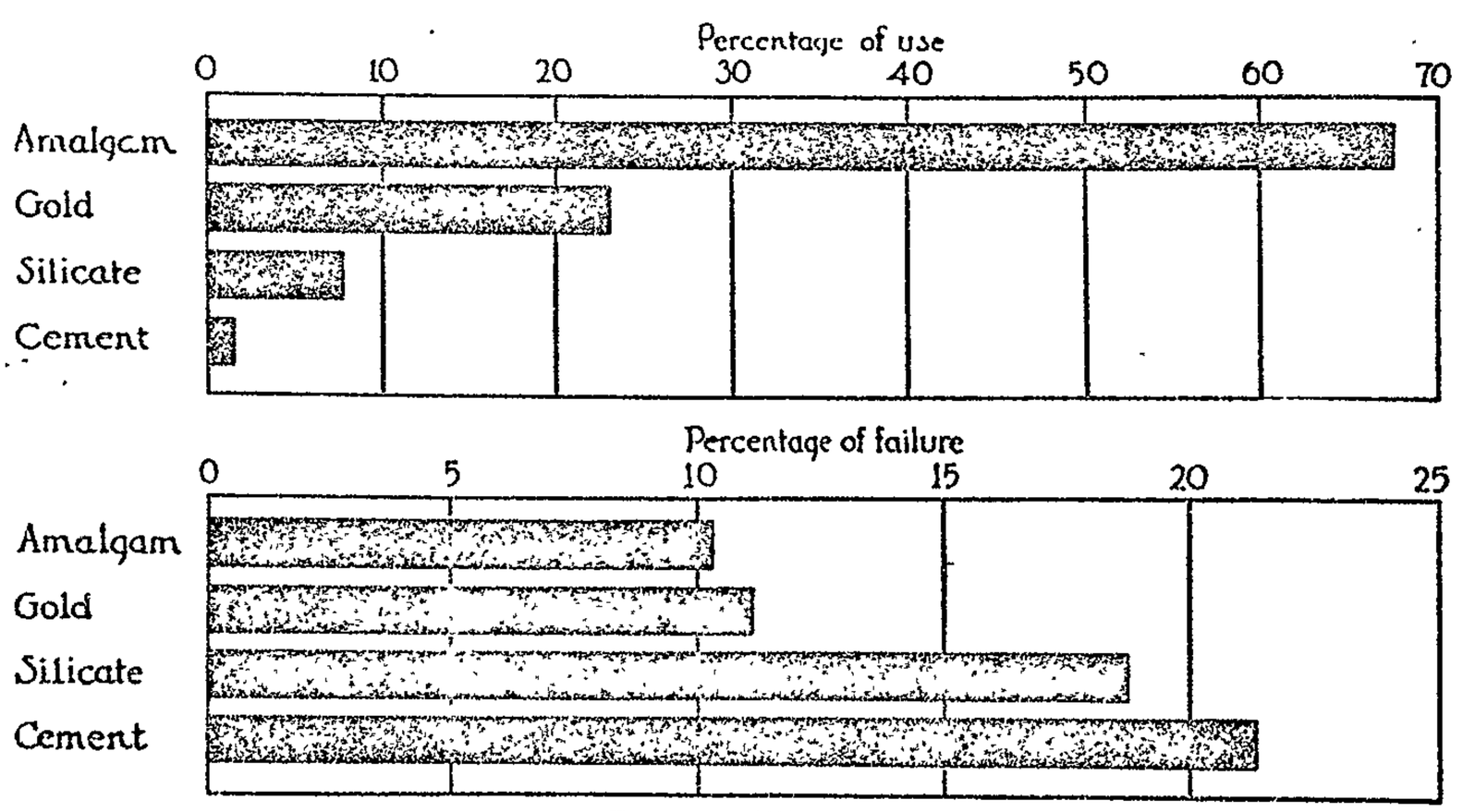
During the period 1925-1938, strong debate appeared in American dental journals concerning the use of silicate cement as a permanent restorative material. Despite severe criticism, clinical surveys showed that the use of silicate cement was widespread. Brekhus and Armstrong (1936) published quantitative data concerning the types and respective failure rates of restorative materials used at the School of Dentistry, University of Minnesota over a two year period. Their results appear in Fig. 1. Paffenbarger et al (1938) commenting on this study stated that: "When one considers that this survey included both anterior and posterior teeth, it can be easily seen that a very large percentage of the fillings in anterior teeth are of silicate cement. The survey shows that

Fig. 1 : Data on filling materials



Total number of teeth examined: male, 208,684; female, 209,468

Dental condition of clinic patients, School of Dentistry, University of Minnesota.



Data on filling materials.

(From Brekhus and Armstrong, 1936)

approximately 19% of the silicate fillings have failed. The criteria by which success or failure of the silicate cement restorations was judged are not given in the report, but Dr. Brekhus, in a personal communication (to George Paffenbarger) says:

> .....criteria used in determining failures in fillings were that, when fillings or tooth margins were so disintegrated that they ceased to preserve tooth, they were adjudged failures. Contour, contact, color and other minor deficiencies were not taken into consideration."

A survey by Paffenbarger (1940) supported the contention that silicate cement was being widely used by the American dental profession.

Huff, (1935), an ardent opponent of the material urged the National Bureau of Standards to draw up a specification. In 1938, Paffenbarger et al published the findings of comprehensive in vitro studies on dental silicate cement. They attempted to set out clearly the manufacturer and operator variables that influenced the physical and chemical properties of the material which were of clinical significance. A tentative specification for dental silicate cement was drawn up.

With a greater understanding of the physical and chemical properties and consequent advantages and disadvantages, rational clinical procedures were developed for the use of the material. By 1940, the use of silicate cement, in certain clinical situations, was firmly established.

DEVELOPMENT OF SILICATE CEMENT - Summary

(i) The history of restorative, tooth-coloured cements has been short and controversial.

(ii) After many attempts to produce an aesthetic material which was physically, chemically and biologically acceptable, Thomas Fletcher (1878) introduced a restorative cement remarkably similar in composition to modern silicate cements. However, the material was neglected for over twenty-five years.

(iii) In 1904, Steenbock and Ascher reintroduced the cement which was marketed as "Ascher's Artificial Enamel." Silicate cements became extremely popular; Charles Voelker (1916) suggested that they approached the "ideal" restorative material.

(iv) The initial enthusiasm was replaced by doubt and condemnation (Huff, 1928; Black, A.D. 1928). Dentists noticed that the clinical life of restorations varied considerably and that silicate cement seemed irritating to the pulp. The material fell into disfavour.

(v) Manufacturers began to control the composition of their products more rigidly and a few investigators, among them Eberly (1934), explored the possibilities of modifying the components of the cement in an attempt to reduce the prolonged acidity of the setting reaction. Placement of cavity varnishes and bases prior to insertion of the cement was also suggested. (Mamlet, 1936).

(vi) Despite the severe criticism of opponents of the material, Brekhus and Armstrong (1936) and Paffenbarger (1940) showed that silicate cement had been widely accepted by American dentists.

(vii) Paffenbarger et al (1938) at the National Bureau of Standards published the results of exhaustive laboratory studies on the physical and chemical properties of silicate cement. They attempted to define the manufacturer and operator variables influencing the clinically important physical and chemical properties of the cement. A tentative specification was drawn up.

(viii) The use of silicate cement in certain clinical situations was firmly established by 1940.

CHAPTER II : CHEMICAL COMPOSITION OF THE MATERIAL

Dental silicate cement consists of two components, a powder and a liquid, which when mixed, react rapidly to form a hard cement. The chemical composition of the components will be considered separately.

POWDER

Silicate cement powders are finely ground, complex acid-soluble glasses (Crowell, 1927; Paffenbarger et al, 1938; Wilson et al, 1967a). Fletcher's 1878 material was a "combination of fused silica (SiO_2), alumina (Al_2O_3) and lime (CaO)." (Peyton, 1968, p. 431) This powder was mixed with an aqueous solution of orthophosphoric acid.

"Ascher's Artificial Enamel" (1904) was of a similar nature; fused silica, alumina and beryl (BeO) instead of lime. The cement liquid was an aqueous solution of orthophosphoric acid (50%) saturated with aluminium phosphate and small amounts of zinc and strontium phosphate. (Ray, 1934). The early powders were produced by precipitation of $BeO.SiO_2$ (empirical formula) by adding SiO_2 to a solution of basic beryllium nitrate. The precipitate was washed, dried and calcined at red heat. The preparation was then finely ground and mixed with powdered Al_2O_3 (Doubleday, 1926).

Paffenbarger et al (1938) reported on the chemical composition of twelve commercially available cement powders. The simplest in composition was probably produced "by fluxing the given amounts of silica, alumina and lime with sodium carbonate." The powders investigated could be broadly divided into two groups - (i) those fused with a fluoride flux (NaF, CaF_2 or Na_3AlF_6), which was by far the larger group (75%).

(ii) powders fused by means of other fluxes;

the particular powders investigated had probably been fluxed with Na_2CO_3. All powders investigated contained alumina and silica. The alumina : silica mole ratio varied from 0.7 - 0.9. Ca and Na were also present in all powders either as the oxide (in those cements fluxed with Na_2CO_3) or more generally as fluorides (cements fused with fluorine-containing fluxes). With the exception of one cement powder, P_2O_5 was found in all powders. The average amount of P_2O_5 was 4.1% by wt (excluding one cement powder which had 24% by wt P_2O_5). "This unusual amount of P_2O_5 appeared to have a very deleterious effect on the physical properties." (Paffenbarger et al, 1938). It was thought that aluminium or calcium phosphate was added to the powder to retard the cementing reaction as the setting time of the cement, not containing phosphate, was too rapid.

Compounds such as beryllium oxide, (BeO), nickel oxide (NiO), ferric oxide (Fe_2O_3), magnesium oxide (MgO), lithium oxide (Li_2O) and zinc oxide (ZnO) were also found in small quantities in the cement powders.

As Paffenbarger has reported, a number of fluxes were used to aid the fusion of SiO_2, Al_2O_3 and other components. Crowell (1927) reported that most silicate powders manufactured in the U.S.A. were fluxed with a fluoride (corroborated by Paffenbarger et al in 1938), although other fluxes were available and occasionally used. The reason given by Crowell for this was that glasses fluxed with fluorides were more translucent and hence possessed better optical properties than glasses fluxed with carbonates. Modern powders as reported by Wilson and Batchelor (1967a) are all fluxed with fluorides. It is thought that perhaps the leaching of F^- ions into the surrounding dentine and enamel may be the most important factor relating to the "anticariogenic" nature of silicate cement.

(Phillips and Swartz, 1957; Norman et al, 1961).

Wilson and Batchelor (1967a) reported on the physicochemical characteristics of fourteen commercial silicate powders using spectrochemical, wet-chemical and particle size analyses and X-ray diffraction techniques. They showed "that all were finely ground (median particle size range 6.6 microns to 15.5 microns) sodium calcium fluoro-aluminosilicate glasses. Minor amounts of phosphate were found in twelve, beryllium in two and zinc in one of the powders. In some powders minor amounts of crystalline compounds and glass fibres were detected."

They noted that the composition of present day cements does not vary as much as those reported by Paffenbarger et al in 1938. At present, powders are generally formed from glasses prepared by fusing silica and alumina in a mixed cryolite (Na_3AlF_6) - Fluorite (CaF_2) flux containing some phosphate (Wilson and Batchelor, 1967a).

LIQUID

Silicate cement liquids have always consisted basically of aqueous solutions of phosphoric acid.

Asch and Asch (1911) applied the terms "alpha" and "sigma" to silicate cement liquids in use during or before 1910. So called "alpha" liquids consisted of aqueous solutions of phosphoric acid, whilst "sigma" liquids consisted of aqueous phosphoric acid solutions which had been "partially neutralized" by the addition of metallic salts singly or in combination.

Tompkins (1922) found that alpha liquids were much more irritating to the pulp than the "partially neutralized" sigma liquids and by the mid-1920's only the sigma liquids remained in use (Doubleday, 1926; Crowell, 1927).

"Modern" liquids are all modified with metallic ions, usually in combination, and have a pH of approximately two. The water content is slightly greater than that found in zinc phosphate cement liquid being 40 $\pm$ 5%. "There is no such thing as a 'neutralized' silicate cement liquid" (Paffenbarger and Stanford, 1958). "Analysis of seventeen liquids showed that all were based on phosphoric acid (47 - 66% H_3PO_4) modified by salts of aluminium, zinc, beryllium, and magnesium, singly or in combination." (Wilson and Batchelor, 1967a).

CHAPTER III : MODIFICATIONS TO COMPONENTS

Many attempts have been made to modify the components of silicate cements in order to overcome the physicochemical and biological deficiencies inherent in the material.

Eberly (1934) reported on the effects of the addition of dielectrics to silicate powder on the physical properties of the hardened cement. He hoped "that increasing the dielectric properties of the material would render the set cement more chemically inert." Approximately 5% by wt of white petroleum jelly was incorporated into the powder without seriously affecting its handling characteristics. "The result was most gratifying in that the addition of the jelly did not interfere with the reaction. In fact, in some specimens the reaction was accelerated, the petroleum jelly apparently acting as a catalytic agent. Color and shade were not changed and a more tooth-like appearance was given to the cement. Specimens left in the open air never dried out to a chalky white." Using electrical conductivity tests as a measure of completion of reaction of the cement, he asserted that the modified cement powder set at a rate approaching zinc phosphate cement. The pH of the setting cement was measured with a Quinhydrone electrode and compared with unmodified silicate cement and zinc phosphate cement at various times after mixing. His results appear in TABLE I.

Eberly concluded that it was desirable to reduce the early high acidity of silicate cement, two general methods being applicable:-

a. "obtaining a better balance in the chemical reaction of the powder and the liquid and;

b. introduction of neutralizing agents."

TABLE I

pH Determinations, Quinhydrone Electrode Method

Cement Washings

0.2 cc. cement liquid. Penny thick pieces.
Soaked in 0.4 cc. distilled water.
Washed in 5 cc. distilled water between readings.
60 seconds mixing time unless otherwise noted.

	Silicate cement typical of 7 kinds tested	Zinc cement	Copper cement	Silicate cement 5% petroleum jelly	Mixing time reduced to 30 seconds	3% powdered soap
	pH	pH	pH	pH	pH	pH
pH of cement liquid...	0.8	0.6	0.6	0.8	0.8	0.8
Time						
Minutes—20.....	4.2	6.0	3.0	5.1	6.3	6.0
30.....	5.4	6.3	5.3	5.7	6.4	6.8
60.....	5.5	6.3	5.7	6.0	6.4	6.8
Days — 1.....	5.5	7.1	5.2	6.2	6.4	6.9
7.....	5.3	7.1	5.2	6.2	6.5	6.9
30.....	5.5	7.3	4.8	6.2	6.5	6.9

(From Eberly, 1934)

A total of 205 modified silicate cement restorations were placed in patients attending the University of Pennsylvania, (apparently without protective bases) and after one year "there were no cases of pulpal irritation. This is very gratifying in view of the fact that some cases were selected which were very close to the pulp" (Eberly, 1934). Diagnostic methods used to determine the state of the pulp were not mentioned.

Another liquid modifier appeared in Germany in the early 1930's called Durosim. "Durosim appears to be an oily liquid and gives off an odor strongly suggestive of castor oil.

Saenger (1935) reported that there was less irritation of the pulp under silicate cement fillings when Durosim was used. Walter (1935) believes that the addition of Durosim greatly benefits the silicate cement and in fact has solved the so-called silicate cement question. Both of these reports are very optimistic about the benefits derived from the

use of Durosim" (Paffenbarger et al, 1938).

Paffenbarger et al (1938) reported that the presence of oily substances:

1. did not seriously affect the setting time.

2. reduced the seven day compressive strength by approximately 25 - 30%. They pointed out that this reduction in strength may not be of clinical significance for Class III and V type restorations.

3. affected the dimensional changes which occurred during the hardening of the cement. Shrinkages of modified cements (Durosim and petroleum jelly respectively) after one hour in air were approximately 70% and 40% less than normal cement. After approximately three months in air at 21°C and 65% R.H., there was no real difference between normal cement and cement modified with petroleum jelly; each showed shrinkage of approximately 125 microns/cm. Cement modified with Durosim under the same test showed a shrinkage of approximately 60 microns/cm.

One hour setting shrinkages in water at 37°C of the modified cements (Durosim and petroleum jelly) were approximately 25% less than the unmodified cement. After 24 hours under these conditions, the modified cements still showed less shrinkage (approximately 30%).

The difference reported for in vitro specimens (cylinders, 10 mm. long x 5 mm. diam.) produced from unmodified and modified cements were no doubt significant under the test conditions. However, Paffenbarger et al pointed out that when the dimensions of an average silicate cement restoration are considered , then the

apparent differences between modified and unmodified cements become questionable.

Perhaps, where silicate restorations may dry out to some degree (as in mouth-breathers), then the lesser shrinkage of a cement modified with Durosim may become clinically important. The advertising statement that "Durosim prevents shrinkage of the filling material after setting" is misleading. (Paffenbarger et al, 1938).

4. has no significant effect on the pH of the setting cement. This was in direct opposition to the results of Eberly (1934) who reported the pH of cement modified with 5% petrolatum to be 5.1 at 20 minutes and 6.2 at 24 hours. These high initial pH readings reported by Eberly were not substantiated by Paffenbarger et al.

5. did not change substantially the specification solubility of the particular silicate cement (K) used. The manufacturer's claim that "Durosim by essentially reducing solubility assures a constant hardness and long life of the filling" could not be established. (Paffenbarger et al, 1938).

6. tended to increase opacity - petrolatum increased the opacity considerably. Paffenbarger et al (1938) found that a cement modified with petrolatum, when exposed to a drying atmosphere, increased in opacity. This again, seems opposed to the statement made by Eberly (1934) that "specimens left in the open air never dried out to a chalky white." The quantitative data pertinent to the above assertions of Paffenbarger et al (1938) can be found in TABLE II.

TABLE II : EFFECTS OF OILY SUBSTANCES ON THE PHYSICAL PROPERTIES OF CEMENT K

Column	1	2	3	4	5	6	7	8	9	10						11
	Powder: Liquid Ratio	Time of Setting		Compressive Strength	Shrinkage on Setting			Acidity‡‡		Solubility and Disintegration###						Opacity
		21°C. (70°F.)#	37°C. (99°F.)##	One§ Week	One Hour in Air**	One Hour in Water††	24 Hours in Water††	15 Minutes	24 Hours	1	2	3	4	5	Total	One Week
	Grams‡	Minutes	Minutes	Lbs./In.²	Microns per Centimeter			pH	pH	Per Cent####						$C_{0.70}$§§
Cement K	1.4	6.0	3.5***	19,500	45	12	17	3.4	5.6	1.3	0.4	0.3	0.3	0.2	2.5	0.21
Cement K with Durosim*	1.3	5.5	3.5	14,500	13	9	12	3.5	5.2	1.1†††	0.6	0.2	0.2	0.2	2.3	0.25
Cement K with petrolatum†	1.7	6.5	4.5	13,500	28	8	13	3.5	5.6	1.7	0.8	0.4	0.3	0.2	3.4	0.33

*Durosim was added to the liquid in the ratio of 3 parts to 10 parts of liquid.
†Five per cent by weight of petrolatum was added to powder.
‡Grams of powder in 0.4 cc. of liquid which produced mix of standard testing consistency.
#Relative humidity of the air was 65 per cent.
§Specimens stored in distilled water at 37°C. (99°F.).
**At 21°C. (70°F.) with relative humidity at 65 per cent.
††At 37°C. (99°F.).
‡‡Of 25 cc. of distilled water (5.6—6.0) in which a cement disk 2 mm. thick and 20 mm. in diameter was immersed.
##Relative humidity of the air was 100 per cent.
§§Ratio of the daylight apparent reflectance of the cement with a black backing to the daylight apparent reflectance of the cement with a white backing having an apparent daylight reflectance relative to MgO of 0.70.
***Not identical with value for cement K, Table 6, column 4, because of slight variation among batches.
†††Values obtained with the Durosim cement mixture for the first week were very erratic, which indicates non-uniformity among specimens.
###At 37°C. (70°F.).
####By weight.

(From Paffenbarger et al, 1938)

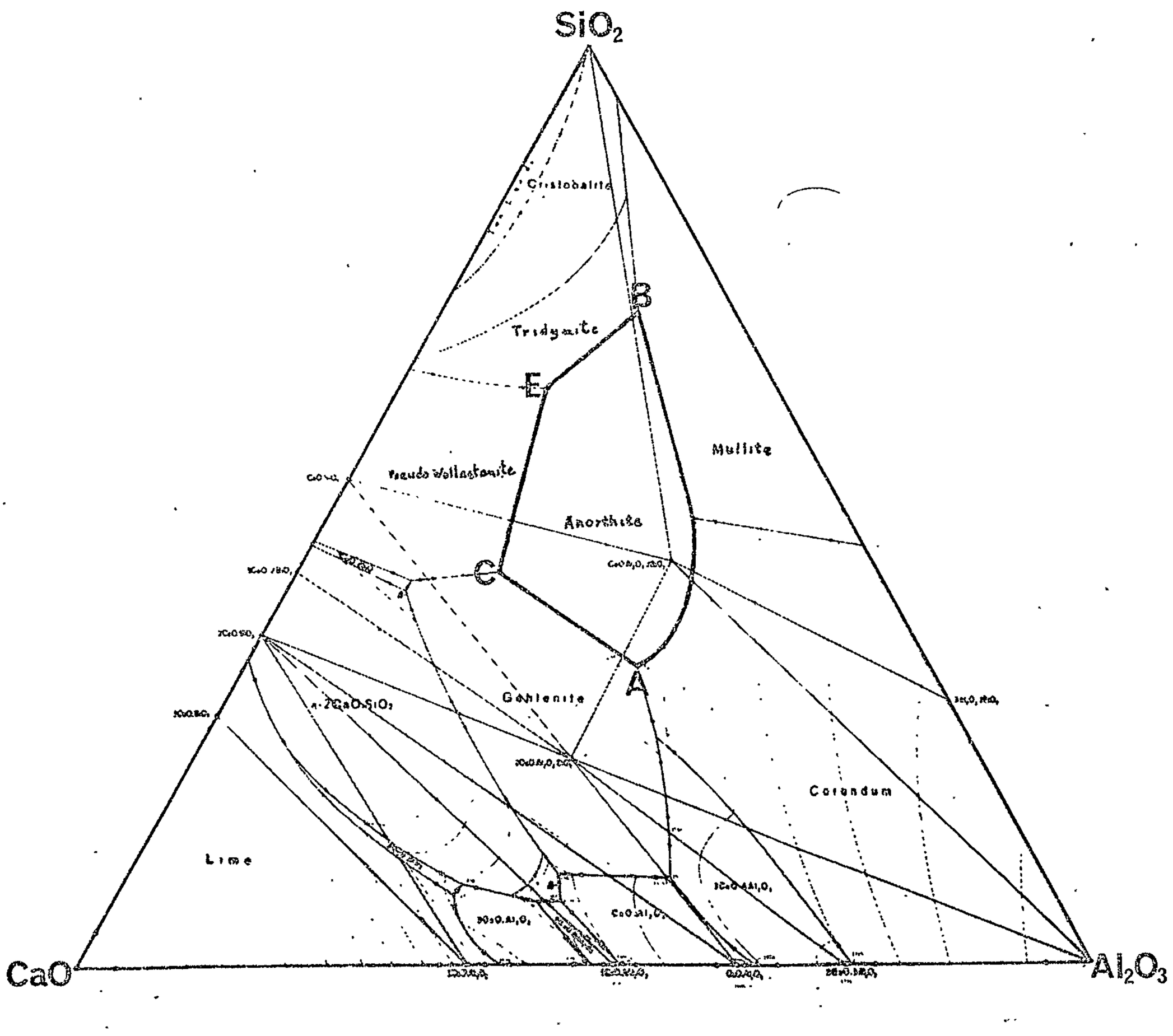
The feelings of the American National Bureau of Standards towards modifying agents were clearly stated. "The effective life of a silicate cement is sometimes short, consequently all dentists may reasonably expect to encounter a number of failures at one time or another when using them. At such times the dentist may be susceptible to appeals to try one of the modifying preparations which may have been recommended from time to time as necessary to improve the properties of silicate cements.....So far no American manufacturer has been convinced that the modifying agents advocated do materially improve the cements.....All in all one can say that the addition of petrolatum did neither definite harm nor good to the cement. Its use should certainly be confined to experimental fillings. There is always the danger that these added ingredients may break down in a few months and cause serious discolorations. The same may be said of soap and other agents which, when added to a silicate cement, are said to improve it." (Souder, W. and Paffenbarger, G.C. 1942, p. 133).

Manly et al (1951) conducted a comprehensive survey into the possibilities of improving the properties of silicate cements by altering the kind and amount of modifier in the liquid and by varying the kind and amount of flux and the proportions of usual oxides found in the powder; these being silica, alumina and lime. Twenty experimental powders were produced by fusing the basic oxides alone or with a known amount of flux between the approximate temperature range 1,300°C - 1,500°C. "Compositions for fusion without flux were selected from a composition temperature phase diagram of $CaO-SiO_2 - Al_2O_3$ system" shown in Fig. 2.

The first unfluxed powders produced represented compositions of

the four eutectics bounding the anorthite range (Points A, B, E and C in Fig. 2).

Fig. 2 : Composition temperature phase diagram of $CaO - SiO_2 - Al_2O_3$ system



(From Manly et al, 1951)

Fluxed powders were made by using ratios of CaO, Al_2O_3 and SiO_2 corresponding to the anorthite and mullite ranges fused with one of the following fluxes:- sodium carbonate, sodium fluoride, calcium fluoride, boric oxide, beryllium compounds, or metal phosphates. "The mullite

range was tested because most commercial powders have oxide ratios similar to mullite" (Manly et al, 1951). Possible metallic modifiers of the cement liquid were reduced considerably by rejecting metals which formed coloured sulphides or which were insufficiently soluble in phosphoric acid. Ions considered included Be^{2+}, Li^{+}, In^{3+}, Mg^{2+} in addition to the commonly employed Zn^{2+} and Al^{3+}.

Experimental powders were mixed with SS White Filling Porcelain liquid and those showing a setting reaction were tested for consistency using the method described in Amer. D.A. specification No. 9 to determine standard testing powder : liquid ratios. Setting time and solubility in water were determined as set out in the above specification. The seven day solubility of experimental cements in an acid solvent was also determined. The solvent used was a buffered solution of ammonium-acetate - acetic acid at pH_4. "An indication of the strength of the set cement was obtained from indentation hardness tests with a Wilson Tukon Tester using a Knoop diamond indenter" (Manly et al, 1951). Indentation tests were made on one hour old cements and after one week water solubility tests. The refractive index of some experimental powders was determined as well as the translucency of a few experimental set cements.

The results and conclusions show that: "When aluminium or zinc was used alone as a modifier, the physical properties of the cement were approximately the same as that prepared from a special control liquid and that prepared from a commercial liquid. Magnesium, indium, calcium, barium, titanium and beryllium proved to be unsuitable as single modifiers in the liquid. Barium, calcium and indium oxides could be used as comodifiers with zinc oxide without deleterious effect on the physical

properties, but there was no indication of general improvement.

Only a very narrow range of compositions containing CaO, SiO_2, and Al_2O_3 could be fused to clear glasses which would set within the proper length of time with silicate liquids. Several different compounds could be used as fluxes for increasing the range of compositions that would set. No composition was found which was appreciably superior in properties to representative commercial products and all powders tested were deficient in translucency." (Manly et al, 1951).

Brauer et al (1958) have also investigated possible modifications to silicate cement. Silanes and silicones were added to cement mixes in an attempt to reduce the water solubility. Small amounts of silicone reduced the Amer. D.A. specification "solubility and disintegration" by approximately 20%, had no effect on setting time but generally reduced the compressive strength of the set cement. Reduction in solubility was rationalized : "The added silicone apparently combines with the free silica in the mix, but does not react with the sodium to form an insoluble product".

At about this time, the Vivadent Co. (Liechtenstein) attempted to increase the strength and decrease the solubility of their product (Achatit) by the addition of glass fibres to the powder. Claims made by the manufacturer have not been substantiated. (Commonwealth Bureau of Dental Standards, 1960; Swartz et al, 1963; Phillips, 1965).

Wilson et al (1968b) have thoroughly investigated the effect of phosphoric acid modifiers on the physicomechanical properties of the cement mix and on the durability and strength of set silicate cements. They aimed to produce a cement liquid which would give the set cement optimal physical properties. "Cations suitable for use as modifiers of phosphoric

acid must (1) possess moderate solubility in phosphoric acid (2) must not form coloured sulphides (3) must be nontoxic, and (4) must be capable of retaining a vitreous form in the final cement.

To satisfy criterion 4, the cation must be capable of tetrahedral coordination; otherwise, the phosphates would crystallize. Hence, cations of fairly large charge-size ratios are required. This requirement limits the choice to such amphoteric or weakly basic metals as aluminium, beryllium, magnesium and zinc; i.e. the network dwellers of Volf."

In this study aluminium and zinc were investigated either as single liquid modifiers or in combination at various concentrations. The effect of boric acid as a comodifier was also established as Lefforge and Atteberry (1954) had reported that boric acid stabilized the solution of aluminium in phosphoric acid. The chemical composition of seventeen commercially available silicate cement liquids showed that the modifying ions most commonly employed were Zn^{2+}, Al^{3+}, and Mg^{2+} respectively. The concentration range for Zn^{2+} was 1.5% - 9.1% (by wt), whilst Al^{3+} was 1.4% - 2.5% (by wt). In most cases the modifying ions were used in combination. "The stability of a mixed zinc-aluminium dihydrogen phosphate in solution confirms the deduction of Manly et al (1951) that this enabled the concentration of the salts to be maintained at a level well below saturation. It is probably for this reason that manufacturers use liquids of the mixed type." (Wilson et al 1968b). It was noted that commercial liquids containing a phosphoric acid concentration 44.7% - 49.2% by wt produced cements which were stronger, more resistant to aqueous attack and less acid in reaction than cements formed from liquids containing higher concentrations of phosphoric acid. There was one

exception to this, a cement designated as C13; the composition of the liquid L-13 was 46.8% H_3PO_4 by wt and it contained Zn^{2+} 8.4% wt as the only modifier. Two other commercial liquids from the superior phosphoric acid concentration category were modified only with Zn^{2+}, whilst another cement from this group had a higher concentration of Zn^{2+} but was also modified with Al^{3+}. A chemical description of the powder P-13 was not stated. The cement produced (C-13) was lower in 24 hour compressive strength and was significantly less resistant to aqueous attack with respect to amount of P_2O_5 leached. See TABLE III below.

TABLE III

CHEMICAL COMPOSITION OF COMMERCIAL LIQUIDS

Liquid Material	Percent				
	PO_4	Al	Zn	Mg	Be
L-1	46.8	2.3	4.9	...	...
L-2	47.3	1.6	6.1	...	...
L-4	47.8	1.9	4.2	...	...
L-6	49.2	1.5	8.7	...	...
L-8	53.8	2.0	9.1	...	...
L-9	47.6	2.0	5.0	...	...
L-10	63.8	1.8	...	1.3	...
L-11	63.9	...	...	1.6	0.65
L-12	63.0	1.4	1.5	0.4	...
L-13	46.8	...	8.4	...	...
L-14	46.7	...	8.4	...	...
L-15	51.1	...	2.4	0.3	...
L-16	52.6	...	2.4	0.3	...
L-17	44.5	2.2	5.3	...	...
L-18	50.3	2.5	5.5	...	...
L-19	47.2	...	6.9	1.1	...
L-20	47.0	...	7.9	1.1	...

PROPERTIES OF COMMERCIAL CEMENTS

Liquid		Cement					
Designation	Phosphate Content (%)	Designation	P/L Ratio (gm/ml at D = 20.0 mm)	Compressive Strength (kg/cm^2)	Species Eluted: t/ = 0 to 7 Days (mg/gm Cement) P_2O_5	SiO_2	pH
L-17	44.7	C-17	4.1	2,550	3.03	0.99	...
L-13	46.8	C-13	3.9	1,750	9.38	0.95	4.7
L-20	47.0	C-20	3.5	3,100	1.23	1.19	...
L-19	47.2	C-19	3.5	2,480	1.39	1.72	4.9
L-2	47.3	C-2	4.0	3,100	3.20	1.20	4.7
L-4	47.8	C-4	3.9	2,600	3.27	0.93	4.8
L-6	49.2	C-6	4.1	2,570	1.74	0.92	4.8
L-8	53.8	C-8	3.3	2,100	3.73	1.62	4.3
L-12	63.0	C-12	3.6	2,270	7.89	2.62	3.5
L-11	63.9	C-11	2.7	700	38.6	4.49	3.8

(From Wilson et al, 1968b)

Nineteen experimental liquids were prepared having a phosphoric acid concentration of 49.0% by wt. "The liquid type code was P for liquids containing phosphoric acid only; PA for liquids modified with aluminium salts only; PZ for liquids modified with zinc salts only; PAZ for liquids modified with both aluminium and zinc salts; and B added to the prefixing code letters to indicate the addition of boric acid as a comodifier." Descriptions of experimental liquids are set out below in TABLE IV.

TABLE IV

COMPOSITION AND STABILITY OF MODIFIED PHOSPHORIC ACID CEMENT LIQUID

Type and Designation†	Modifiers in 49.0% H_3PO_4 Al(%)	Zn(%)	H_3BO_3(%)	Stability
Al, R>1				
PA-3	6.0	0.0	0.0	Could not be prepared.
PAB-6	6.0	0.0	2.5	Slow crystallization after 2—3 weeks.
PAB-5	6.0	0.0	5.0	Clear, glassy semisolid.
Al, R=1				
PA-1	4.5	0.0	0.0	White precipitate formed after 6—20 weeks.
PAB-1	4.5	0.0	2.0	Stable for at least 12 months.
PAB-2	4.5	0.0	2.5	Slow crystallization after 2—3 weeks.
PAB-3	4.5	0.0	5.0	Precipitation after 3 days.
Zn, R=1				
PZ-1	0.0	16.35	0.0	Could not be prepared.
PZB-2	0.0	16.35	2.5	Precipitate formed after 3 days.
PZB-1	0.0	16.35	5.0	Gradual precipitate soon after preparation.
Al, Zn, R=1				
PAZ-1	2.25	8.2	0.0	Stable for at least 12 months.
PAZ-5	1.13	12.25	0.0	Some precipitation after 24 hours.
Al. R<1				
PA-0*	2.5	0.0	0.0	Stable for at least 12 months.
Al, Zn, R<1				
PZ-0*	0.0	13.0	0.0	Borderline stability, slight precipitation after 12 weeks.
PZB-0	0.0	13.0	2.5	Stable for at least 12 months.
PZ-1	0.0	12.0	0.0	Stable for at least 12 months.
Al, Zn, R<1				
PAZ-0*	1.25	6.5	0.0	Stable for at least 12 months.
PAZ-3*	0.625	9.75	0.0	Stable for at least 12 months.
PAZ-4*	1.375	3.25	0.0	Stable for at least 12 months.

* Generic formula 13.0(*x*)% Zn, 2.5(1−x)% Al, and 47.5% PO_4.

† *R*, equivalents of total metal per mol of H_3PO_4.

(From Wilson et al, 1968b)

Eight of the experimental liquids were stable for at least a year. Of

these only two were modified with one metallic salt; a PZ having 12.0% (by wt) zinc concentration and a PA having 2.5% (by wt) aluminium concentration. If zinc and aluminium salts were used in combination, a stable PAZ liquid (PAZ-1) was produced having an aluminium concentration of 2.25% and zinc concentration of 8.2% When boric acid was used as a comodifier, the concentrations of Zn^{2+} and Al^{3+} could be increased somewhat, without jeopardizing the stability; e.g. PZB-0 13.0% Zn^{2+} 2.5% BO_3^{3-}, PAB-1 4.5% Al^{3+} 2.0% BO_3^{3-}. These concentrations of Zn^{2+} and Al^{3+} were well above those found in commercial liquids, the maximum concentrations for the respective ions found in this study for commercial liquids being 9.1% and 2.5% by wt. When the concentration of Al^{3+} and Zn^{2+} with or without BO_3^{3-} was increased above 4.5% and 13.0% respectively, the liquids produced were unstable, forming either precipitates, crystallizing slowly or being extremely viscous. Super Syntrex powder was used with the experimental liquids and the solubility and disintegration of the cements in water and buffered organic acids was determined by quantitative chemical analysis of the ions eluted in the solvent. "Phosphate P_2O_5 and silicate SiO_2 were of particular interest because they are major constituents of the powder, liquid and gel matrix of the prepared cement" (Wilson and Batchelor, 1967a).

The effect of modifying ions in the liquid on the rheology of the cement pastes formed, the setting times, and subsequent compressive strengths of the cements was also investigated. Wilson et al (1968b) concluded that "the addition of zinc or aluminium salts to phosphoric acid considerably reduces the amount of soluble material in the prepared cement. There is, however, an optimum concentration; cements

prepared from liquids saturated with metallic salts contain more soluble material than those prepared from undersaturated liquids. The use of mixed metallic salts is probably based on this fact. In liquids containing approximately equivalent amounts of metallic salts, increase in the Zn/Al ratio increases the setting time, perhaps from the reduction of free water content. Boric acid as a comodifier to stabilize cement liquids is of doubtful value.

Cements prepared from liquids modified only with aluminium were significantly more resistant to acid attack than other types. Thus, they would be expected to last longer in the mouth, as acids probably cause failure. Clinical evaluation would be valuable.

Evidence from the pH-ion elution curves indicates that metal phosphates and fluorides are important constituents of the cementing gel matrix, possibly at least partially in combination with the siliceous phase. The structure of the matrix is complex and is being investigated further, the results may suggest possible improved formulations".

Wilson, as a highly trained physical chemist, is quite pessimistic about improving the physical properties of silicate cement. Modification of present day powder and liquid components is fundamentally restricted by the chemistry of the setting reaction. The dentist requires a glassy, acid soluble powder which will form a strong, translucent cement. From the studies of Manly et al, it has been shown that there is a restricted range of calcium-aluminosilicate glasses which meet these requirements.

The solubility and disintegration of silicate cement in the mouth

is probably improved somewhat by the addition of liquid modifying ions. However, "it is certain that the dental silicate cement is a form of phosphate bonded material, where aluminium is the principal binding cation. Dissolution of such a material in both acidic and citrate media is to be expected and must be regarded as an inherent defect which stems from the fundamental chemistry of the system." (Wilson 1969a).

CHAPTER IV : CHEMISTRY OF THE SETTING REACTION

Although there is a wealth of literature surrounding the development and use of silicate cements in dentistry, only a few studies have been carried out to elucidate the chemistry of the setting reaction.

1. TRADITIONAL CONCEPTS

The basis of "traditional" ideas on the chemistry of the setting reacton seems to be found in papers published by two physical chemists, Crowell (1927) and Hurd (1938).

One of the first workers to publish a theory on the subject was Charles Voelker (1916). He studied the chemical composition of the powder and liquid of five commercial silicate cements which he asserted "as being used now almost exclusively in this country" (U.S.A.) and found that all powders contained large amounts of alumina as well as silica. Thus, "they might with equal propriety be named aluminate cements." Voelker reports that Abraham (1912) "suggests as a better name for the silicate cements the term aluminium-phosphate cements, as describing them more satisfactorily from a chemical standpoint after the phosphates have been precipitated by the mixing of the powder and liquid, and the mass has set."

Perhaps Abraham was suggesting that the set cement was a phosphate-bonded material. For Voelker, the chemistry of the setting reaction was far from mysterious; "we may state as the consensus of opinion of those who have given the silicates detailed study, both here and abroad, that a silicate mix contains calcium and aluminium or beryllium phosphates admixed with silicates, aluminates, fluorids, and other compounds, and that

chemically they are allied to the older type of oxyphosphate cements, especially the zinc oxyphosphates. In the latter we have a reaction analogous to the following, assuming for the sake of simplicity that the powder is only zinc oxid, and the liquid unmodified ortho-phosphoric acid:

$4ZnO + 2H_3PO_4 = Zn_3(PO_4)_2.ZnO + 3H_2O.$

In other words, the older types of oxyphosphate cements are chemico-mechanical mixtures of zinc phosphate and zinc oxid, no true chemical compounds known as oxyphosphates and expressible by means of exact chemical formulae being recognized in chemical terminology." Voelker then reported a communication with Steenbock who described how he arrived at the chemical composition of the powder. The aim was to find "compounds which had to be translucent, easily decomposable by the cement acids, and had to furnish insoluble translucent decomposition products." He found that the silicates proved suitable. "Instead of the simple oxids we therefore combined silicic acid compounds of the oxids with the old cement liquids - that is to say, we put up the older cements in a new form. I was therefore not a little astonished when everybody fell to imagining that there must be some secret behind the new cements; yet we have done nothing more than to conduct a well-known process along lines which brought about a definite physical effect. Hence the silicate cements must be described, as regards their chemistry, as identical with the older oxyphosphate cements, with the sole difference that in the oxyphosphate cements the fixing of the acid takes place rather more quickly initially, and that silicate cements require close observance of the mixing ratio. The hardened silicate cements are mixtures of phosphates, silicates, and silicic acid," (Voelker, 1916).

This explanation was not fully accepted by later workers who suspected that the setting reaction of silicate cement could not be related simply to that of zinc phosphate cement. (Doubleday, 1926; Crowell, 1927). "In the aluminium-silicate fillings a much more complex reaction occurs and the bases are relatively inert, the resulting chemical reaction is much less complete and acid salts are present in larger proportions. The formation of a silicate cement takes place in two main stages. The first is a primary setting occupying about ten minutes and probably largely due to the formation of phosphates of aluminium; the hydration of the silicates is a much slower process and is not completed for weeks." (Doubleday, 1926).

Crowell (1927) in an extensive article, distinguished clearly between the chemical reactions taking place in the setting of zinc phosphate cement and silicate cement. He drew attention to the crystalline nature of set zinc phosphate cement whilst set silicate cements were "gelatinous or collodial." Crowell stated that the "powders are complex acid-soluble glasses. Their constitution is unknown. When acted on by acids, silicic acid is liberated, but the base to which it was attached in the glass is difficult to determine. In our opinion, it is alumina. When a large amount of alumina is present, the powder is quick setting. Reducing the quantity retards the set." He pointed out that silicate cements set by gelation of silicic acid and that "most of the good and bad properties of silicate cement are due to silicic acid." Hence, the "traditional" concept that setting of dental silicate cement results from polymerization of monosilicic acid to polysilicic acid gel and that the set cement is of the silica-gel bonded type.

Ray (1934) reported that "when the liquid and powder are mixed, the acid of the liquid attacks a part of the powder, forming colloidal aluminium phosphate and a colloidal silicic acid.....After a certain amount of the silicic acid has been formed and the acidity of the liquid has decreased, the silicic acid gels, or partly sets."

Matthews (1935) using acid/base theory, explained why one would expect the set silicate cement to be more acidic than zinc phosphate cement. He considered the setting reaction of zinc phosphate cement to be:-

"Zinc oxide + phosphoric acid = zinc phosphates + water

i.e. base + acid = salt

whereas, in the case of the silicate cement, we have:-

Aluminium silicate + phosphoric acid = silicic acid + aluminium phosphate

i.e. salt + acid = weaker acid + salt

Mamlet (1936) spoke of the set cement containing both amorphous and crystalline phases in the matrix. "The completed filling when fully hardened consists of undecomposed particles of the fused powder embedded in a matrix of colloidal silicic acid in which aluminium and calcium phosphates crystallize in a more, or less, vitreous form."

Hurd (1938) reviewed and discussed in a general way the chemistry of silicic acid gels. He showed that silicic acid gels result from sols of hydrated silica under a wide range of conditions. Silica concentrations should be above 0.5% and sols undergo gelation more readily in an acid environment. "Certain conditions, such as concentration of silica, temperature, hydrogen ion concentration, and concentration of other substances, will be found to govern the time required for gelation or "time of set", as it is called, but it is safe to say that any sol

containing over 2% SiO_2 will set eventually to a gel, unless it is strongly alkaline." Data concerning the $Si(OH)_4$ molecule strongly suggested that it underwent polymerization, condensation or coalesced to form large chains with the lapse of time. Hurd (1938) quoted a number of investigators who found that the apparent molecular wt of $Si(OH)_4$ increased rapidly with time. Other investigators have used albumin to test the silicic acid formed. When first formed $Si(OH)_4$ does not coagulate albumin, a characteristic of simple molecules; however, on standing, the test becomes positive, indicating the increase in molecular wt of $Si(OH)_4$. "When first formed, considerable silicic acid passes easily with the electrolytes through the membranes used for dialysis. With the lapse of time, all of the silicic acid becomes unable to pass through the membrane." (Hurd 1938). This fact, together with the above observations, indicated that when $Si(OH)_4$ was first formed, it consisted of simple molecules which polymerized into large groups upon standing.

Hurd described and discussed a number of theories of gel structure; he favoured the "polysilicic acid fibrillar theory." "This theory suggests that a silicic acid gel consists of an interlaced fibrillar or brush heap structure consisting of very large polysilicic acid molecules, the spaces being filled by liquid. The structure is produced by condensation, water being split out between two simpler silicic acid molecules to form a more complex structure." The formation of more and more complex structures ultimately caused the complete immobilization of the fluid. The gel had now set. "This interconnected branched polysilicic acid structure is almost certainly heavily hydrated. It holds the fluid in its structure by capillarity. This structure explains, better than any

other, the properties of silicic acid gels."

A mechanism of condensation of silicic acid can be put forward if it is assumed that:

"(1) a monosilicic acid is formed in the first step of the process, or perhaps more correctly, silicon hydroxide.

(2) this acid, or hydroxide is amphoteric giving either hydrogen or hydroxyl ions.

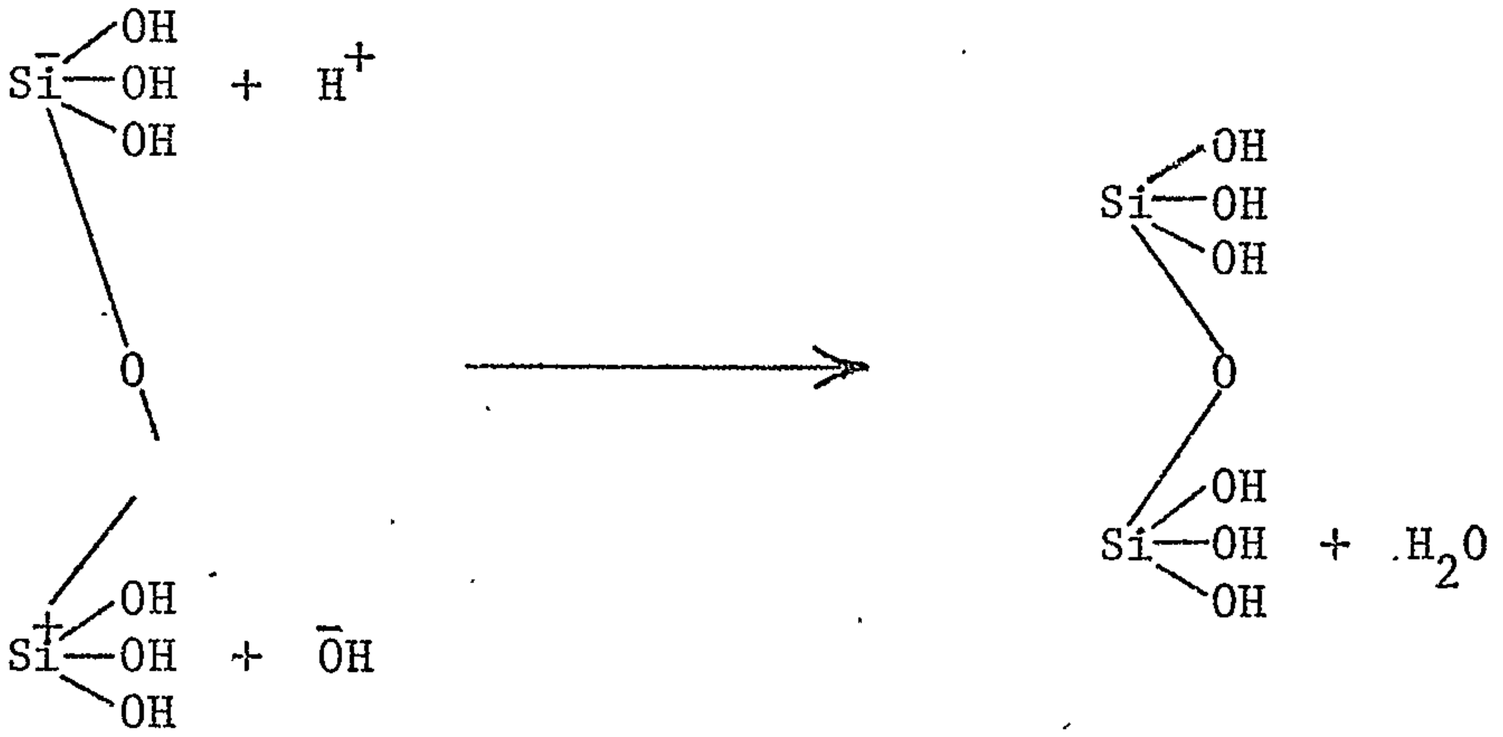
i.e. $\bar{O}H + Si(OH)_3^+ \longleftarrow Si(OH)_4 \longrightarrow SiO(OH)_3^- + H^+$

in acid solution ← favoured → in basic solution

(3) condensation occurs when the positive and negative ions containing the silicon come into contact.

(4) water remains combined, or adsorbed, in the structure.

The first three assumptions can be fairly well established by laboratory observations. Thus, condensation of monosilicic acid to a polysilicic acid gel can be described as :



"

(Hurd, 1938)

Hurd did not present much evidence concerning the role of water in the complex gel structure. He mentioned Schwarz (1926) who claimed that there were two different kinds of water in the gel - free water and bound water. This bound water is chemically combined whilst the free water presumably

is held in the structure simply by capillarity. "While it is perhaps not possible to prove that water remains either chemically combined or strongly adsorbed by the filamentous structure, the facts point strongly towards such a condition. Van Bemmelen's observation (1908) that from 0.5 to 1.0 moles of water per mole of silica remained very strongly attached to the silica and could be removed only by vigorous heating, is significant."

Dental materialists drew heavily upon these generalizations and applied them directly to dental silicate cement. Thus, from Hurd's theories of gel structure and mechanisms of condensation, the concept that dental silicate cement was basically a silica gel bonded material has been accepted until very recent times.

The comprehensive report by Paffenbarger et al (1938), gave a detailed physico-chemical analysis of representative powders and liquids; however, no mention was made of the possible chemical reactions taking place during the setting of silicate cement. Souder and Schoonover (1939) suggested that "reaction is assumed to be colloidal with molecular reactions similar to those in the setting of silica gel." The silica-gel bonded nature of set dental silicate cement is quoted or assumed by Souder and Paffenbarger (1942, p. 111); Paffenbarger and Stanford (1958); Skinner and Phillips (1967, p. 492); Peyton et al (1968, p. 434); and Phillips et al (1969, p. 58).

2. NEW CONCEPTS

During the years 1967-1971, there appeared in the Journal of Dental Research, a series of fourteen articles written by A.D. Wilson, a British government chemist and his associates. Wilson's work was initiated by the variation in clinical results produced by the wide use of silicate cement within the National Health Service. It was therefore of economic importance to define clearly the factors affecting the significant clinical properties of the material. (Wilson and Batchelor, 1967a). Using sophisticated physical and chemical techniques, Wilson et al were able to elucidate the chemistry of erosion, factors influencing the durability of the cement, and the complex chemistry of the setting reaction. Many parameters thought to affect cement durability were also studied.

From the outset, Wilson suspected that dental silicate cement was not simply a silica-gel bonded material as was the traditional concept. "The high compressive strength of the dental silicate cement - 3000 Kg/sq.cm. can be attained - compared with that of known silica-gel bonded cements (150-270 Kg/sq.cm.) and its observed tendency to dissolve in acidic and citrate media is at variance with this model." (Wilson, 1969a).

From ion elution studies (Wilson and Batchelor 1967a, b; 1968a; Wilson et al 1968b), a general theory regarding the chemistry of the cementing reaction was evolved. The acid-base nature of the reaction was hypothesized from observations of ions eluted in water. "A considerable amount of material is eluted from dental silicate cements in the 24 hours after contact between the cement and solution. The chemical composition of this eluate bears little relationship to that of the parent cement and may be regarded as a solution of the mixed sodium salts of dihydrogen

phosphate and complex fluorides. Sodium dihydrogen phosphate is the soluble product of a neutralization reaction between powder and liquid..... The leaching pattern of phosphate from cements, in which the amount eluted is initially considerable and eventually drops to trace proportions, suggests that the process is a simple washing out of soluble salts from the cement gel. The amount of phosphate salt varies considerably between cements; it probably depends on the degree of attack by the liquid on the powder and is greatest when the relative amount of liquid used in cement preparation is high and its phosphate concentration is high. Since the amount of phosphate salt eluted is related to clinical performance, initial conditions must be of considerable importance. The difference between cements becomes less as the age increases.

The leaching pattern of silica is entirely different from that of phosphate; decrease in the amount eluted as the cement ages is much less and suggests that the process of solution is from slow peptization of silica from the cement gel.

The amounts of aluminium, zinc, and calcium eluted are small and elution rapidly decreases to negligible proportions in the cements.

The elution pattern of sodium and fluoride is generally similar to that of phosphate and may also be ascribed to the simple washing out of soluble salts. However, even when the cement has aged three months, these ions are still being eluted and may come from unreacted powder rather than the gel matrix. The continuing elution of fluoride no doubt accounts for the anticariogenic properties of these cements." (Wilson and Batchelor, 1967a).

The observations of Wilson et al (1968a and b) on the effects of

acidic, alkaline and complexing medias on cement durability also support the hypothesis that phosphates are important reaction products found in the cement matrix. The test medias used were various compounds and substances similar to those that might be found in the mouth. Using an acid lactate buffer (pH = 4.0) it was noted that there was a significant increase in the amounts of silicate and phosphate leached. "Not only was the initial rate of solution during the first 24 hours increased but, more important from the clinical aspect, the rate of solution of silicate showed little decrease after several weeks. This was in contrast to the performance in water (pH = 5.7), in which, after several weeks, the solution of phosphate was negligible and that of silicate was slight" (Wilson and Batchelor, 1968a).

Thus, there are two distinct and chemically different types of erosion or disintegration of dental silicate cement; a simple washing out of water soluble reaction products and a definite chemical attack on the cement. The first process is one which can be controlled to a large extent by the operator and will be discussed in a later section. The chemical attack, particularly by acidic and complexing agents "strongly suggests that the lifetime of a restoration is greatly influenced by environmental factors."

The results of these studies (Wilson and Batchelor, 1968a) are feasible, based on the assumption that precipitated phosphates form an important constituent of the cementing matrix. "Aluminium, zinc, and calcium phosphate are soluble in acid solution, and both aluminium and zinc phosphate are soluble in alkaline conditions. Citrate forms soluble complexes with both these metals and phosphate. Thus, from basic chemical

considerations, the observed drastic effects of acids and citrate on dental silicate cements are to be expected and it can be seen that there are fundamental limitations on improving this type of material. The elution of silicate ion together with phosphate ion in acid solution suggests that these may be chemically linked in the gel matrix, because silica gel is not normally soluble in acid." (Wilson and Batchelor, 1968a).

From these first ion elution studies, results could only be explained in terms of phosphate chemistry. A model for the cementing reaction was formed from these studies, electrical conductivity observations and data from infrared absorption spectroscopy of setting pastes. The model is complex but seems basically irrefutable in the light of corroborating evidence from observations and data collected about

(i) alternative liquid cement formers,

(ii) the acid-base aspect of the setting reaction,

(iii) wet chemical techniques used to study the initial stages of decomposition of the powder, and

(iv) ion extraction data from the setting cement.

The hypothesis is further supported by exhaustive studies of the fully hardened cement using optical and electron microscopy, electron probe microanalysis, infrared spectroscopy and X-ray diffraction analysis.

(i) Initial Rapid Phase - Formation of the Paste

"The cement-forming reaction may be divided into two overlapping stages : an initial phase, where most of the extractable ions are rapidly extracted from the powder by the liquid, and a subsequent more prolonged phase, where the pH rises with comparatively little further powder/liquid interaction. This causes insoluble metal phosphate to precipitate and the

cement to set, the final pH of the system, about 5, being in the region where phosphates of aluminium, calcium, and zinc are insoluble." (Kent and Wilson, 1969).

The initial reactions within the paste have been studied extensively by Wilson and Kent (1970a) using a wet chemical technique. "The present method was designed to obtain information concerning the early stages of the reaction. Since this process is rapid, allowing no time for crushing and extraction of ions from the cement, this study was carried out by reacting the powder and liquid in a dilute aqueous phase. Although this model, where the reaction is carried out in excess water, is considerably different from the actual cement, it represents the only feasible method of study."

This study defined the initial stages of decomposition of the powder and Wilson and Kent (1970a) suggested a possible mechanism of glass lattice degradation.

"The initial stage of the cement-forming reaction is therefore an extraction of cations, fluoride ions, and orthosilicic acid from the glass powder, accompanied by an increase in the concentration of $H_2PO_4^-$ ions (from infrared spectrum studies, 1968d) and pH.

The rapid extraction of cations accompanied by a rise of pH in the system shows that the initial stage of cement formation is a type of acid-base reaction, with the liquid clearly acting as the acid, and the powder, which is amphoteric, as the base. The extraction of soluble ions from the powder is therefore the result of an electrophilic attack by the liquid on the powder in the early stages of the reaction. It is of interest to establish the mechanism of attack on the glass.

Dental silicate powders are opal glasses containing calcium fluoride as the main opacifier. For the purpose of this part of the discussion, the main glass phase can be considered as essentially an oxide glass, although some fluoride will substitute for oxygen anions. Chemical analysis shows that these glasses are aluminosilicates where the ratio of Al/Si is approximately 1:1. Since aluminium as well as silicon can act as a glass-network-former, the lattice will be an aluminosilicate structure. The extraction of aluminium ions and orthosilicic acid, reported in this and previous papers (1967a and b), is therefore evidence that the glass lattice has been decomposed. Weyl and Marboe (1962) consider an attack on a glass by aqueous reagents a process of hydrolysis initiated by proton penetration into the oxygen anion accompanied by the addition of a hydroxyl ion. Weyl (1953) has suggested that anions predominate at the glass surface, and Livey and Murray (1956) considered that this results from retraction of cations of high field strength.

The tendency for this process to occur depends on the acidity of the solution and the "polarizability" of the anion. Polarizability is the capacity of the electron cloud of an anion to be "tightened" by a cation. It has been related to basicity of O^{2-} anions.

In an $Si^{4+} - O^{2-} - Si^{4+}$ linkage the electron cloud of the O^{2-} anion is tightened by the strong field of the Si^{4+} cations, has little residual polarizability, and is not, therefore, appreciably attacked by electrophilic reagents, i.e. acids. When one of the Si^{4+} ions is replaced by a cation of weaker field strength, for example Al^{3+}, the polarizability of the O^{2-} anion is increased and it becomes more basic, and is hence more susceptible to electrophilic attack.

The aluminosilicate lattice carries a negative charge, since some Si^{4+} are replaced by Al^{3+}, and is more basic and more susceptible to acid attack than the electrically neutral silica lattice. Decomposition of an aluminosilicate lattice at $Si^{4+} - O^{2-} - Al^{3+}$ links, which for the reasons outlined contain more polarizable and more basic O^{2-} anions, yields orthosilicic acid and aluminium ions. It is known that some naturally occurring aluminosilicate minerals break down in the presence of mineral acids and form gels, which suggests that they may be models for dental silicate glass. Breakdown of the lattice is probably preceded and accompanied by a kind of ion exchange process between sodium ions in the interstices of the glass lattice and protons in the attacking solution with the sodium ions diffusing through the solid to the surface. The mechanism is that proposed by Douglas and Isard (1949) for glass surfaces, and has been described as a form of electrophilic attack by Budd (1961). De Vore (1956), studying the decomposition of naturally occurring aluminosilicates, considers that exchange of Na^{+} by H^{+} has little effect on lattice breakdown. However, there must be some slight disruption for, as Weyl and Marboe (1967) pointed out, simple ion exchange between sodium and protons is unlikely to occur since the latter are hydrated and cannot occupy the same sites as Na^{+} ions." (Wilson and Kent, 1970a).

(ii) Subsequent Prolonged Phase - Precipitation Hardening of the Paste

The British, Australian, American and F.D.I. specifications for silicate cement determine "Time of Setting" using a Gillmore needle; acceptable setting times ranging from a minimum of three minutes to a maximum of eight minutes after the start of mixing. "The cement shall be deemed to have set when the needle fails to leave a perceptible

circular indentation on the surface of the specimen" (Australian Standard Specification for Dental Silicate Cement No. T.8 - 1953, Appendix B, p.5).

This has led to a "set" cement being arbitrarily defined as a paste system in which a rapid precipitation of metal phosphates and fluorides and a polymerization of silicic acid to form an aluminosilica gel have occurred simultaneously, followed by sufficient hardening of the complex gel matrix to resist deformation by the Gillmore needle. In the transition from paste to hard cement, X-ray diffraction analysis and electrical conductivity studies indicated that "the structure of the set cement does not differ greatly from that of the unset paste.....

Changes in electrical conductivity provide a sensitive method of determining the course of the cement hardening process and give direct evidence of a slow reaction that continues for several weeks. Results are consistent with an acid-base reaction that leads to precipitation of insoluble salts. Water is a critical rate-controlling factor, possibly because these salts are hydrated. There are no discontinuities at the setting time; therefore, the parameter cannot be measured by this technique. Considerable residual conductivity at this point indicates that a cement is only partially reacted at the time of setting." (Wilson and Kent, 1968c).

Data from infra-red absorption spectroscopy studies by Wilson and Mesley (1968d) added further weight to the assumptions of Wilson et al (1967a, b; 1968a, b) regarding the chemistry of the cementing reaction in dental silicate cement.

"From the observations of Norman et al (1966a and b) on pH changes, and of Wilson and Kent (1968c) on electrical conductivity changes, it may

be inferred that both an acid-base reaction and a precipitation reaction take place during cement hardening. The studies made by Wilson et al (1967a, b; 1968a, b) on the leaching of ions from dental silicate cements under various conditions of pH, suggest that the cementing matrix is a complex metal fluoro-silico-aluminophosphate gel." (Wilson and Mesley, 1968d).

The cementing reaction was studied using Super Syntrex powder mixed with unmodified orthophosphoric acid and liquids modified singly with aluminium and zinc salts. The respective liquids were designated "P-O (49% H_3PO_4), PA-O (2.5% Al, 49% H_3PO_4) and PZ-O (13.0% Zn, 49% H_3PO_4)" (Wilson and Mesley, 1968d). The infrared spectrums of P-O and PA-O liquids were essentially the same and had similar absorption maximums. However, the spectrum of PZ-O liquid was completely different. Wilson and Mesley indicated that in P-O and PA-O liquids, the orthophosphoric acid was basically undissociated. They presumed that the aluminium in PA-O had formed an aluminium-phosphate complex and that PZ-O liquid gave a different spectrum because zinc was present in simple solution. There was also strong evidence of increased dissociation of H_3PO_4 to $H_2PO_4^-$ ions.

"For reaction studies, cements were prepared at 20°C. A low powder:liquid (P/L) ratio of 2.0 gm/ml. was used to slow down the progress of the cement reaction so that changes in the infrared spectrum could be recorded. (The above P/L ratio can be expressed as 0.8 gms/0.40 mls. This would give a fluid mix, the normal clinical consistency for this material being approximately 1.5 gms/0.40 mls.) This is a valid technique, for even with such a low P/L ratio there is sufficient powder for all liquid to be utilized so that the reaction goes to completion." (Wilson

and Mesley, 1968d).

From observations made on setting pastes; "It may thus be inferred that the initial reaction on mixing is an electrophilic attack on active centres in the aluminosilicate glass, from which silicic acid, cations, and $H_2PO_4^-$ ions are released. The resulting silicic acid then polymerizes to form a silica gel matrix (in which some Si atoms are probably replaced by Al). During the subsequent hardening phase, the ionic dihydrogen phosphate undergoes further reaction to form covalent aluminium phosphate (sometimes containing a proportion of zinc), which can readily be incorporated into the silica or aluminosilica gel matrix and has the effect of bonding it together. At set, some $H_2PO_4^-$ ions remain and the subsequent hardening of the cement is associated with its further reaction.....The final gel is a form of aluminosilicophosphate, in which P-O-P and Si-O-P bonds are excluded." (Wilson and Mesley, 1968d).

Wilson examined a number of possible alternatives to orthophosphoric acid and established significant rules for the chemical composition of cement-forming liquids. Liquids capable of producing a cementing reaction with a conventional silicate cement powder (e.g. Super Syntrex) must have:-

1. an acidic function
2. chemical groupings capable of forming complexes with trivalent and divalent cations (Wilson, 1968e).

To which could possibly be added

3. be in aqueous solution.

Important conclusions were drawn from comparisons of the infrared spectrums of cements and nonsetting pastes formed from citric, tartaric,

tannic, acetic and hydrochloric acids.

"The transmission infrared spectrums of cements formed from tartaric, citric and tannic acids contained bands in the regions of 6.05 to 6.20 microns and 7.15 to 7.20 microns. These bands are attributable to $C0\bar{0}$, the carboxylate ion, evidence that is consistent with chelate formation. Changes recorded in the ATR (attenuated total reflectance) infrared spectrums of the setting tartaric acid cement showed that the reaction was rapid; the C = 0 band at 5.9 microns, from free carboxylic acid, virtually disappeared within three minutes of mixing. This period corresponded to the setting time of this cement and strongly suggests that setting results from chelate formation.

The results show that the acid anion plays an important role in cement formation and may be the bonding agent, an inference further substantiated by the effect of water on these cements. Citric acid, which forms a soluble complex with calcium or aluminium, yields a cement that rapidly and completely disintegrates on contact with water. In contrast, tartaric and tannic acids, which form insoluble or barely soluble compounds with calcium and aluminium, yield cements that disintegrate only slightly on contact with water. Thus, it must be concluded that the anion is, at least in the early hardening stages, an important bonding agent. This conclusion is in agreement with theories previously advanced for conventional silicate cement, which suggest that the character of that cement depends on the acid anion phosphate.....

The band at 9.5 microns, found in the infrared spectrums of all cements and nonsetting pastes examined, has been assigned to silica gel, possibly with some aluminium replacing silica, by Wilson and Mesley

(1968d). Hence, silica gel must be considered a constituent of the cementing matrix. Previously, the theory had been advanced that silica gel is responsible for the setting of conventional silicate cement. However, with these alternative cements, the view advanced here is that the initial setting is from formation of a metal chelate, silica gel supplementing the bond as the cements age. If the initial setting of these cements was from silica gel, then all pastes in which the formation of silica gel was observed would be expected to set. This was not observed, because both hydrochloric and acetic acid formed non-setting pastes that contained silica gel. The presence of a continuous silica gel is also to be discounted, because these alternative cements disintegrate (as do conventional silicates) in acid and sometimes in water. Such behaviour is not consistent with the chemistry of silica gel. The great variation in the properties of the cement pastes when using different acids in aqueous solution strongly suggests that the character of the cement depends on the variable character of the metal chelate and not on silica gel, which is common to all.

The exact nature and function of the silica gel cannot be exactly ascertained. Most probably, some of the silicon is replaced by aluminium, forming an aluminosilicate gel. There is evidence that substitution of aluminium for silicon occurs at the surface of the silica micelle at tetrahedral sites. If such a structure is formed, the surface aluminium could be chelated readily to complexing agents, so binding the whole structure together. This might account for the absence of crystallinity in these amorphous cements, in which the siliceous gel imposes disorder on the whole matrix. The superior strength of the phosphate-bonded cements,

and to a lesser extent the fluo-borate cements, may be attributed to geometric similarities in the basic structural units; aluminium, silicon, and phosphorus are all capable of tetrahedral co-ordination toward oxygen." (Wilson, 1968e).

The hypothesis that some aluminium substituted for silicon into tetrahedral sites at the surface forming an aluminosilica gel was substantiated in electron probe microanalysis of a fully set coarse-particle cement. (Kent et al, 1970). An explanation of the bonding of the complex phosphatic matrix to the aluminosilica gel, (which represents glass lattice disruption a few micrometers thick on the surface of the original powder particles), was suggested. "The absorption of phosphate as $H_2PO_4^-$ ions on aluminosilica gel has been reported. A similar reaction may occur during the cement-forming process, rather than a simple phosphate precipitation. The mechanism of phosphate adsorption has been described as one of hydroxyl-phosphate exchange and has been observed in the pH range 3.0 to 8.0 with basic aluminium phosphate being formed. According to Shishniashvili (1956), maximum adsorption occurs at pH3, at which level phosphate occurs mainly as $H_2PO_4^-$. Scarseth (1935) considered that the phosphate became bonded to aluminium atoms at the aluminosilica surface, forming phospho-aluminosilicates." (Wilson and Kent, 1970b). Amorphous aluminium phosphate has been identified in infrared studies of the setting paste (Wilson and Mesley, 1968d). It is probable that zinc also forms complex insoluble phosphates in the matrix.

Simultaneously in the paste, aluminosilica gel polymerizes on the surface of the glass powder. Its presence, together with the colloidal phosphate, is positive evidence of lattice disruption.

As mentioned previously, physicochemical examination of dental silicate cement powders showed them to be powdered fluorine-containing alumino-silicate glasses, where the F : Si ratio was higher than any other type of opal glass recorded. It is probable that fluorine exists as a dispersed fluorite (CaF_2) phase within the glass, giving rise to the typical opacity observed. (Wilson, 1969a). In hardened dental silicate cements, Wilson et al have strongly inferred the existence of fluorine in the gel matrix as precipitated complex fluorides or fluorophosphate salts. (Wilson and Batchelor, 1967a; Wilson et al, 1968b; Kent and Wilson, 1969; and Wilson and Kent, 1970a and b). The presence of fluorine as a microcrystallite fluorite phase in the gel matrix of the fully hardened cement has been substantiated by Wilson using X-ray diffraction analysis and observing polished surfaces optically under crossed polarisers. (Wilson, 1969a).

The role of water and pH, as critical rate-controlling factors in the chemistry of the cementing reaction of dental silicate cement, will be discussed in the following section.

(iii) Effect of Liquid and Powder Parameters on the Chemistry of the Cementing Reaction

Liquid Parameters

I H_3PO_4 : H_2O Ratio

Water is an essential component of silicate cement liquids since non-aqueous solutions of phosphoric acid when mixed with a conventional silicate powder (e.g. Super Syntrex) do not form cements. (Wilson, 1968e). "Water is required to act as a solvent base for the setting reaction, to hydrate protons and to be available for the formation of cementing hydrates. Hence a deficiency of water results in an arrestment of the reaction, and

the acidity of the cement remains high." (Wilson et al 1970c).

The rate controlling effect of water concentration of the liquid on the cementing reaction has been known for a long time. Worner and Docking (1958) have published quantitative data on this subject. Precipitation of hydrated phosphates and fluorides will progressively remove water from the system, and a stage will be reached when insufficient water remains for the acid-base reaction to continue. This phenomenon was observed by Kent and Wilson during studies of apparent pH (pHβ) of a young, partially hardened, uncertified dental silicate cement. (Terralux Ultra, Zahn-Porzellan, K.G. Hamburg, Germany). When the young cement was crushed and mixed with a minimum amount of water, the apparent pH dropped sharply (to approximately 2.5) and then began to steadily rise. "Thus, when a cement is prepared from a liquid of high phosphoric content (i.e. low water content), the reaction is arrested while still strongly acid, presumably because of lack of water; when water is added after crushing, thereaction proceeds once again." (Kent and Wilson, 1969).

The pH dependent nature of the cementing reaction is related to the conditions (pH) in the paste system which initiate precipitation of phosphate and fluoride salts.

"Rate of increase of pH is not a direct indication of the rate of interaction between powder and liquid. Because of buffering action, pH changes in the region of pK_1 (=2.1) are indicative of considerable interaction between powder and liquid. In contrast, in the region $pK_1 + pK_2$ (= 4.7), large pH changes result from comparatively small interactions.....

Because the major fraction of ions available for cement formation are released prior to set, subsequent increase in pH causing precipitation

may be regarded as a major rate-controlling parameter in the setting and hardening reaction. These final increases in pH are the result of comparatively minor additional powder/liquid interaction, results explicable in terms of the phosphoric acid neutralization curve." (Kent and Wilson, 1969). These statements are substantiated by considering the Henderson-Hasselbach equations involving the first and second dissociation constants (pK_1 and pK_2) of phosphoric acid. (Wilson and Kent, 1970a).

The H_3PO_4 : H_2O ratio in the liquid has considerable effect on cement properties. Its relationship to "setting time" of paste systems is evident; the rate of the cementing reaction increases with increased H_2O concentration in the cement liquid; the converse is also true. Precautionary steps to maintain the H_3PO_4 : H_2O balance established by the manufacturer will be discussed in Part B. Wilson et al (1970c) also explain observed changes in compressive strength and disintegration in aqueous and acid media in the fully hardened cement in terms of the effects of H_3PO_4 : H_2O ratio of the cement liquid on the chemistry of the cementing reaction.

II Metallic Modifying Ions

The effect of the typical metallic modifying ions, Al^{3+} and Zn^{2+} found in most silicate cement liquids, on the chemistry of the cementing reaction, has been reported (Wilson and Kent, 1970a). It was shown that when powder and liquid are mixed to form a paste, there was attack by hydrated protons on "active centres" in the glass. This gave rise to rapid extraction of cations, fluoride ions and orthosilicic acid from the original powder. "The presence of modifiers considerably reduces the amount

of attack on the powder by the liquid.....Clearly, with modified liquids, since metal ions are already present in the liquid phase, less has to be extracted from the powder in order to achieve a sufficiently high concentration and pH to cause precipitation."

Powder Parameters

I Powder Particle Size

Particle size analysis of fourteen commercial dental silicate cements available in Britain showed that they were all finely ground. The median particle size range was 6.6 - 15.5 microns. (Wilson and Batchelor, 1967a). The effect of powder particle size on the cementing reaction is well known. The surface area of the particle exposed to the cement liquid has a direct relation to the rate of the reaction. (Crowell, 1927; Swanson, 1936; and Charbeneau, 1961). "As the reaction proceeds and the finer particles dissolve, the specific surface area of the powder and the reaction rate decrease." (Wilson and Batchelor, 1967b). Kent et al (1970) found that the rate of reaction was greatly decreased when a coarse-particle cement (Super Syntrex, 45 - 105 microns) was reacted with 49% w/w H_3PO_4. The setting time for this cement was one to two days.

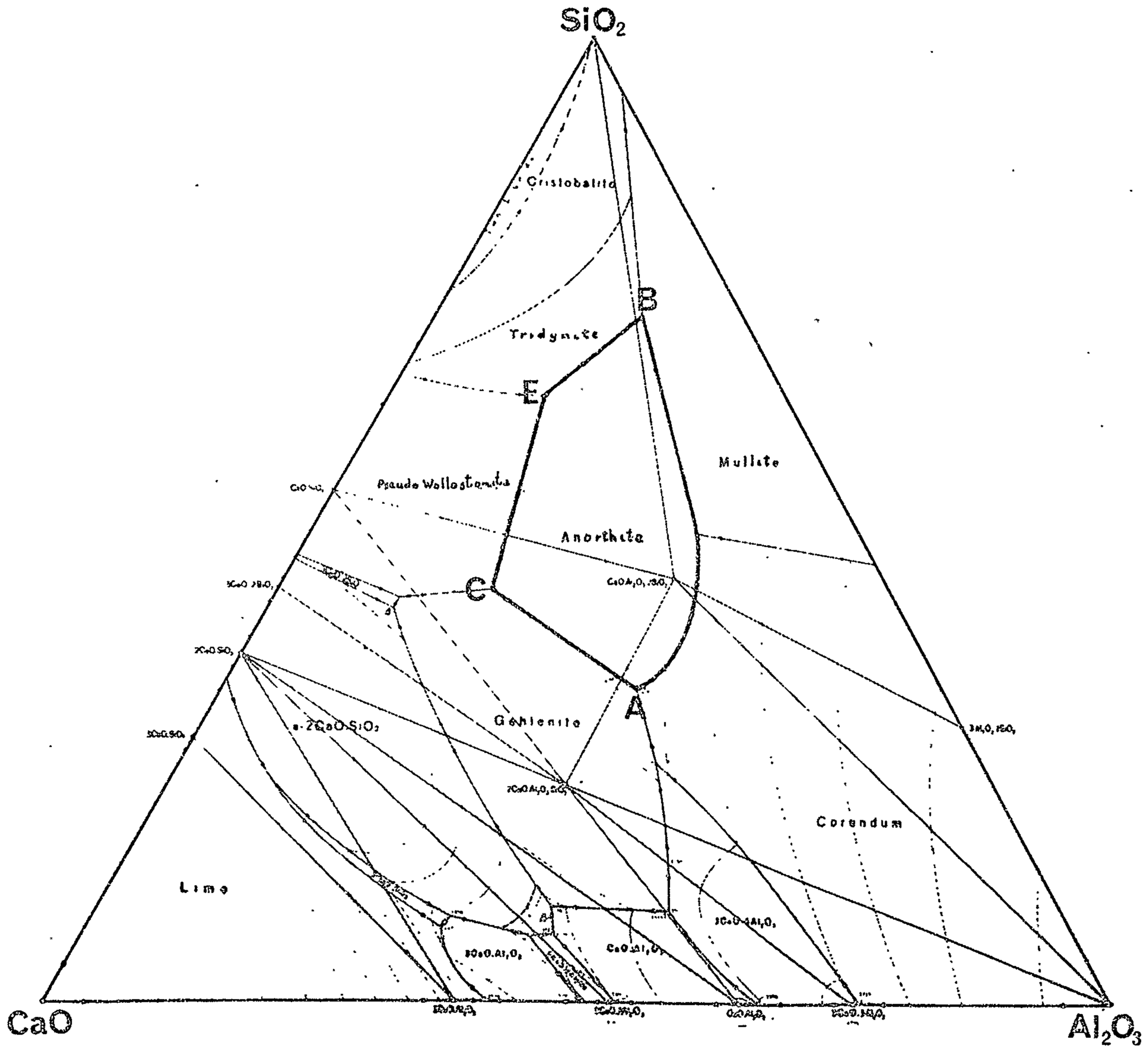
Theoretically, powders may be so coarse that cementing of the paste fails to occur since the greatly reduced surface area of the original particles does not expose enough glass to the liquid. The amount of matrix formed would be decreased to the point where original powder particles fail to bond. The converse, that reaction rate increases with increase in surface area of the powder, should also be true. Kent et al (1970) have shown that particles below five microns in diameter are completely degraded to aluminosilica gel.

II Powder Composition

"The problem with silicate cements is to prepare a powder and a liquid which will set rapidly enough for practical use. The activity of the powder is controlled to some extent by the amount of alumina in it." (Crowell, 1927). The inferred increased activity of the powder with increase in Al_2O_3 concentration was not explained. A paper by Manly et al (1951) represents the most comprehensive study attempting to show the effect of powder composition on the cementing reaction and on some physical properties of the hardened cements. Fifty-three experimental powders were produced which fell into two groups: (i) unfluxed glasses (20) and (ii) fluxed glasses (33). "Compositions for fusion without flux were selected from a composition temperature phase diagram of $CaO-SiO_2-Al_2O_3$ system" shown in Fig. 3.

"All unfluxed glasses (with 1 exception) were chosen from the Anorthite region. Tridymite compositions were not tested because preliminary results from adjacent Anorthite glasses, (having high SiO_2 concentrations), lacked setting properties when mixed with a commercial silicate cement liquid (S.S. White Liquid for Filling Porcelain). The 20 compositions fused to clear, opaque glasses which were subsequently crushed until they passed a standard mesh. The powders were mixed with the above liquid and the resulting pastes were divided into 4 categories : I Non-Setting, II Slow-setting, III Moderate-setting and IV Fast-setting. "The non-setting compositions occurred in the high silica area of the anorthite range with SiO_2:CaO ratios of approximately 2.08 or greater.....

Fig. 3 : Composition temperature phase diagram of $CaO-SiO_2-Al_2O_3$ system



(From Manly et al, 1951)

The slow-setting compositions occupy a narrow region just below the non-setting range. Their composition approximately corresponds to a range of alumina from 11 to 28% in composition with SiO_2:CaO ratio of about 1.95 (Setting times of these pastes ranged from 11 to 18 minutes).....

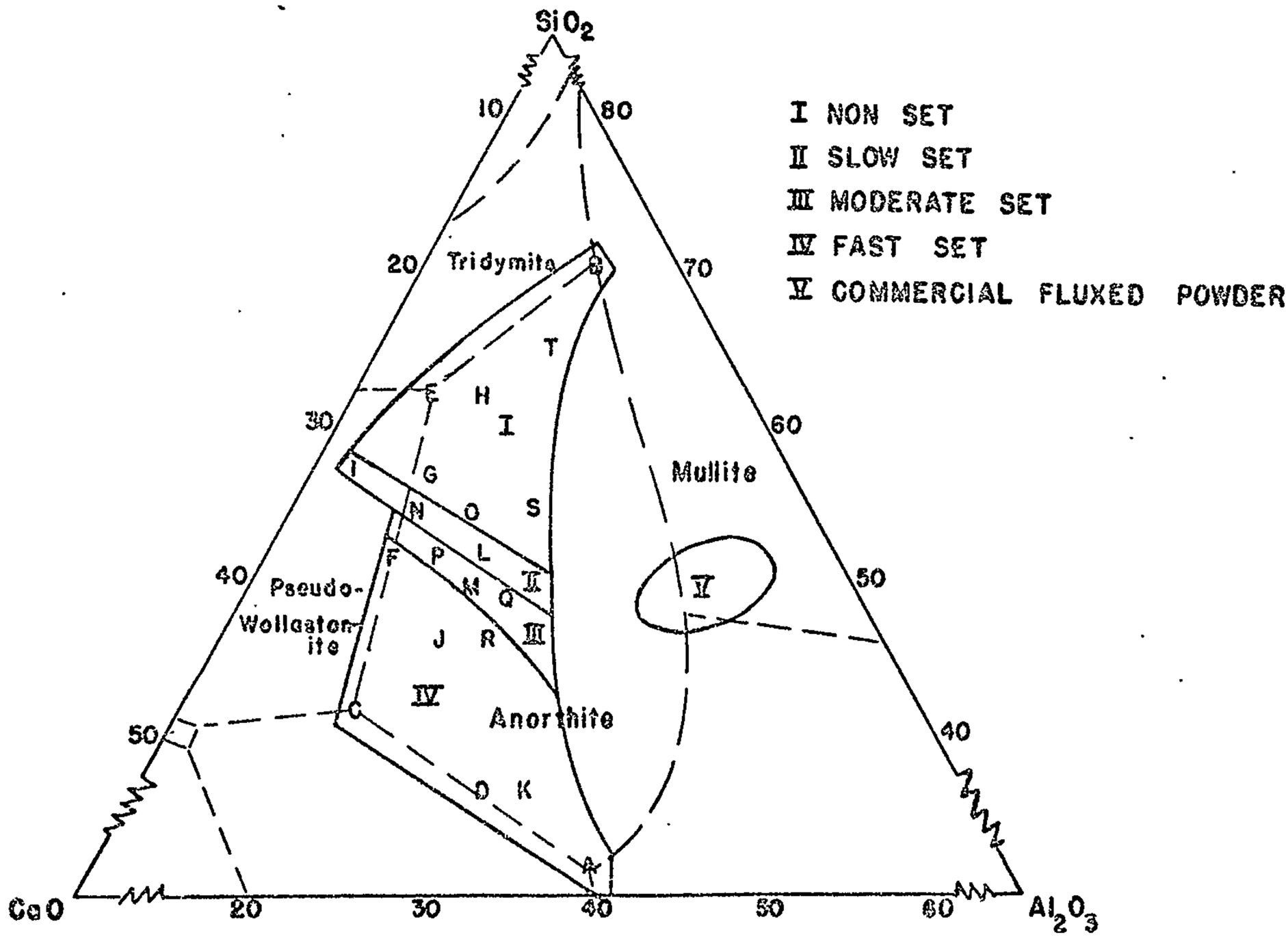
Moderately rapid setting compositions have somewhat lower

SiO_2:CaO ratios than the slow-setting compositions. The samples occupy a narrow region just below the slow-setting group. The band has a SiO_2:CaO ratio of approximately 1.83 $\pm$ .06 and an Al_2O_3 content of 16 to 30%. (Setting times were not mentioned, but these compositions gave cements which had the best physical properties).....

The fast-setting compositions had SiO_2:CaO ratios lower than 1.74, and were located in the lower third of the anorthite range. (These cements had poor physical properties). See Fig. 4.

Fig. 4

SETTING OF $CaO-Al_2O_3-SiO_2$ COMPOSITIONS



(From Manly et al, 1951)

Sodium carbonate and chloride, sodium and calcium fluoride, beryllium compounds, boric oxide and metal phosphates were used to produce the 33

fluxed experimental powders. "Data on commercial silicate powders indicates that their $CaO:SiO_2:Al_2O_3$ ratio would correspond to the mullite range of the ternary system. For this reason some of the compositions with flux were prepared with the mullite ratio of the oxides, and the remainder had oxide ratios corresponding to the anorthite range." (Manly et al, 1951). The powder producing the most acceptable cement was in the mullite region and was fluxed with the highest tested amount of calcium fluoride. Its composition was $SiO_2 \approx 40\%$, $Al_2O_3 \approx 28\%$, $CaO \approx 11\%$ and $CaF_2 \approx 21\%$. "The hardness was lower than the control, but the water solubility was lower than any other composition tested and was within specifications. Non-setting compositions were converted to rapid-setting powders when sufficient flux was used. It thus appeared that addition of flux would cause cementing actions in a powder of high silicate content." There was an exception to this (i.e. increased flux gives decreased setting-time). When metal phosphates were used as fluxes with rapid and moderate-setting compositions, setting-times were lengthened rather than shortened.

Manly et al (1951) concluded that "only a very narrow range of compositions containing CaO, SiO_2, and Al_2O_3 could be fused to clear glasses which would set within the proper length of time with silicate liquids. Several different compounds could be used as fluxes for increasing the range of compositions that would set. No composition was found which was appreciably superior in properties to representative commercial products and all powders tested were deficient in translucency."

Wilson et al compared an uncertified material C-11 (Terralux Ultra; Zahn-Porzellan, K.G. Hamburg) with certified cements such as C-2 (Super Syntrex; Amalgamated Dental Co. Ltd., London) in a number of studies.

(Wilson and Batchelor, 1967a; Wilson et al, 1968b, c and d; Kent and Wilson 1969; Wilson and Kent, 1970a; and Wilson et al, 1970c). From ion elution data (test media distilled water), it was found that the material eluted from C-11 differed significantly from C-2, the eluate was more acidic and there was a substantial increase in the amounts of phosphate and sodium leached. This indicated that the degree of attack on P-11 had been greater than on P-2 (Refer to TABLE III p. 24). It was noted that the sodium content (14.5% Na_2O) of the powder P-11, and hence the amount of cryolite (Na_3AlF_6) flux used in glass preparation, was particularly high. (Wilson and Batchelor, 1967a). From electrical conductivity and infrared studies of C-11 (Wilson et al 1968c and d) it was clearly shown that in the young set cement (6-24 hrs), there was still a considerable amount of unreacted phosphoric acid present as $H_2PO_4^-$ ions. "After set, the hardening process is apparently slower than with other cements.

The presence of $H_2PO_4^-$ in the cement accounts for its high electrical conductivity and dissolution rate in water, since not all the phosphate is fixed in an insoluble covalent form." (Wilson and Mesley, 1968d).

The poor durability of Terralux Ultra cement cannot be attributed entirely to the higher concentration of phosphoric acid in the liquid. Wilson noted that there was an increase in the water soluble species $NaH_2PO_4.H_2O$ for this cement. Therefore, a more complete explanation must also include a consideration of the chemical composition of the powder. A high concentration of H_3PO_4 was employed in the liquid ($\approx$65% w/w H_3PO_4) to ensure adequate clinical working time by retarding the cementing reaction. When Terralux Ultra powder (P-11) was mixed with a more conventional silicate cement liquid ($\approx$ 49% w/w H_3PO_4), the reaction was

extremely rapid, the paste setting on the glass slab. (Wilson et al, 1970c). P-11 was the most reactive silicate cement powder tested, the degree of reactivity of any powder being directly related to the concentration of sodium and the powder particle size. Wet chemical analysis of the early stages of the decomposition of P-11 showed that the amount of sodium extracted was far in excess of the amount from other paste systems tested. "This comparatively large attack on the powder, with consequent formation of a considerable amount of gel matrix, accounts for the inferior strength and durability characteristics of this cement system compared with C-2 (Super Syntrex) and the effect is greater than can be accounted for merely by the higher initial phosphoric acid concentration.... The uncertified cement system C-11, which yields inferior cements, is prepared from a powder P-11 containing 10.8% Na compared with 5.7% in P-2. Since Na^{+} ions are of low field strength, the average polarizability and basicity of the O^{2-} anions will be higher for P-11 than P-2; consequently, P-11 will be more rapidly attacked, as was observed." (Wilson and Kent, 1970a).

CHEMISTRY OF THE SETTING REACTION - SUMMARY

1. Traditional Concepts

(i) 1916 Voelker stated that the chemistry of the setting reaction of silicate cement was closely allied to that of zinc oxyphosphate cements. Steenbock agreed with this theory.

(ii) This explanation was thought to be an over simplification by later workers. Doubleday (1926) asserted that a much more complex reaction occurred. He suggested two main stages in the setting reaction: 1. rapid formation of aluminium phosphates and 2. the hydration of silicates, a much slower process extending over some weeks.

(iii) Crowell (1927), using X-ray diffraction analysis drew attention to the amorphous nature of set silicate cement whilst set zinc phosphate cement was crystalline. He concluded that silicic acid was liberated from the glass powder when mixed with the cement liquid and that setting of the cement was due to condensation polymerization of silicic acid to polysilicic acid gel.

(iv) Ray (1934), Matthews (1935) and Mamlet (1936) mention the formation of colloidal aluminium phosphates and colloidal silicic acid. They agreed that setting was due to gelation of silicic acid.

(v) Hurd (1938) reviewed and discussed theories concerning the mechanism of setting of silicic acid gels. Laboratory data strongly suggested that monosilicic acid polymerized

to polysilicic acid forming a complex, irreversible gel. Theories of gel structure were discussed.

(vi) Souder and Schoonover (1939) at the National Bureau of Standards assumed that the reactions which took place in dental silicate cement were similar to those related to the setting of silica gels.

(vii) The traditional concept, that dental silicate cement was a silica gel bonded material, has been propagated in dental materials texts up till recent times (1969).

2. <u>New Concepts</u>

(i) Exhaustive studies by Wilson et al have led to a greater understanding of the complex chemistry of dental silicate cement. Their proposed model for the cementing reaction appears irrefutable. Time and again, it has been corroborated using a variety of physical and chemical techniques.

(ii) The cementing reaction can be divided into two overlapping phases:

1. <u>Formation of the Paste</u> : An acid-base reaction occurs in which hydrated protons degrade the alumino-silicate glass lattice at Al-O-Si linkages. There is a rapid extraction of cations, fluoride ions, and orthosilicic acid from the glass powder, accompanied by an increase in the concentration of $H_2PO_4^-$ ions and a rise in pH.

2. <u>Precipitation Hardening of the Paste</u> : Concentrations of the various ionic species in the paste system increase

until ion products exceed solubility products of the various complex phosphate and fluoride salts. The complex salts are then precipitated. All amorphous metal phosphates are probably hydrated and become less water soluble as the reaction progresses, with the exception of $NaH_2PO_4.H_2O$. Hydrated sodium dihydrogen phosphate remains as a water soluble, deleterious species in the fully hardened cement. Other complex metal phosphates are virtually water insoluble. Amorphous aluminium phosphate has been identified, from infrared spectroscopy, and it is probable that zinc also forms complex phosphates in the matrix. Simultaneously in the paste, aluminosilica gel polymerized on the surface of the glass powder. Its presence, together with the colloidal phosphates, was positive evidence of lattice disruption.

(iii) It was suggested that the amorphous metal phosphates, which form the major component of the matrix, are adsorbed or bonded to the original particles via aluminium atoms at the surface of the aluminosilica gel forming phospho-alumino-silicates.

(iv) The presence of precipitated fluorides in the matrix was established.

(v) The critical role played by some liquid and powder parameters in the rate of the cementing reaction has been reviewed.

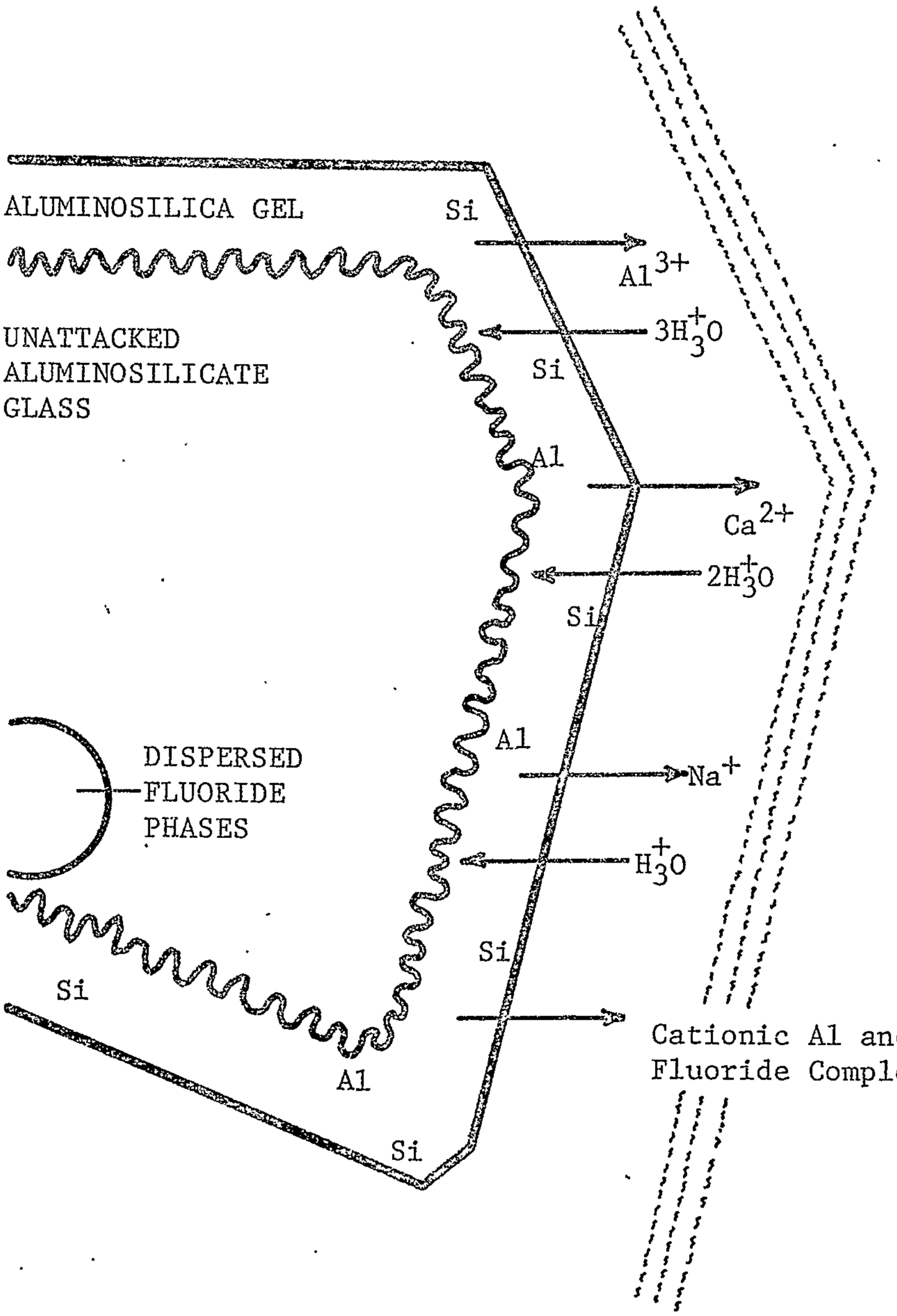
(vi) Fig. 5 shows a schematic representation of the cementing reaction.

Fig. 5 : Schematic representation of the cementing reaction

POWDER + LIQUID ⟶ PASTE

$H_3PO_4 \longrightarrow H_3^+O + H_2PO_4^-$

(Zn^{2+} and Al^{3+} present as modifiers)

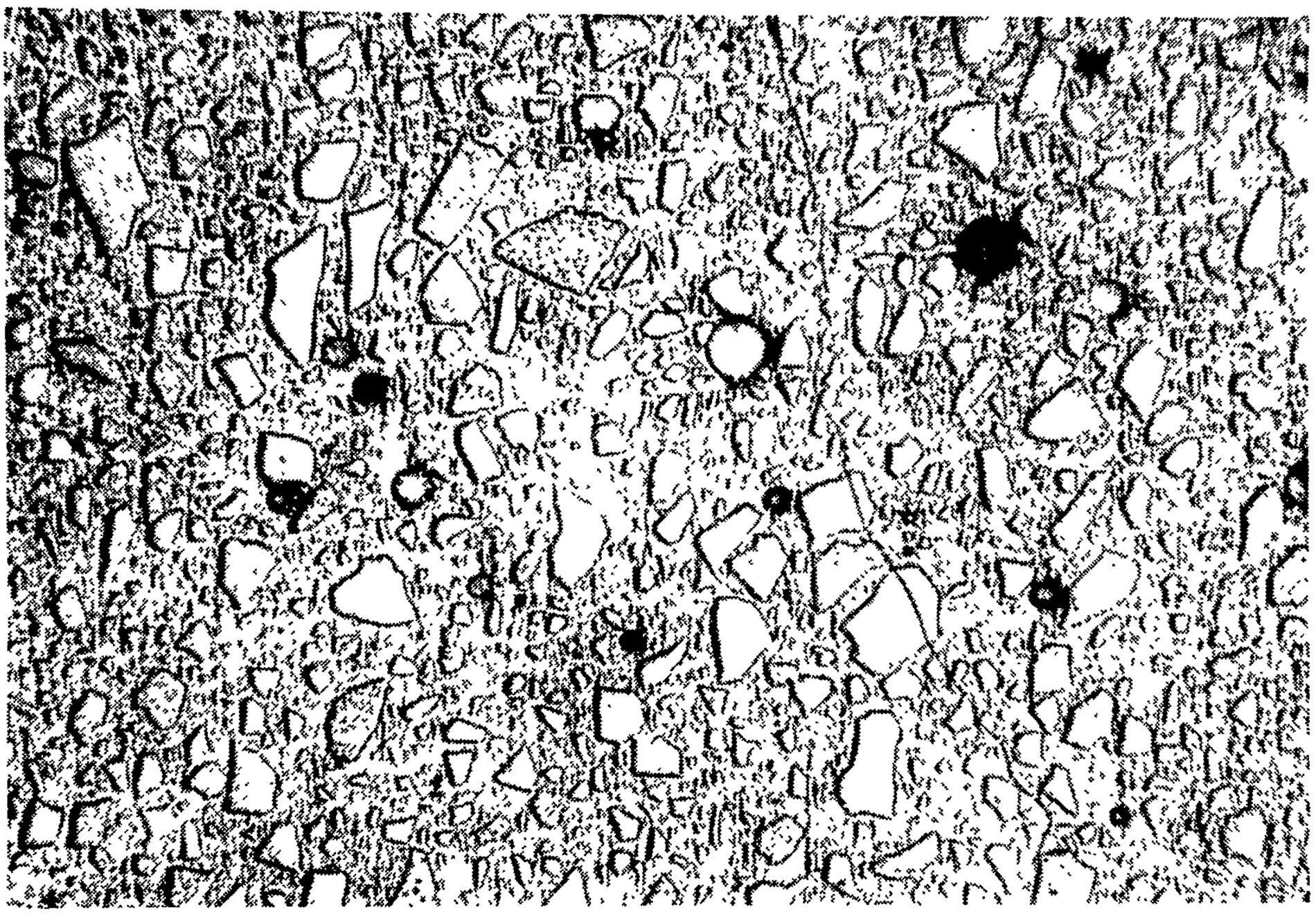


(Modified from Kent et al, 1970)

CHAPTER V : STRUCTURE OF THE HARDENED CEMENT

The cored nature of fully hardened silicate cement has been well established. From optical microscopy, the structure has been shown to consist of original glass particles which have been partially decomposed at the surface to produce a matrix of reaction products. Voids are normally present and are due to air trapped during mixing of the powder and liquid. (Ray, 1934; Mamlet 1936; and Paffenbarger et al, 1938). A typical photomicrograph of the fully set cement is shown in Fig. 6.

Fig. 6



(From Jørgensen et al, 1969)

By X-ray diffraction, the matrix was shown to be largely amorphous. (Crowell, 1927; Souder and Paffenbarger, 1942, p. 110). Although the composition of this gel matrix was thought to be complex, it was held that

the major constituent was condensed polysilicic acid gel. (Souder and Paffenbarger, 1942, p. 110; Peyton, 1968, p. 433). Thus, the traditional concept, that dental silicate cement was a silica gel bonded material, was established.

Electron microscopy was employed by Grant et al (1968) to observe the structure of set silicate cement. They noted that the structure of the remaining unreacted glass particles was not completely homogeneous. Two forms of spherical inclusions were present. The larger inclusions were visible as pits in optical photomicrographs and hence were undoubtedly part of the glassy structure. The distribution of these inclusions was random, some coinciding with the reaction interface indicating that they took part in the setting reaction. Their relative reactivity was similar to all other parts of the reaction interface. It was suggested that "the spherical inclusion bodies in the silicate particles are possibly of some high freezing point component or silicate material into which fluorides were not dissolved as glass formers." (Grant et al, 1968). Their electron micrograph appears in Fig. 7. This theory was not supported by Wilson. Although he reported segregation of two types of droplet, circa 4,000 A^{o} and circa 250 A^{o} in diameter, he suggested that these droplets did in fact represent dispersed fluoride phases within the glass network. (Wilson, 1969a).

The comprehensive studies of Wilson et al have led to a far greater understanding of the complex chemistry of dental silicate cements. The composition of the gel matrix and the chemical nature of the matrix – original particle interface have been fairly well established.

Fig. 7 : Electron micrograph of set silicate cement. A : unreacted portion of original powder particle; B : matrix
Inset: Optical micrograph of set silicate cement. Note marked angularity of the silicate particles.

(From Grant et al, 1968)

"The microstructure of a number of fully hardened cements was studied by a variety of techniques : optical and electron microscopy, electron probe

microanalysis, infrared spectroscopy and X-ray diffraction analysis. All cements examined were found to be largely "amorphous"; the presence of silica or aluminosilica gel and amorphous aluminium phosphate was inferred from infrared spectroscopic data. However, small amounts of well-defined microcrystallites were detected and identified as augelite, $Al_2PO_4(OH)_3$ and fluorite, CaF_2.

Under the optical microscope, polished surfaces of cements appeared as poorly interconnected mosaics of angular grains, which varied in size from 1 - 100 microns. In the intergranular regions of the stronger cements, a fine network of birefringent microcrystallites was observed under crossed polarisers. Scanning electron micrographs confirmed that the glass particles had retained their original shape; however, the presence of surface inhomogenities was indicative of local attack. These particles appeared to be only loosely bonded to the cementing matrix." (Wilson, 1969a).

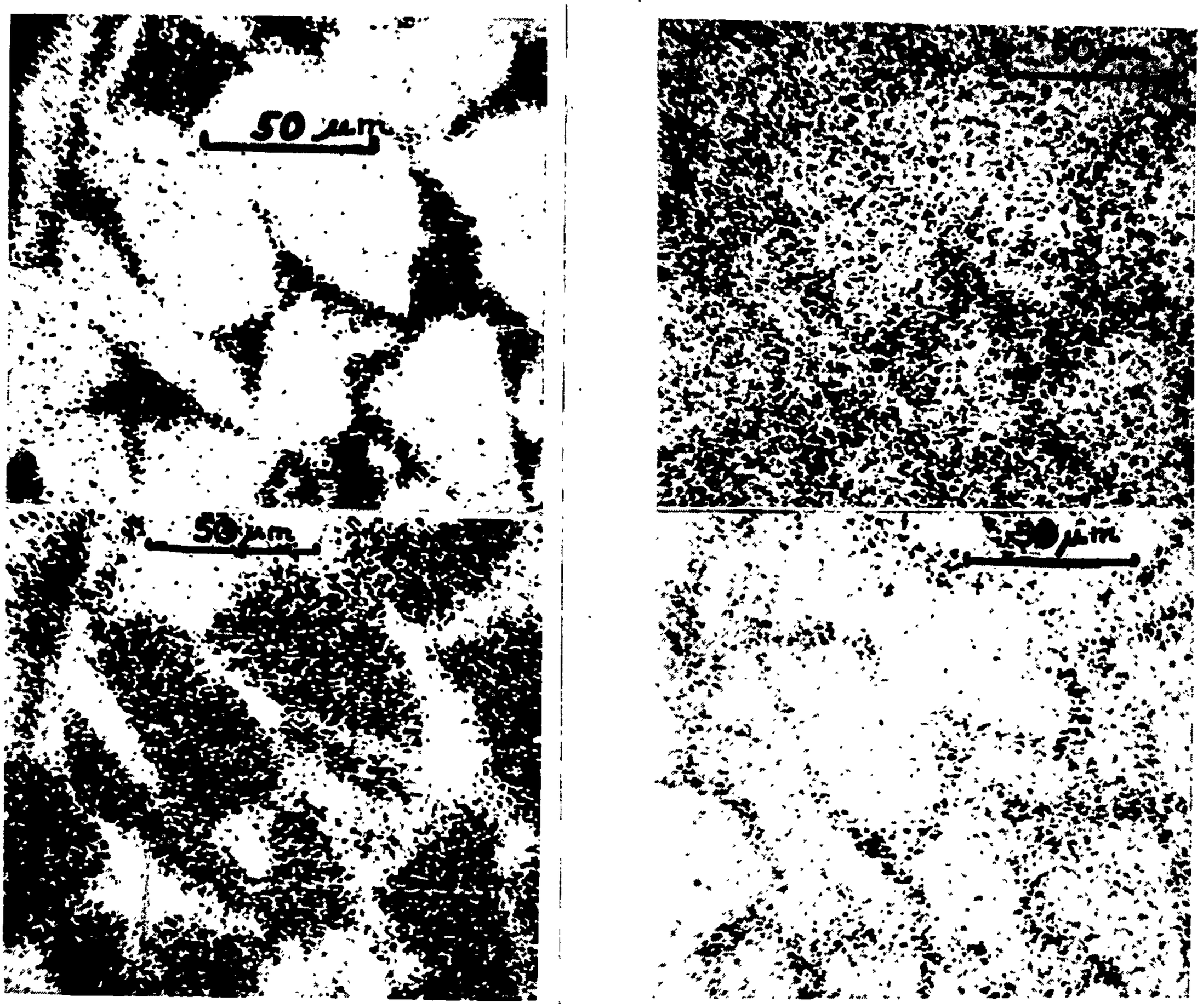
The chemical nature of the cement structure was established, for one cement, using electron probe microanalysis. This technique enables the distribution of certain elements - Si, Al, Ca and P - to be mapped. By comparing these element distributions with an electron image photograph of the same area, it was evident that, as the result of the penetration of protons, some Ca and Al had migrated from the surface of the vitreous particles into the intergranular region where they were associated with P. Si did not migrate but remained in the cation depleted surface as a water-containing gel, an observation which explains why the particles retain their original shape despite chemical interaction. See Fig. 8 and 9.

"Using this evidence a detailed structure for the dental silicate cement can be advanced. The cement consists of cored particles embedded in a largely amorphous matrix where the principal constituent is aluminium phosphate. The particles contain an unattacked glass core which is sheathed by an alumino-silicate gel. A network of augelite and fluorite microcrystallites runs throughout the matrix. The exact mechanism for the formation of the phosphate gel is still a matter of speculation but, aluminium is known to form hydroxy- and phosphato-bridged polynuclear species in phosphoric acid solution as its concentration increases. Thus it is reasonable to suppose that a pH dependent polymerization occurs to give a water insoluble polynuclear species of this type, which acts as the effective bonding medium." (Kent et al, 1970).

Fig. 8 : Reflected electron image photograph of a coarse-particle cement (Super Syntrex), liquid 49% w/w H_3PO_4

(From Kent et al, 1970)

Fig. 9 : Silicon (1), phosphorus (2), calcium (3), and aluminium (4) distribution of the field shown in Fig. 8.



(From Kent et al, 1970)

PART B: PHYSICAL PROPERTIES

INTRODUCTION

The procedure of testing dental materials by either dentists or manufacturers is not new. "G.V. Black (1895) emphasized the necessity for making physical tests and using test data to insure the uniform excellence of a product and to take care of variations in raw materials and in manufacturing processes." (Crowell, 1932). Because inferences are frequently drawn from comparisons of test results, Crowell (1932) stressed the need for standardization of test methods. "The shape and size of the test piece have a marked effect on the numerical value of the test results, particularly when small sizes are tested or used. Test pieces must not differ greatly in dimensions from the pieces actually used in the dental structure.....Also, the rate at which a test is made affects results and must be controlled. If tests are to be used to predict clinical usefulness and for the purpose of comparison, then the following principles must be observed:

1. Test specimens and methods must conform as nearly as possible to the conditions of actual use, particularly in regard to size of specimen and method and rate of loading.

2. Test method should be reproducible, with the unavoidable errors kept to a minimum. Some measurement of dispersion of results is essential.

3. When different testing procedures have been used, comparison of results can only be made when the effects of these different methods can be quantitatively assessed."

The first tentative specification for dental silicate cement was introduced by Paffenbarger et al (1938) who listed time of setting, ultimate compressive strength, opacity and solubility and disintegration as the physical properties of major importance in the paste and fully hardened cement. The American specification was the basis for the present F.D.I., British and Australian standards.

Only strength and solubility and disintegration will be discussed in detail, as they are the subject of the investigation which follows. The arbitrary parameter of setting time of a silicate cement paste is indicative of the rate of hardening or degree of cementation (or setting) of the paste system. Wilson et al (1970c) stated that "compressive strength of cements may be taken as a measure of the degree of cementation." It can be seen readily that setting time is an arbitrary point observed during the development of strength of the hardening cement. Therefore, it follows that the factors generally affecting rate of development of compressive strength will also be those which affect setting time. The factors affecting the physical properties discussed under the general headings of "Strength" and "Disintegration and Erosion" will be considered in a following section.

CHAPTER I: STRENGTH

Traditionally, the strength of silicate cement has been recorded at the point when the test piece failed under compressive stresses, the strength being termed ultimate compressive strength or crushing strength. Poetschke (1916); Ray (1934), and Paffenbarger et al (1938) were among the first workers to determine the compressive strength of silicate cement.

Silicate cement is a brittle material suiting the simple cylindrical design usually used for compressive test pieces. It should be kept in mind that the compressive strength test for silicate cement is probably a form of bend or tensile test, complicated by elaborate geometry as occurs in other glassy materials. (Haward, 1949, p. 64). Comparisons of compressive strength results must account for test method and conditions. With the application of the diametral compression test to various dental materials, values for the tensile strength of silicate cement have been measured. (Appleton, 1964). Mitchem (1967) has also used a bend test to observe the flexural or transverse strength of silicate cement. Mahler and Mitchem (1964) have shown that a definite relationship exists between the measured compressive strength, tensile strength and transverse strength for amalgam, a brittle, heterogeneous material. It is likely that certain relationships between the various types of strength also exist for silicate cement. Jørgensen et al (1969) have shown an almost direct relation between compressive strength and tensile strength for a given fully hardened cement.

1. RATE OF DEVELOPMENT OF STRENGTH

As the rate of development of compressive strength has not been widely studied, data is not readily available for the more modern (1950-1970) materials. Poetschke (1916), one of the first workers to consider this

parameter, used specimens of dimensions 5 mm. diam. x 5 mm. ht; the rate of loading during testing was not specified. (Ray, 1934). He found that the crushing strength of most cements increased rapidly during the first hour after mixing, reaching 60% of the ultimate compressive strength in some cases. Subsequently, there was a slower increase in strength extending over a "considerable period". He also noted that the compressive strengths of some cements actually declined after approximately four weeks or less. Paffenbarger et al (1938) tested one product (Cement D), crushing specimens at different intervals ranging from 15 minutes to 14 months. The cylindrical specimens, 6 mm. diam. x 12 mm. ht, were stored in distilled water at 37°C until crushed. The rate of loading was specified as the strain rate 0.01 in./min. The fifteen minute compressive strength was approximately 40% (9,600 p.s.i.) whilst the three hour strength was approximately 60% (14,400 p.s.i.) of the compressive strength recorded at 14 months, (24,000 p.s.i.). With the exception of Cement D which appeared to have a slightly higher strength at 14 months, all the cements tested by Paffenbarger et al when kept in distilled water were strongest at six months. No decline in compressive strength, as observed by Poetschke, was noted. Data for Cement D appears to have been presented in tabular form in 1958 by Paffenbarger and Stanford and is set out in TABLE V.

TABLE V

CHANGE OF COMPRESSIVE STRENGTH OF A SILICATE CEMENT WITH TIME

Age of Specimens	Compressive Strength (p.s.i.)
15 minutes	10,000
1 hour	12,000
3 hours	15,000
1 day	16,000
1 week	19,500
6 months	22,500
14 months	24,000

(From Paffenbarger and Stanford, 1958)

2. COMPRESSIVE STRENGTH

As mentioned previously, the methods of testing can significantly affect the measured compressive strength of silicate cement. Hence, the rationale of dental materials specifications which adopt standard test procedures. Pertinent parts of various specifications for the testing of compressive strength appear in TABLE VI. Using this information as a guide, the various results for the compressive strength of silicate cement appearing in TABLE VII can be discussed.

The trend, noted by Phillips (1965), towards increased compressive strengths for modern silicate cements can be readily seen. The mean compressive strength computed from results reported since 1960 is approximately 30,900 p.s.i. which is well above the minimum requirements for the specifications listed in TABLE VI. The relatively high strength reported by Poetschke can probably be explained on the basis of specimen size.

TABLE VI

Specification	Size of Compressive Strength Test Piece (mms) ht x diam.	Rate of Testing	Min. 24 hr. Compressive Strength
Aust. Standard No. T.8 Amdt. No. 1 Jan. 1961	8 x 4	140 Kg/min 300 lb/min	1,750 Kg/cm^2 25,000 p.s.i.
F.D.I. No. 5 July 1961	12 x 6	225 Kg/min 500 lb/min	1,700 Kg/cm^2 24,200 p.s.i.
A.D.A. No. 9 Second Revision Dec. 1962	12 x 6	225 ± 50 Kg/min	1,700 Kg/cm^2
British Standard 3365: Part 1, 1969	12 x 6	225 Kg/min 500 lb/min	1,700 Kg/cm^2 24,200 p.s.i.
British Standard 3365: Part 3, 1970 (Draft for capsulated cements)	6 x 4	0.75 ± 0.25 mm/min 0.03 ± 0.01 in/min	1,750 Kg/cm^2 25,000 p.s.i.

TABLE VII

REPORTED COMPRESSIVE STRENGTHS OF SILICATE CEMENTS MIXED AT STANDARD OR MANUFACTURERS RECOMMENDED CONSISTENCY

SPECIMEN SIZE (mms) ht x diam.	INVESTIGATOR	RATE OF TESTING	TIME OF TEST (DAYS)	COMPRESSIVE STRENGTH (p.s.i.)	MEASUREMENT OF DISPERSION (p.s.i.)
5 x 5	Poetschke 1916	?	?	42,500	?
20 x 5	Ray 1934	?	5	5,650 - 8,450	?
12 x 6	Swanson 1936	0.01 in/min	7	8,558	?
12 x 6	Paffenbarger et al 1938	0.01 in/min	7	$\underline{10}$,500 - 25,500 $\bar{x}$ = 17,800 n = 12	?
12 x 6	Souder and Paffenbarger 1942	0.01 in/min	7	24,000	?
12 x 6	Paffenbarger and Stanford 1958	0.01 in/min	1	25,000 $\pm$ 2,000 range for certified mats.	?
12 x 6	McConnell and Brawley 1960	3000 lb/min	1	26,300*	S.D. = 2,470 (n = 5)
9 x 3	Craig et al 1961	0.015 in/min	1	25,600	Mean Dev. = 300 (n = 5)
12 x 6	Rubinstein 1962	0.01 in/min	1	27,200 (Cement A hand-mixed)	Mean Dev. = 558
12 x 6	Swartz et al 1963	0.01 in/min	7	21,100 - 29,600	?
12 x 6	Appleton 1964	225 $\pm$ 50 Kg/min	1	27,000	?
12 x 6	Mueller et al 1967	0.1 in/min**	1	$\underline{26}$,050 ($\bar{x}$ of 10 batches)	Mean Dev. = 2,430 (n = 5)
12 x 6	Wilson et al 1967	225 Kg/min	1	46,500	?
12 x 6***	Eichner et al 1967	225 Kg/min	1	24,200	?
?	Eichner et al 1967	225 Kg/min	1	38,400	?
12 x 6	Swartz et al 1968	0.01 in/min	1	25,000	?
12 x 6	Norman et al 1969	0.01 in/min	1	$\bar{x}$ = 27,000 (n = 10)	S.D. = 3,700
12 x 6	Wilson et al 1969	225 Kg/min	1	37,000	?
6 x 3	Jørgensen et al 1969	10 Kg/sec (1320 lb/min)	1	$\bar{x}$ = 31,840 (n = 10)	S.D. = 2,290
7 x 3.5	Sorensen 1970 et al	0.02 in/min	1	?****	?

* computed from raw data supplied TABLE I.

** assumed typographical error, should be 0.01 in/min. (Mueller et al state that they are testing according to the American Specification; in which case their rate of testing should be 225 $\pm$ 50 Kg/min.)

*** 12 x 6 specimen obtained from four Silicaps; unstated specimen size for one Silicap would be approx. 7 x 3.5.

**** TABLE III - interpretation difficult.

Paffenbarger et al (1933), considered these dimensions "contrary to acceptable engineering practice, which requires that the length be approximately twice the diameter." The squat dimensions of Poetschke's test pieces would tend to increase the measured compressive strength, whilst the relatively long specimens of Ray would tend to decrease the observed strength, all other factors being equal. The strengths reported by Wilson et al (1967b, 1969b) are well above the average, particularly in the case of cement C-2 (Super Syntrex) where the observed compressive strength was approximately 46,500 p.s.i. No explanation can be offered for these seemingly high results.

Most workers have crushed specimens at specification rates of testing. There are, however, two prominent exceptions; McConnell and Brawley (1960), and Jørgensen et al (1969). McConnell and Brawley crushed specimens at an extremely fast rate of loading, (3,000 lb/min), approximately six times the present American specification rate and test pieces would probably have been crushed in ten to twelve seconds. This contrasts with the four to six minutes testing time required when a strain rate of 0.01 in/min. (approx. 100 lb/min.) is employed. The faster rate of testing has not appeared to influence their results. The strengths reported by Jørgensen et al (1969) are above average and perhaps can be rationalized on the basis of the smaller specimen dimensions (6 mm. ht x 3 mm. diam.) and the increased rate of loading employed. (1320 lb/min., approximately two and a half times the American specification rate).

The lack of measurements of dispersion of results is a notable feature of TABLE VII. Of the nineteen studies listed, only six reported mean or standard deviations for strength results. With two exceptions,

the mean or standard deviation was approximately 10% of the observed mean compressive strength. The mean deviations reported by Craig et al (1961) and Rubinstein (1962) were only approximately 1.17% and 2.05% respectively of the measured mean compressive strength.

3. TENSILE STRENGTH

Because of the complex specimens required for tensile testing using the traditional "grips" method, the tensile strength of silicate cement was investigated little till the introduction of the simpler diametral compression test to the field of dental materials.

Brown and Rodriguez (1960) have determined the one week tensile strength of silicate cement using the "grips" method. Specimens were tested at a cross-head speed of 0.02 in./min. and the average tensile strengths ranged from 500-1000 p.s.i. Standard deviations were quite large ranging from 100-300 p.s.i. This spread emphasizes the difficulties inherent in this particular test method when applied to brittle materials. Norman et al (1970), using the "grips" technique, have also reported values for the seven day tensile strength of silicate cement. The cements investigated were S.S. White New Filling Porcelain and M.Q. and Caulk Syntrex, all mixed at standard consistency. Specimens were 6 mm. diam. x 12 mm. ht and were broken under a load applied at the rate of 0.035 in./min. All cements gave tensile strengths of approximately 800 p.s.i.; measurements of dispersion of results were not included. Appleton (1964), used specimens of American specification dimensions to record tensile and compressive strength of silicate cement. He found that the tensile strength of silicate cement, determined by the diametral compression test, was only approximately 5% (1,400 p.s.i.) of the compressive strength of the same cement (27,000 p.s.i.). The rate

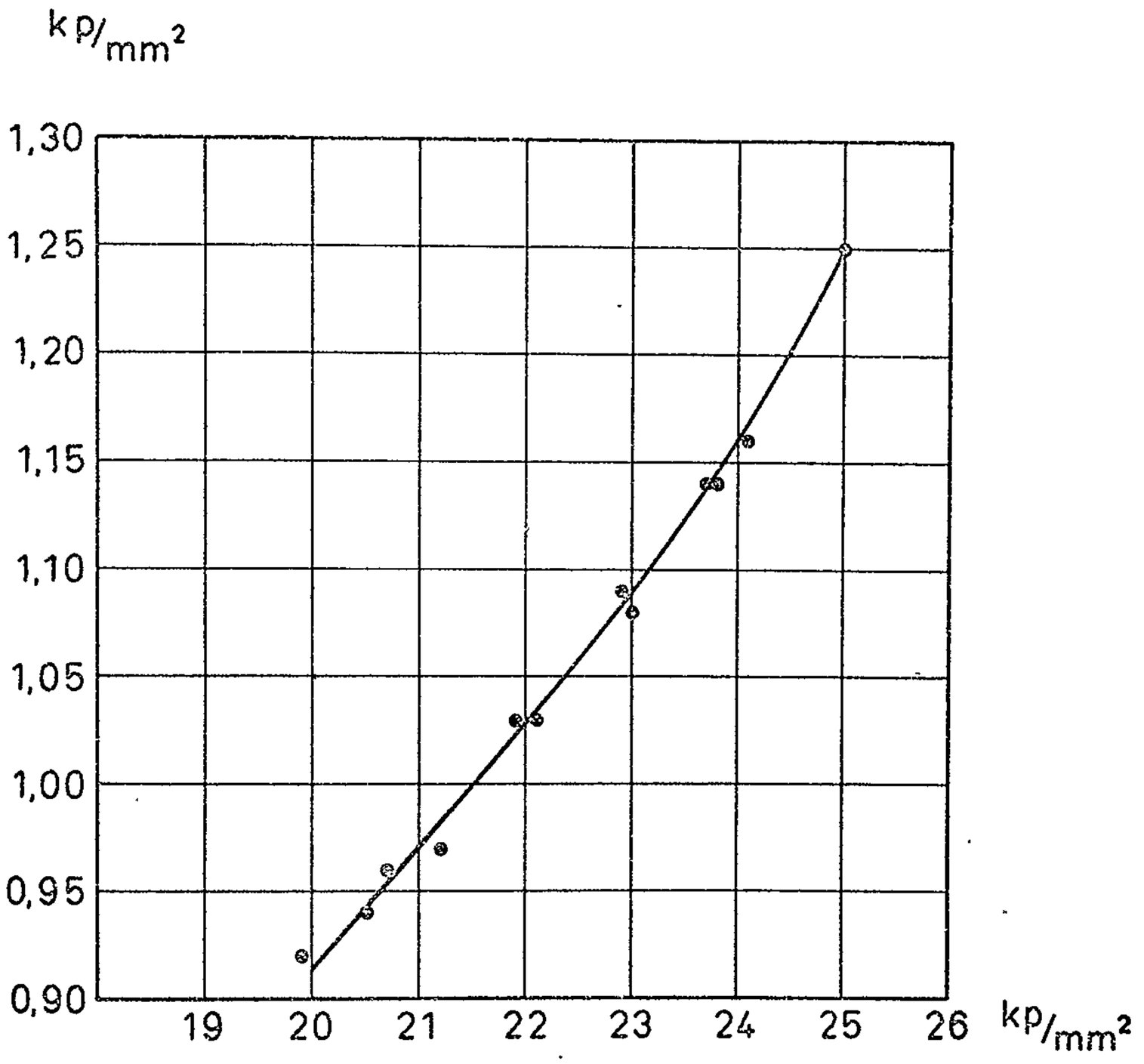
of loading during the diametral test was not specified. Jørgensen et al (1969) have also determined the tensile strength of silicate cement by this indirect method. Using test cylinders of 6 mm. ht x 3 mm. diam. loaded in a Losenhausen machine at a rate of 2 Kg./sec. (265 lb/min.), they found that the tensile strength of a silicate cement (Achatit-Silicap) ranged from 1,310 p.s.i. to 1,780 p.s.i. depending on mixing technique and powder:liquid ratio. The average of all standard deviations reported was approximately 8.6% of the measured mean tensile strength. These results agreed with those of Appleton (1964). The percentage standard deviation for tensile strength was similar to that found for compressive strength by McConnell and Brawley (1960) - 9.4%, Mueller et al (1967) - 9.3% and Jørgensen et al (1969) - 7.2%. Jørgensen et al noted an almost direct relation between the tensile strength and compressive strength of a fully hardened silicate cement (Achatit-Silicap) even when prepared from a range of powder:liquid ratios and mixed under different conditions. Their findings are presented in Fig. 10 or may be expressed as follows:

Tensile Strength x 22 $\approx$ Compressive Strength

By means of the diametral compression test, Williams and Smith (1971) have also investigated the tensile strength of fully hardened silicate cement, as well as the rate of development of tensile strength. They tested S.S. White New Filling Porcelain and Vivadent Achatit with fibres at the manufacturers' recommended powder:liquid ratios. The tensile strengths of the fully hardened cements (72 hours) were 1,950 p.s.i. (S.D. 220 p.s.i.) and 2,130 p.s.i. (S.D. 110 p.s.i.) respectively. The slightly increased tensile strengths and decreased deviations, compared with those of Appleton (1964) and Jørgensen et al (1969), perhaps can be

explained on the basis of the faster rate of testing (0.0625 in./min.).

Fig. 10: The relationship between compressive and tensile strength of Achatit-Silicap



(From Jørgensen et al, 1969)

Williams and Smith contrast the relatively slow rate of development of tensile strength of silicate cement with that of amalgam. However, at half an hour, the earliest time of testing, the tensile strength of the silicate is approximately 70% of its 72 hour value. The authors stated that "the rate of gain of strength of the two silicate cements is slower in relation to the final strength than with dental amalgam; the fiber-containing material shows a slighter higher value. Nevertheless, the tensile strength of silicate is only about a quarter of that of the amalgam, whereas the compressive strength can reach, in each instance,

values in excess of 28,000 $Nm^{-2} \times 10^{-4}$ (40,000 p.s.i.).....These results show clearly that the silicate restoration is much more liable to fracture under tensile stresses than amalgam, a finding that is in accordance with clinical experience and that underlines the value of tensile strength as a criterion as opposed to the less illustrative compressive strength." These comments neither substantiate nor refute the assertion of Jørgensen et al (1969) that a relationship exists between the tensile and compressive strengths of silicate cement. It may also be added that compressive strengths in excess of 40,000 p.s.i. would appear rather high when compared with the compressive strengths reported in TABLE VII.

"If a material is very brittle it is difficult to test in tension; because precise axiality of loading is required and its notch sensitivity tends to make it break at a change in section away from the gauge length. In such cases, a reasonable value for the tensile strength may be found from a test in simple bending to fracture." (Tweeddale, 1964, p. 220). The test is called a transverse or bend test and the observed ultimate strength is usually termed modulus of rupture, bend strength, flexural strength or transverse strength. Haward (1949, p. 30) stated that "the bending strength is a stress, and is in principle the same as the tensile strength, though in actual tests, different and usually higher figures are obtained." The accuracy of bend test results is dependent on many factors, the discussion of which is beyond the scope of this review. Mitchem (1967) has evaluated the modulus of rupture of a silicate cement (S.S. White New Filling Porcelain mixed at the manufacturer's recommended powder:liquid ratio), which he called "transverse strength." The twenty-four hour modulus of rupture of specimens of dimensions 9 mm. (span) x

1 mm. (depth) x 2.5 mm. (width), tested at a rate of 0.01 in./min, through the centre with a 1/16 in. hardened steel ball, was approximately 3,800 p.s.i. The mean deviation was approximately 300 p.s.i. This relatively high figure for tensile strength reflected the view expressed by Haward (1949, p. 30).

Both the transverse test and the diametral compression test are methods of estimating the tensile strength of a brittle material. Mitchell (1961), Rudnick et al (1963), Addinall and Hackett (1964), and Williams and Smith (1971) believed that the diametral compression test (Brazilian test or indirect tension test) offered definite advantages over the older "grips" method or transverse test. Essentially, the merit of the diametral compression test lies in its simplicity. "Quality of results, ease of casting, ease of testing, simplicity of shape, and the relatively simple expressions that can be developed to determine the stress conditions should lead to widespread acceptance of this test" (Mitchell, 1961). "Conventional methods of measurement of tensile strength using 'dumbbell'-shaped specimens suffer from difficulties of specimen grip eccentricity and surface stress concentrations that are particularly severe with brittle materials. Likewise, flexural tests give results that are affected by the surface condition of the specimen and its geometry. The stress distribution across the bent specimen is nonlinear and values of tensile strength or modulus of rupture obtained in the bend test are frequently higher by a factor of two or more than those obtained in the conventional test." (Williams and Smith, 1971).

These different test methods for determining "tensile strength" give widely divergent results. The technically difficult "grips" method gives lowest values, diametral compression test values are intermediate,

and bend tests give significantly higher results. Results using different methods of determining the "tensile strength" of silicate cement are summarized in TABLE VIII.

TABLE VIII: "TENSILE STRENGTH" OBSERVED USING VARIOUS EXPERIMENTAL METHODS

"GRIPS" METHOD (p.s.i.)	DIAMETRAL COMPRESSION TEST (p.s.i.)	BEND TEST (p.s.i.)
Bowen and Rodriguez 500 - 1,000 (100-300)*	Appleton 1,400	Mitchem 3,800 (300)
Norman et al 800	Jørgensen et al 1,310 - 1,780 (85 - 228)	
	Williams and Smith 1,950 (220)	

* Standard deviations appear in brackets.

4. SURFACE HARDNESS

No generally accepted and all-embracing definition of hardness exists. (Haward 1949, p. 122). However, it can be defined as "the resistance to localized indentations of a surface by a standard indenter under standard conditions" (Tweeddale 1964, p. 142). The hardness is therefore a surface characteristic of a material and the many tests in existence have led to various hardness scales. The following discussion will be confined to mirco-hardness tests most frequently employed in the dental materials field. These fall generally into two groups : (i) diamond indentation tests e.g. Vickers and Knoop hardness and (ii) diamond scratch tests e.g. Bierbaum scratch

hardness. Many factors can influence the observed hardness using these tests; among the most important for a heterogeneous material such as silicate cement are surface preparation of the specimen and the load employed. Generally, when the surface consists of more than one phase, relatively high loads (above 200 gms) are used to insure that the indentation produced incorporates all phases. In this way, phase hardness differentials are averaged out and a mean hardness can be quoted. The relation of surface hardness of silicate cement to other physical properties is not entirely clear; it would appear however, to be fairly closely related to strength and possibly wear resistance, parameters which have definite clinical implications. (Swartz et al, 1963).

Ray (1934) used a scratch test employing a diamond stylus to determine the surface hardness of fully hardened silicate cement. The load applied to the stylus was not stated. He found that the matrix was much softer than the original powder particles; typical figures were 182 and 1125 respectively, which Ray termed "micro-units". Ray also observed that cements produced from "thick" mixes were appreciably harder than those produced from "thin" mixes. (Powder:liquid ratios for the mixes were not given). The hardness of the fully set cement was approximately 24% of that of enamel. (The softest surface enamel is about 1300 "micro-units"). Paffenbarger et al (1938) tested twelve silicate cements. The Knoop hardness number (K.H.N.) for one year old specimens varied from 42-79, the mean was 64. (The load used was not stated). The authors noted that the hardness of silicate cement was similar to that of human dentine, but only approx. 20% of the hardness of enamel when tested under similar conditions. These results agreed with those of Ray (1934) even though different test methods were used.

Manly et al (1951) used a Wilson Tukon tester with a 600 gms load to determine the K.H.N. of S.S. White New Filling Porcelain at one hour and one week. The one hour surface hardness was found to be approx. 95% of the surface hardness of the cement after one week, mean K.H.N.'s being 50.8 and 53.8 respectively. Swartz et al (1963) used a Tukon tester loaded at 200 gms to investigate the hardness of a number of cements at one day and one week. The K.H.N. ranges were 59-64 and 62-73 respectively. One day and one week K.H.N.'s for S.S. White New Filling Porcelain were 64 and 73, (the one day Knoop hardness was approximately 88% of the seven day Knoop hardness). In the absence of standard deviations, it appears unlikely that there is a significant difference between the one day and one week hardness values. The higher seven day results and the apparent slight decrease in rate of development of surface hardness reported by Swartz et al compared with those reported by Manly et al for this material are most likely due to the different loads used. Kent et al (1971 a and b) used a Wallace Rubber Micro Hardness tester which employed a standard Vickers pyramidal diamond loaded at 300 gms. Results were expressed as Woxen hardness numbers (W.H.N.). At nine minutes after the commencement of mixing, the W.H.N.'s for Biotrey and Super Syntrex were 28 and 17 respectively. The investigators have shown that crazing and dulling of the surface of silicate cements was closely related to several factors, among them rate of development of surface hardness. The greater the rate of development of surface hardness, the less the chance of surface disruption of the cement. The effect of compositional and manipulative variables on rate of development of surface hardness will be discussed in a following section.

CHAPTER II: DISINTEGRATION AND EROSION

INTRODUCTION:

Disintegration and erosion or "solubility and disintegration" as it has been traditionally termed is probably the most important clinical physical property of silicate cement. During the 1920's, when the material was used widely in the U.S.A., dentists noticed that silicate restorations tended to disintegrate (Huff, 1928; Black, 1928), though the rate of disintegration was extremely variable. The debate surrounding the use of silicate cement has been dealt with previously. (PART A: CH. I).

In this thesis, the terms "solubility and disintegration", "disintegration and erosion", and "dissolution" will be used synonymously. The term "specification solubility" will refer only to the observed disintegration and erosion as determined by the indirect gravimetric method.

The rationale of the specification test depends on the assumption that inferences regarding the durability of different cements in the oral environment can be drawn from the comparison of in vitro results of these cements. The use of distilled water as a solvent has been controversial. While most of the early investigators, including Voelker, 1916; Rosthj, 1929; Naeslund, 1934; and Matthews, 1935, recognised the limitations of distilled water, they used this solvent as a control, so that comparisons could be made with many other solvents known to occur in the mouth. For example, Naeslund (1934) used solvents which included distilled water, saliva, fruit juices and wines, sour milk, organic acids and solutions of citric acid buffered with sodium tartrate. Mitchem (1967) validated the use of distilled water as a test solvent, whilst Jørgensen (1962) showed that some certified cements did not perform as well as some uncertified

products under conditions which he thought more closely represented the oral environment. Stralfors and Eriksson (1969) asserted that the validity of the Amer. D.A. specification technique for determination of "solubility and disintegration" of silicate cement was questionable because distilled water lacked phosphate salts normally present in saliva. They showed that the addition of phosphate salts to distilled water dramatically reduced the "apparent solubility." Wilson and Kent (1968c) concluded that "specification solubility tests are in fact a measure of the degree of reaction" of the cement at twenty-four hours.

Bowen et al (1968) at the National Bureau of Standards attempted to correlate Amer. D.A. "solubility and disintegration" with clinical durability. A total of 74 silicate restorations using cements "A" and "B", with 24 hr specification solubilities of 1.1% and 0.4% respectively, were placed in proximal surfaces of adjacent teeth. After a period of six years, no significant difference between types "A" and "B" restorations could be detected. (There was a tendency for more of the type "A" restorations [higher solubility] to be judged in better condition than cement "B" restorations).

Thus, the problem of solvent type has not been resolved and highlights the basic limitation of many laboratory tests, namely the difficulty of reproducing the complex oral environment.

There are two basic methods of determining the disintegration and erosion of silicate cement: (i) the traditional gravimetric methods, and (ii) chemical techniques where apparent disintegration is estimated from quantitative analysis of specific ionic species eluted from the cement specimen, present in the solvent. These techniques will be referred to

as:

(i) Traditional Gravimetric Methods

a. Indirect gravimetric method (Specification solubility)

b. Direct gravimetric method (dry and wet)

(ii) Chemical Methods

Hochstrasser (1961) has also determined the disintegration and erosion of silicate cement by measuring the depth of the erosion on the surface of the specimen in a light sectioning microscope.

(i) Traditional Gravimetric Methods

a. Indirect gravimetric method (Specification solubility)

Australian, British, American and F.D.I. test methods for determination of "solubility and disintegration" are virtually identical. The "solubility and disintegration" of a silicate cement is defined as the amount of material leached from two disks (20 mm. diam. x 1.5 mm. ht) in 50 mls of distilled water after twenty-four hours. The leached material is said to be the residue left after careful evaporation of the water from the weighing bottle. "The difference between the final mass of the weighing bottle and its initial mass shall be the amount of disintegration. The gain in mass divided by the mass of the specimen, multiplied by 100, gives the percentage of disintegration." (British Standard 3365: Part I: 1969, p. 10). Results of some investigations which have employed this technique are shown in TABLE IX. TABLE IX shows that all investigators, using the indirect gravimetric method, recorded apparent weight losses in the first twenty-four hours. With the exception of Jørgensen (1963) and Sorensen et al (1970), the range of percentage weight losses listed fell within the Amer. D.A. specification limit of 1.3% (max.) reported by Paffenbarger et al (1958,).

TABLE IX: 24 HR SPECIFICATION SOLUBILITY OF SILICATE CEMENT
(INDIRECT GRAVIMETRIC METHOD)

INVESTIGATOR		DISINTEGRATION IN DISTILLED WATER (% loss by wt)		MEASUREMENT OF DISPERSION (% by wt)
		Range	Mean	
Manly et al	1951	0.80-1.03	0.95	
Correa	1955	0.7-2.0		
Norman et al	1957		0.91	
Worner, Docking	1958		0.7	
Paffenbarger, Stanford	1958	0.7-1.3	1.0	
Griffith, Ware	1960	0.35-0.70	0.55	
Rubinstein	1962	0.8-1.2	1.0	Mean Dev. 0.03-0.07 ($\bar{x}$ 0.05)
Jørgensen	1963	0.4-4.2	1.1	
Norman et al	1963	0.4-0.5	0.4	
Mueller et al	1967	0.6-1.2	0.7	
Mitchem	1967	0.48-0.56	0.53	Mean Dev. 0.04-0.10 ($\bar{x}$ 0.06)
Eichner, Dressler	1967	0.37-0.59		
Eichner et al	1968	0.5-1.0	0.7	
Swartz et al	1968	0.94-0.97	0.96	
Norman et al	1969		1.3	
Sorensen et al	1970	0.8-1.7	1.3	
		MEAN	0.87	

(The second revision in 1963 now limits maximum "solubility and disintegration" to 1.0%). The high weight loss (4.2%) reported by Jørgensen (1963) was due to the uncertified material Terralux (Zahn-Porzellan, K.G., Hamburg). The 1.7% weight loss reported by Sorensen et al (1970) was caused by mixing certified cements at decreased powder:liquid ratios. Despite these inflated results, the average specification "solubility and disintegration" for all studies was approximately 0.87%. Current specifications require a maximum "solubility" of 0.8 - 1.0%. As with TABLE VII, measurements of dispersion of results were rare. Rubinstein (1962) and Mitchem (1967) reported average mean deviations of 0.05 and 0.06 per cent respectively.

The observed specification solubility is increased when cements are immersed in distilled water for periods in excess of 24 hours. The seven day specification solubility has been reported by a number of workers and is shown in TABLE X.

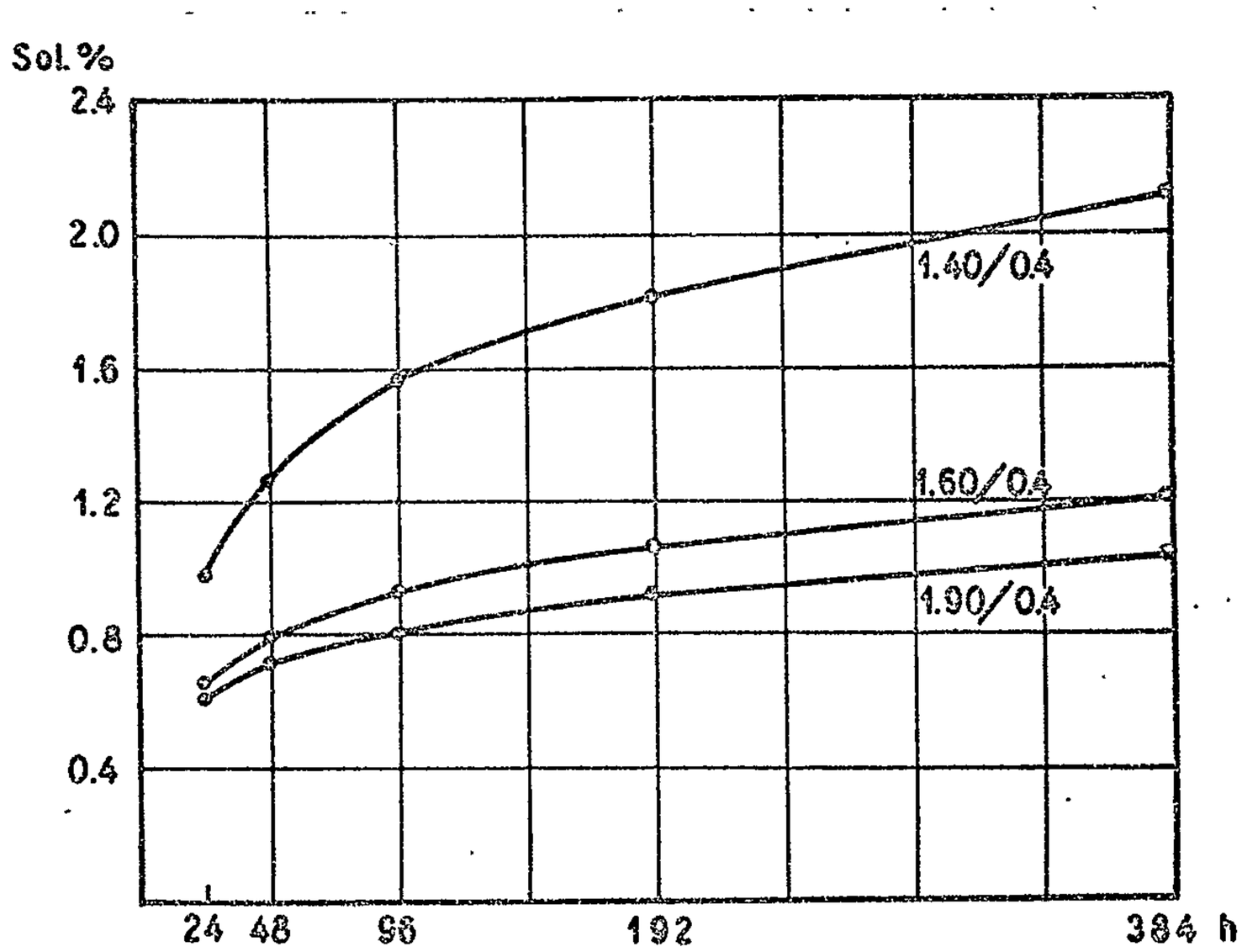
TABLE X: 7 DAY SPECIFICATION SOLUBILITY OF SILICATE CEMENT

INVESTIGATOR		DISINTEGRATION IN DISTILLED WATER (% loss by wt)		MEASUREMENT OF DISPERSION (% by wt)
		Range	Mean	
Paffenbarger et al	1938	0.6-5.0	2.4	
Worner	1940	0.13-5.00	1.60	
Norman et al	1963	1.24-3.40	2.22	
Eichner et al (8 days)	1968	0.7-1.7	1.2	
		MEAN	1.86	

Disintegration and erosion does not increase proportionately with time. After the first day, there is a marked decline in rate of disintegration. Jørgensen (1963) made a close study of this phenomenon and found that the rate of disintegration decreased not only when the water was left unchanged during the test period but also when fresh water was introduced daily. However, the retardation was less when the water was changed than when it was left undisturbed. His results are shown in Figs. 11 and 12. Similar results were obtained by Norman et al (1957) and Eichner et al (1968).

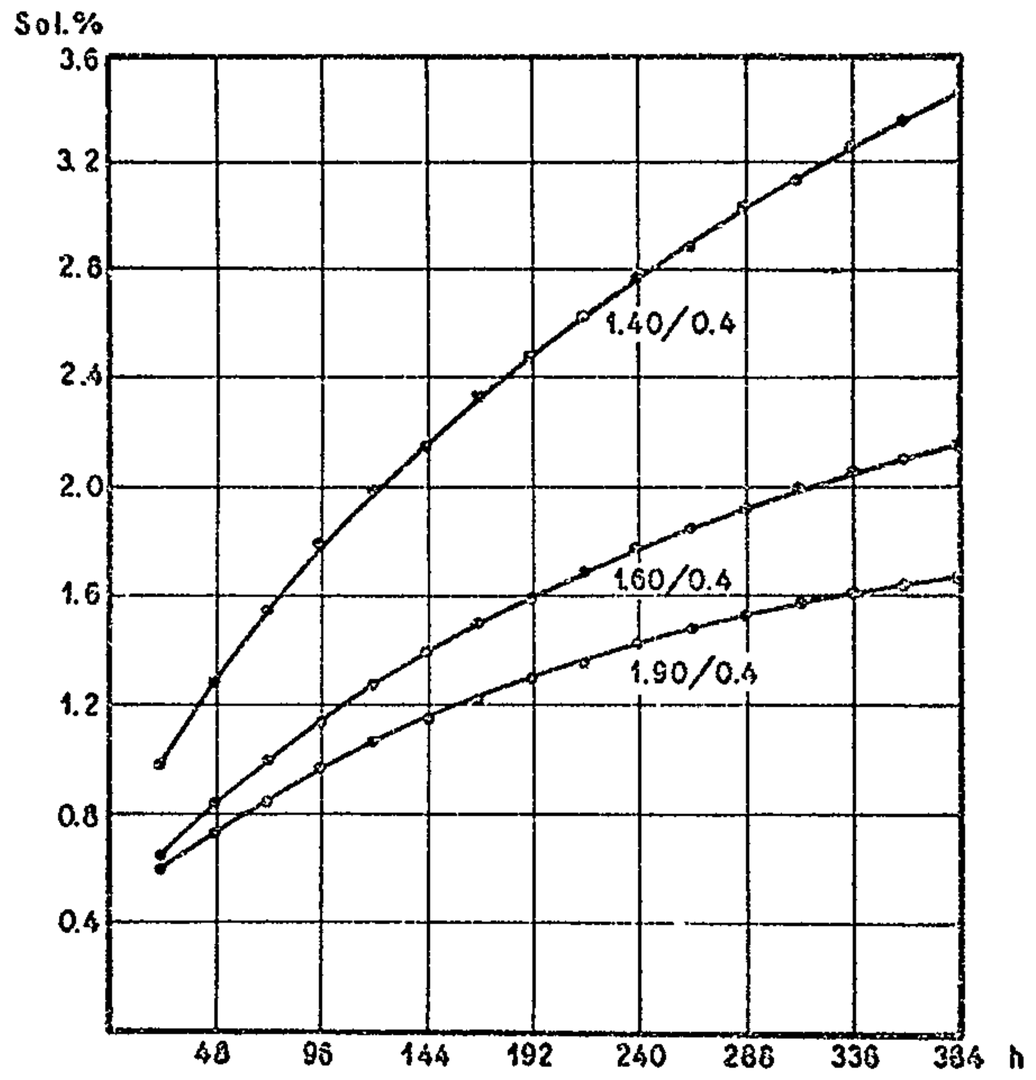
Fig. 11: Specification solubility for Super Syntrex over a 16 day period (384 hrs.)

The water was not changed during the experimental period. The different powder:liquid ratios are shown, the middle curve represents a mix of standard consistency.



(From Jørgensen, 1963)

Fig. 12: As above, but water changed daily



(From Jørgensen, 1963)

Time elapsing from the start of the mixing procedure to the immersion in water may be called the specimen age or pre-immersion time, tp. The effect of this period on disintegration has been investigated by Jørgensen (1963) and Wilson and Batchelor (1967b). From their results, it appears that the rate of disintegration decreased when the specimen age was increased. This effect was especially strong for the first hours of specimen age and it has important clinical implications which will be dealt with in CH. III.

(i) b. Direct gravimetric method

Determination of disintegration and erosion by direct weighing of the specimen before and after the "solubility" test has been employed by many of the early investigators. In the more popular "direct dry" technique, the weight of the specimen before and after immersion in the solvent is noted. (The final weight of the specimen is taken as the constant weight achieved

after careful evaporation of the solvent and subsequent drying of the specimen). The disintegration and erosion is defined as the direct apparent weight loss of the specimen. This method has been used by Voelker (1916), Matthews (1935), and more recently by Stralfors and Eriksson (1969). That the results are quite variable, is basically due to the different surface areas of the specimens employed and to the different experimental times involved. However, all studies report apparent weight losses. This is not surprising, as it is almost certain that some free and perhaps bound water (water of hydration of the phosphate salts) is driven off in the drying process. For example, Stralfors and Eriksson dry the silicate cement disks to constant weight at 110°C.

The "direct wet" gravimetric technique has been employed by Manly et al (1951) and Jørgensen (1963). The solvents used in both studies were buffered organic acids. The results of these experiments will be considered in a later section.

(ii) Chemical methods

Norman et al (1957) were among the first investigators to use analytical chemical techniques to determine the "products of dissolution" of silicate cement in various organic solvents. Using mass spectrographic analysis, they showed that the major constituents of the leach included "large quantities of silica as well as lesser amounts of phosphorus, aluminium, calcium, magnesium, zinc and fluoride." Brauer et al (1958) employing a spectrochemical technique, found that the major ionic species eluted were sodium, phosphorus and aluminium. Mannerberg and Bratthal (1968) placed young cement disks (tp = 15 mins) in 50 mls of redistilled water for one hour, the disks were subsequently placed in fresh 50 mls solutions for

three hours, then twenty hours, and finally for twenty-four hours. The total phosphorus leached from the unprotected disk after the forty-eight hour period was determined by means of a flame spectrophotometer. The range, expressed as mg. phosphorus/100 mls distilled water, was 9.9-16.3 (mean 14.0).

Wilson and Batchelor (1967a) used analytical techniques to determine the various ionic species eluted from silicate cement. "Phosphate was determined photocolorimetrically as molydenum-blue (Riley, 1958); a similar method was used to determine silicate (Wilson, 1963). These were the most frequently determined ionic species. Sodium and calcium were determined with a flame spectrophotometer and aluminium by a spectrographic arc technique. Zinc was determined polargraphically, using phosphoric acid as the base electrolyte (Milner and Slee, 1957), and fluorine was determined by the well-known (sic) distillation method. (Willard and Winter, 1933)". Results obtained from some commercial products are shown in TABLE XI. The major ionic species eluted from these cement systems were P_2O_5 and Na_2O and agreed with the results of Brauer et al (1958).

Wilson and Batchelor (1967a) showed that elution of various ionic species occurred at different rates over a three week period. After a period of three months in distilled water, the only ionic species eluted in significant amounts were silicate and fluoride. These results are shown in Figs. 13 and 14.

TABLE XI: MATERIAL LEACHED INTO SOLUTION FROM CEMENTS DURING INITIAL 24 HRS IN WATER (37°C, pH 5·7 tp = 65 MINUTES

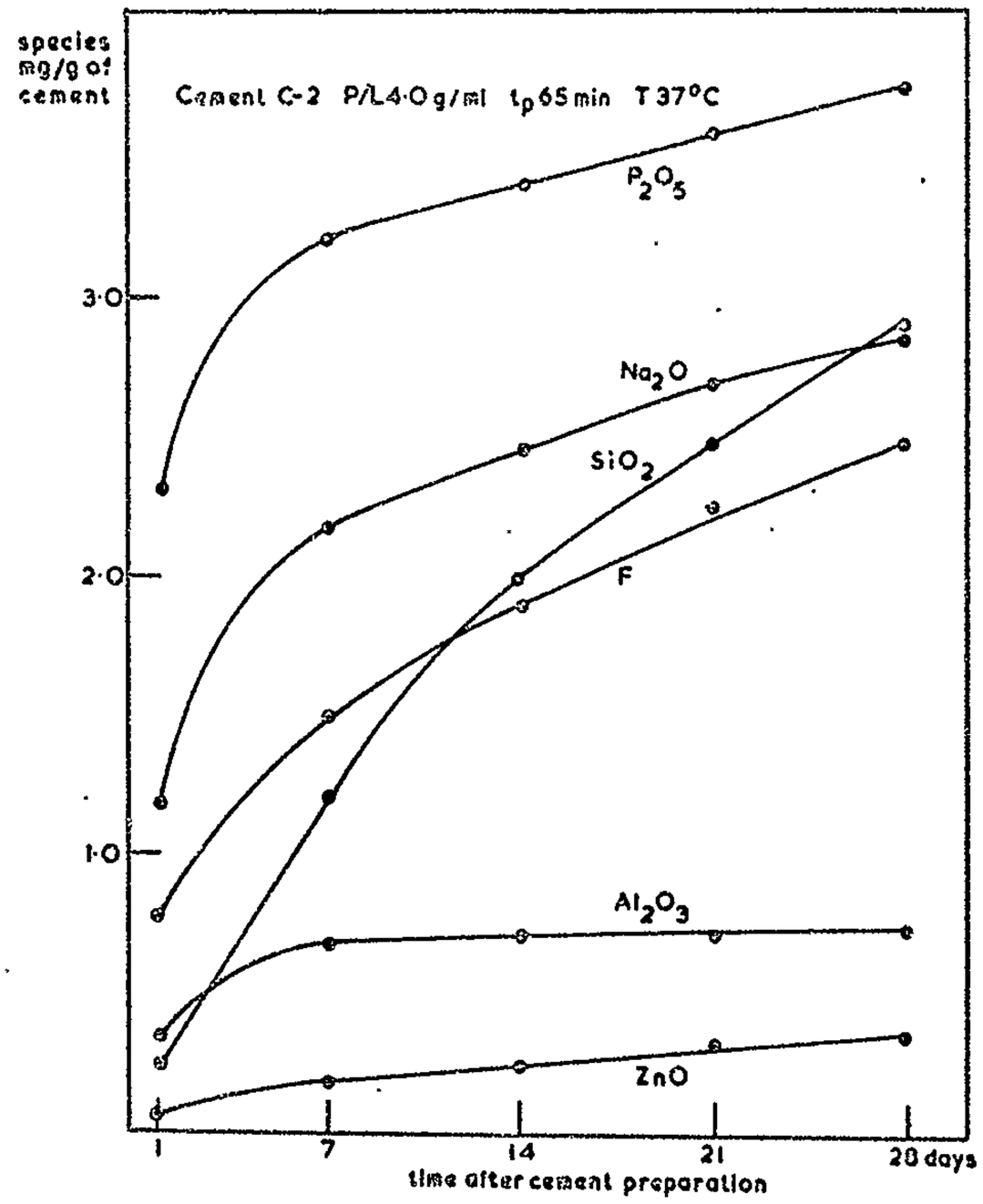
	Cement					
	C-2	C-4	C-6	C-8	C-11	C-19
P/L (Gm./ml.)	4.00	3.75	4.25	3.50	2.75	3.50
pH of eluate	5.7	5.8	5.8	5.5	5.1	5.8
Species (mg. eluted per Gm. cement)						
SiO_2	0.28	0.37	0.20	0.70	1.58	0.64
Na_2O	1.54	1.75	0.90	1.69	15.0	0.59
F	0.71	0.63	1.67	1.61	1.42	1.28
Al_2O_3	0.36	0.45	0.95	1.15	1.70	0.45
ZnO	0.09	0.17	0.25	0.37	0.06	0.15
CaO	0.02	n.d.	0.10	0.01	—	0.07
BeO	—	—	—	—	—	0.20
P_2O_5	2.47	2.80	1.38	3.32	31.6	1.22
H_2O*	0.62	0.70	0.35	0.84	8.0	0.31
	6.09	6.87	5.80	9.69	59.4	4.91
Less O for F	0.30	0.27	0.70	0.67	0.7	0.54
Calculated solids	5.79 (0.58%)	6.60 (0.66%)	5.10 (0.51%)	9.02 (0.90%)	58.7 (5.9%)	4.37 (0.44%)
Solids found	0.6%	0.6%	0.4%	0.9%	5.8%	0.4%

*Calculated H_2O associated with phosphate, assuming it to be present in the diacid form.

(From Wilson and Batchelor, 1967a)

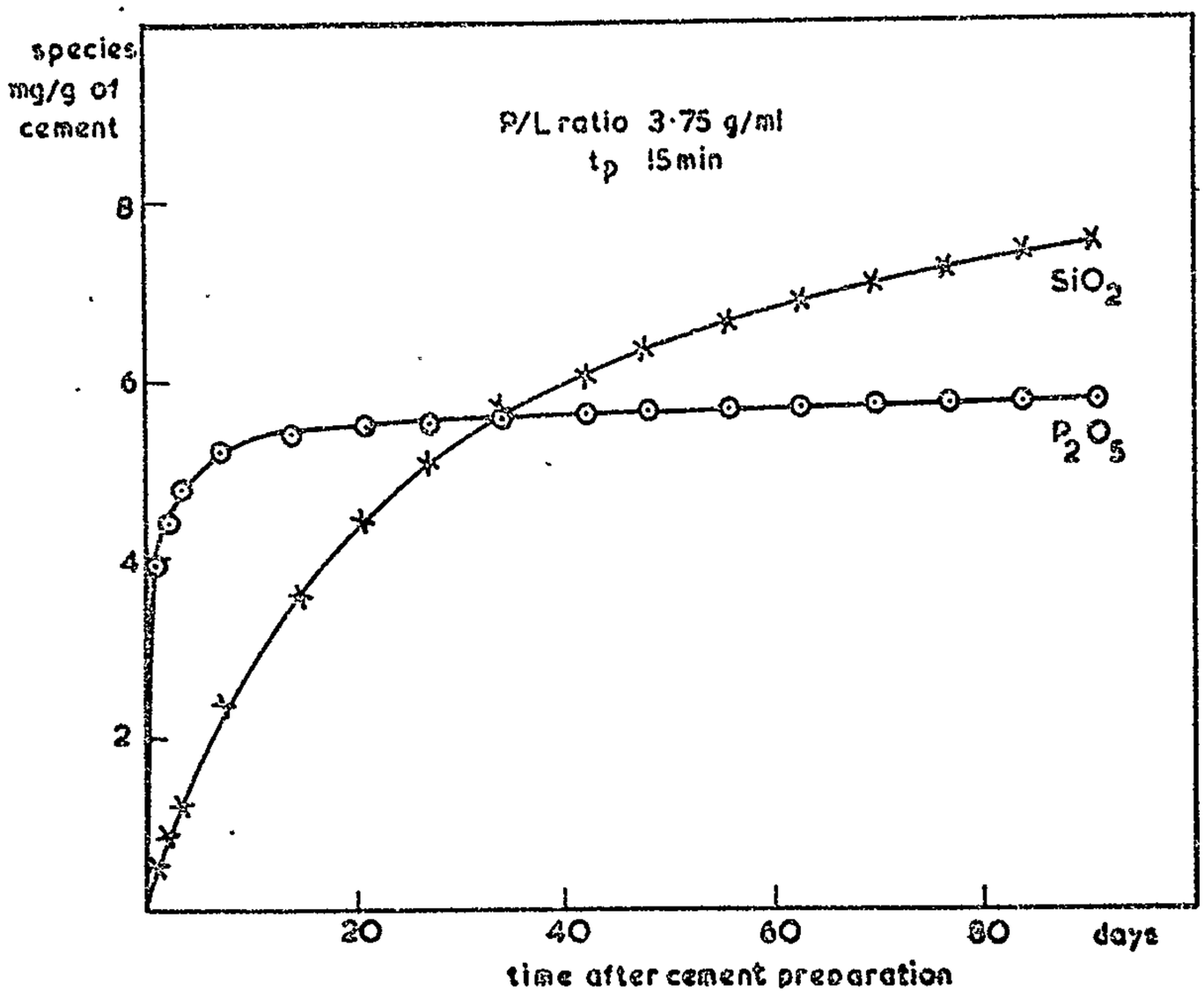
C-2 SUPER SYNTREX, Amalgamated Dental Co. Ltd, London
C-4 NEW FILLING PORCELAIN, S.S. White Dental Manuf. Co. (G.B.) Ltd, London,
C-6 ACHATIT, Vivadent, Schaan, Liechtenstein
C-8 TRUE SHADE, Dental Fillings Ltd, London
C-11 TERRALUX ULTRA, Zahn-Porzellan K.G., Hamburg
C-19 DIAFIL, Pfingst and Co., Inc., New York, N.Y., U.S.A.

Fig. 13: The elution of various ions from a dental silicate cement disk (Super Syntrex, P/L 1.6 gm/0.4 mls) into water (37°C, pH = 5.7) during a 3 week period after preparation. Solutions (50 mls) were changed 1, 7, 14, 21 and 28 days after initial immersion of the cement.



(From Wilson and Batchelor, 1967a)

Fig. 14: The erosion of a dental silicate cement in water (37°C, pH = 5.7) during a 3 month period, as measured by the elution of phosphate and silicate from a cement disk (New Filling Porcelain, P/L 1.5 gms/0.4 mls). Solutions (50 mls) were changed 1, 2, 3, and 7 days after initial immersion (tp = 15 minutes) and thereafter at weekly intervals.



(From Wilson and Batchelor, 1967a)

From Fig. 14 it can be concluded that "the final dissolution of dental silicate cements in water (pH = 5.7) was extremely small. The only matrix-forming species going into solution was silica; the elution of phosphate dropped to negligible proportions. Clearly, the phosphate part of the gel matrix is almost insoluble in water (pH = 5.7). Under similar conditions of pH, dental silicate cement restorations should last indefinitely. Causes for failure must be sought elsewhere.

The small but significant amount of fluoride that continues to go into solution even after three months may explain the caries-preventive properties of these materials.

The small amounts of ionic material eluted after three months, which varied little between cements, supported the view that erosion in near neutral conditions is a simple washing out of soluble reaction products" (Wilson and Batchelor, 1967a). That "erosion in near neutral conditions is a simple washing out of soluble reaction products" is of fundamental clinical importance and explains the longevity of some silicate restorations. Compositional and manipulative variables are closely associated with this effect and will be discussed in CH. III.

DISINTEGRATION IN ACID SOLVENTS

The effects of acid solvents on disintegration and erosion of silicate cement have been well documented by investigators who have used previously mentioned experimental techniques. Generally, it has been found that silicate cement is more soluble in acid solvents than in distilled water. It has been shown in PART A: CH. IV that this fact stimulated Wilson and his associates to think of the gel matrix in terms of phosphate chemistry.

Henschel (1949) observed the pattern of disintegration of several thousand silicate cement restorations over a period of twenty years. He strongly advocated the theory that disintegration and erosion was caused by the acid environment produced by dental plaque. He noted that restorations were eroded in "stagnant areas" not washed by saliva and emphasized the effect of environmental factors such as buffer capacity of saliva, amount and frequency of carbohydrate ingestion and relative oral hygiene on the durability of silicate restorations. Darnutzer (1951) shared these views as did McLean, who, in a written communication to Wilson and Batchelor (1968a), reported that the respective failure rates for Cl. V and Cl. III restorations were 22.0% and 5.3%. McLean contended that Cl. V restorations

occurred in areas more susceptible to plaque formation and mechanical abrasion.

The observed disintegration and erosion is affected by many variables and these must be considered before a true comparison of test results is possible. These factors include:

(i) pH of solvent

(ii) molarity of solvent

(iii) type of organic acid

(iv) age of specimen before immersion

(v) surface area of specimen exposed to solvent

(vi) volume of solvent and if changed, how often

(vii) temperature of solvent

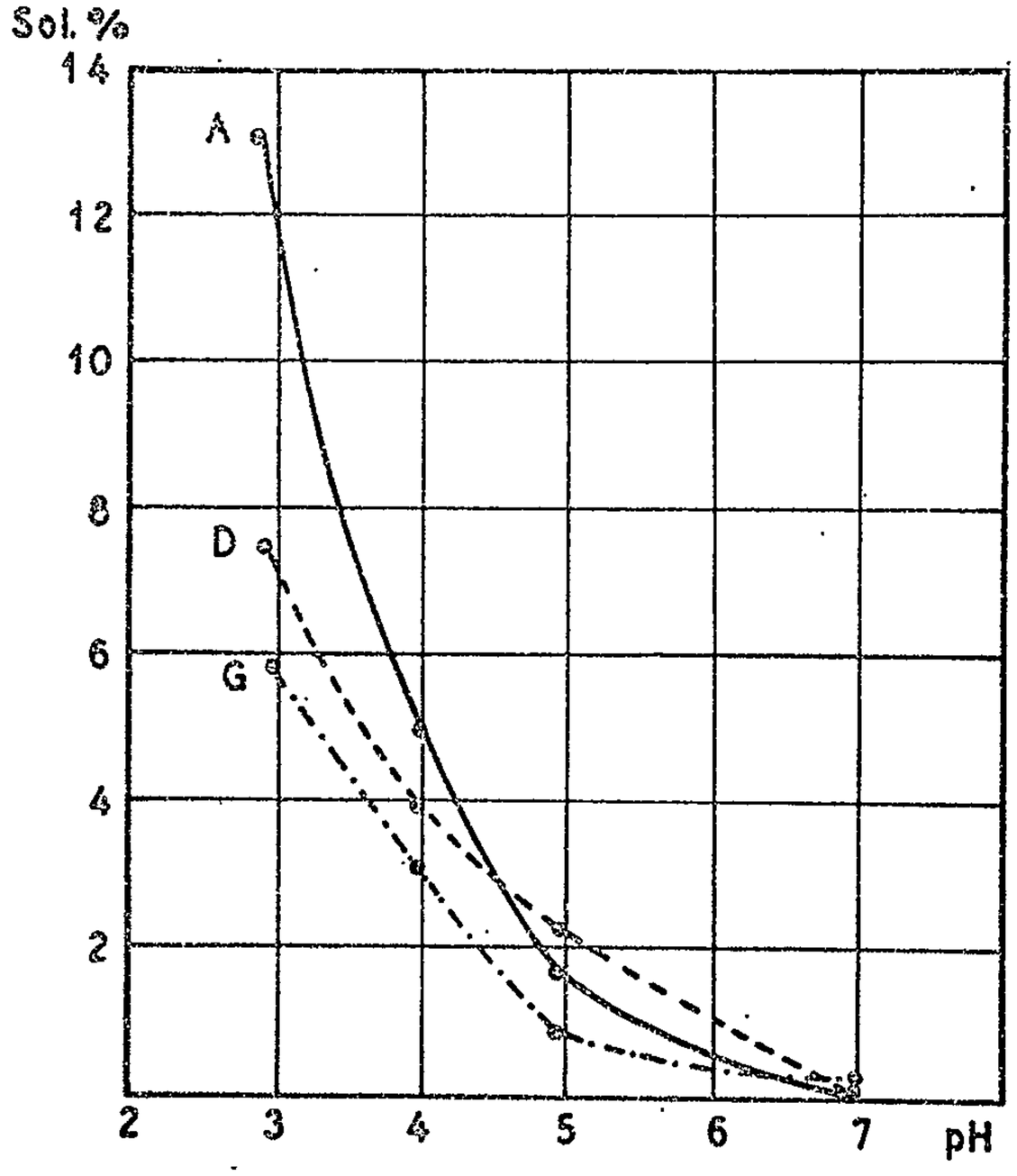
(viii) time of immersion.

The first three variables are particularly relevant when considering cement durability in acidic conditions.

Manly et al (1951) have attempted to determine disintegration and erosion of silicate cement in acid solvent using a "direct wet" technique. The solvent employed was a volatile buffer of ammonium acetate-acetic acid at pH 4.0 (molarity and solvent volume were not stated). "The disks were immersed in acid for a period of time, then removed, and blotted with a wet chamois. It was surprising to find that the disks constantly gained in weight, suggesting that the disks were expanding and absorbing water..... An explanation of the weight increase in the acid cannot be offered at this time." (Manly et al, 1951). When these investigators used the "indirect" gravimetric method, the values for disintegration and erosion of the control

cement in the acidic solvent and in distilled water were 3.40% and 1.03% respectively. Jørgensen (1963) also used the "direct wet" technique for determining disintegration and erosion of silicate cement. "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." (Jørgensen, 1963). Jørgensen employed a 0.2M conc. of sodium lactate buffer at pH ranges from 3-7. His results are shown below in Fig. 15. "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 or D, but was less soluble than these cements when tested in an acidic solvent. 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 cast doubt on the clinical relevance of the Amer. D.A. specification for 'solubility and disintegration'. Undoubtedly it would be more expedient to study the dissolution of silicate cement in environments more biologically appropriate than distilled water." (Jørgensen, 1963).

Fig. 15: 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.



(From Jørgensen, 1963)

*A - Achatit Biochromatic, Etablissement Vivadent, Liechtenstein
B - Super Syntrex, De Trey Bros. S.A., Zurich
G - Diasilic, Jota Dental u. Schleifmittel - GMBH, Dusseldorf.

Norman et al (1957, 1959, 1963), Jørgensen (1963), Wilson and Batchelor (1968a) and Stralfors and Eriksson (1969) have also examined the effect of pH and molar concentration of the solvent on the observed disintegration and erosion of silicate cement. All show that disintegration increased with increase in molarity and decrease in pH. Results of Stralfors and Eriksson (1969) are shown below in TABLES XII, XIII and XIV.

TABLE XII: 24 HR DISINTEGRATION AND EROSION OF SYNTREX : COMPARISON OF WATER AND LACTATE BUFFER pH 4.0

MEDIA: Water and lactate buffer, 0.2M pH 4.0	SOLVENT (6 specimens/750 mls)	
POWDER/LIQUID RATIO : 1.44 gm/0.4 mls	WATER	LACTATE BUFFER
Number of Specimens	6	6
Average disintegration mg/cm^2	0.8	36.4
Stand. Dev. of the average	0.04	0.5

TABLE XIII: 24 HR DISINTEGRATION AND EROSION OF SYNTREX IN LACTATE BUFFER: EFFECT OF pH

MEDIA: Lactate buffer 0.2M of pH values 4.0, 5.0 and 6.0	LACTATE BUFFER (6 specimens/750 mls)		
POWDER/LIQUID RATIO : 1.44 gm/0.4 mls	pH 4.0	pH 5.0	pH 6.0
Number of Specimens	6	6	6
Average disintegration mg/cm^2	45.9	18.2	4.5
Stand. Dev. of the average	0.34	0.11	0.15

TABLE XIV: 24 HR DISINTEGRATION AND EROSION OF SUPER SYNTREX IN LACTATE BUFFER : THE EFFECT OF BUFFER CONCENTRATION

MEDIUM: Lactate buffer, pH 4.0	MOLAR CONCENTRATION OF BUFFER (6 specimens/750 mls)					
POWDER/LIQUID RATIO : 1.44 gm/0.4 mls.	0.001	0.003	0.01	0.03	0.1	0.3
Number of Specimens	6	6	6	6	6	6
Average disintegration mg/cm^2	2.6	4.2	6.2	13.4	30.8	52.5
Stand. Dev. of the average	0.18	0.17	0.21	0.13	0.69	0.48

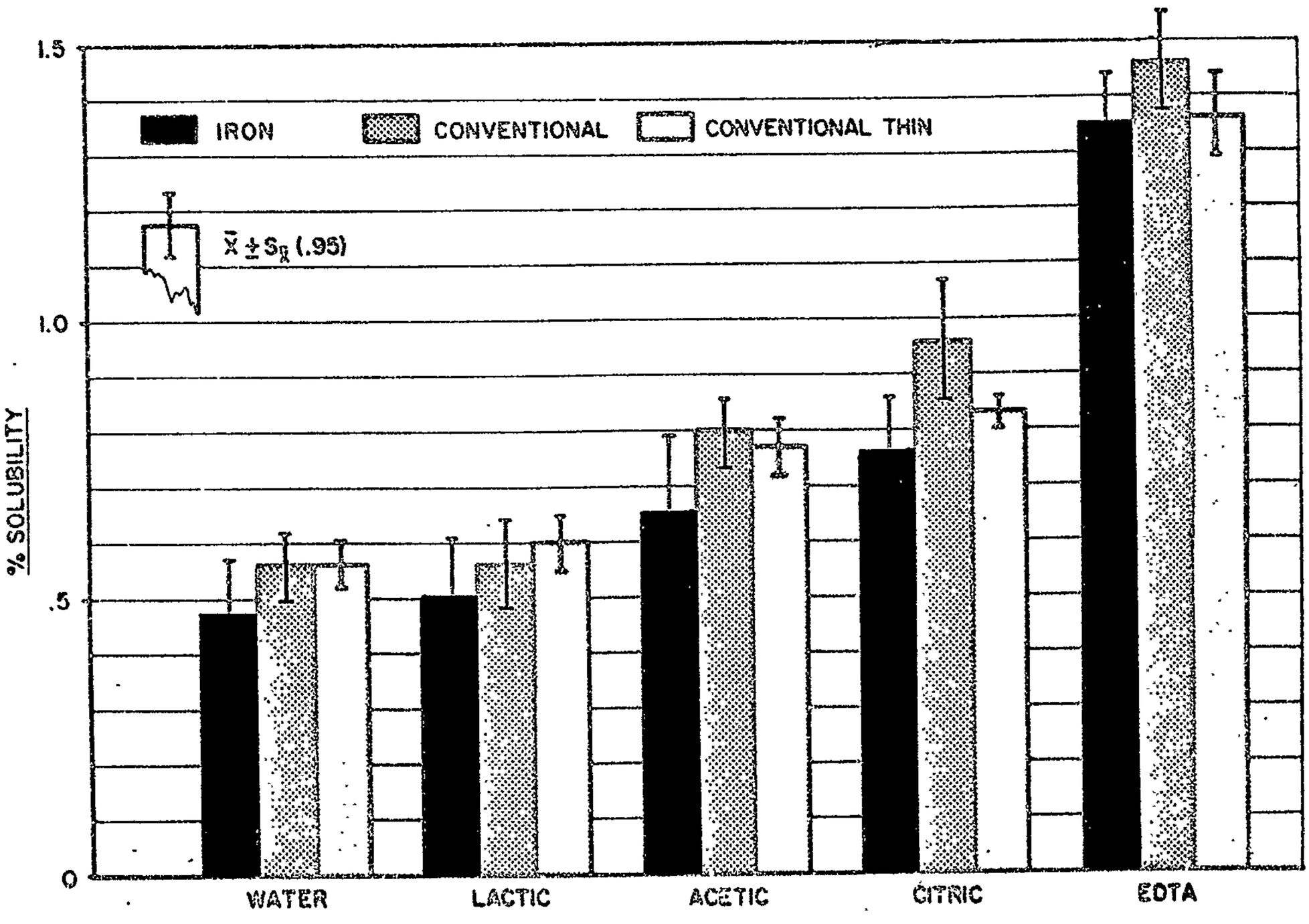
(From Stralfors and Eriksson, 1969)

The effect of organic acid type has been well established. Naeslund (1933) noted the severe deleterious effect of citric acid. Norman et al (1957, 1959, 1963), using very weak buffer solutions (0.001M), noticed a marked "solubility in citric acid, yet the disintegration in acetic and lactic acids was not greater than in water. Mitchem (1967) stated that the "solubility" increased in the order - lactic acid, acetic acid, citric acid and EDTA (0.001M). Wilson and Batchelor (1968a) studied the disintegration in 0.01M solutions as measured by the elution of phosphate and silicate from cement disks. They found that acetic acid was less harmful than pyruvic or lactic acids. Citric acid, which has a complex forming ability, was by far the most aggressive test medium and this was consistent with their hypothesis that the major constituents of the gel matrix were phosphates. Eriksson (1970b) corroborated these findings.

Mitchem (1967) suggested from results shown in Fig. 16 that, "if it

is assumed that the predominate acid in the dental plaque is lactic acid and it is this acid which causes the majority of the solubility of a silicate restoration, then the fact that the solubility of silicate cement is the same in lactic acid and distilled water is of practical interest. The reason for this is that distilled water provides a more stable and convenient solvent to use in the laboratory as well as being the solvent used in the present Amer. D.A. specification test (No. 9) for silicate cement."

Fig. 16: The influence of insertion technique and solvent (0.001M) on the "solubility" of S.S. White New Filling Porcelain



(From Mitchem, 1967)

It must be noted that very weak buffer solutions were used (0.001M). "The buffer capacity of dental plaque is high. Stralfors (1948) found that the amount of acid required to lower the pH values of plaques to 5.0 varied

from 0.03M - 0.09M. The acid required to reach a pH value of 4.0 varied from 0.08M - 0.17M. For approaching the conditions in the dental plaque the range of concentrations from 0.03M - 0.20M should be applied in dissolution experiments." (Stralfors and Eriksson, 1969).

From this evidence it would appear that a more accurate estimation of clinical performance could be obtained by using an organic acid solvent in the molar concentration range recommended by Stralfors and Eriksson (i.e. at a molar concentration related to the typical buffering capacity of dental plaque). "Many kinds of acids have been identified in the dental plaque and it seems probable that different acids are produced from different foods. Individual differences might thus be expected. The quantitative proportions of the acids have not yet been completely ascertained. It therefore seems difficult to design a test for silicate cement which is adequate for mouth conditions." (Eriksson, 1970b). It must also be remembered that acids, such as citric and tartaric, though not produced by plaque bacteria, are present in several acid foods (e.g. citrus juices, acid beverages, and fruits).