THE CHEMICAL STRENGTHENING OF DENTAL PORCELAIN

Thesis submitted to the University of Sydney as a requirement for admission to the degree of Master of Dental Surgery

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Peter Harold Adair, B.D.S., 1971
ACKNOWLEDGEMENTS

I wish to express sincere appreciation to my supervisor, Dr. D.E. Southan, for his guidance in conducting this investigation.

I would also like to thank Miss J. Dunstan and Miss B. Bischoff who assisted in the technical aspects of the presentation of this thesis.
PREFACE

The development of modern dental porcelain from traditional whiteware materials has been determined primarily by requirements for fine aesthetic qualities. Over the years, dental porcelain became more glass-like, so that the highly aesthetic translucent materials of today are predominantly vitreous. As such, dental porcelains, in common with other glasses, have had some disappointing deficiencies, particularly in regard to their durability.

So impressive has been the failure rate of porcelain jacket crowns in the mouth, that many dentists seem to have virtually discarded this type of restoration in favour of porcelain fused to metal crowns. However, the concept of a porcelain jacket crown has so many desirable features that efforts were made to correct the strength deficiencies of this type of restoration, and so make it acceptable for wider use.

Southan, in 1968, presented a method for strengthening dental porcelain by low temperature ion exchange, and it was this method upon which the present work has been based.

It is not our aim to make porcelain jacket crowns which will never break. Such an achievement is not likely, nor is it desirable. The fracture of a crown as a result of excessive stress may be an important 'safety valve' to prevent irreparable damage to the teeth themselves. Our purpose is, however, to produce porcelain jacket crowns which the dentist can use with confidence, perhaps in situations where he would not have previously thought them feasible.
(ii)

All of the experimental work described in this thesis was carried out by me in the Department of Operative Dentistry within the University of Sydney.
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PART A

REVIEW OF LITERATURE

I DENTAL PORCELAIN

1. INTRODUCTION

Porcelain was first produced in China more than twelve hundred years ago. Most of this original material was made from kaolin (white china clay) and petuntse, a feldspathic rock (Southan, 1970a).

In 1774 a French chemist, Duchateau, having seen the dentists of the time using carved ivory, ox bones and hippopotamus tusks to replace human teeth, conceived the idea of making artificial teeth of porcelain (Lee, 1961, p.68). A porcelain manufacturer in Paris constructed a denture of porcelain teeth for Duchateau.

By 1788 the process had been improved by Dubois de Chemant, a Paris dentist, who then obtained a patent to manufacture porcelain teeth. These teeth apparently were of one colour. (Capon, 1927).

Dubois Faucon conducted the first recorded experimental investigation into the colour problem in porcelain and published his results in 1808.

Also, in 1808 an Italian dentist Guiseppangelo Fonzi invented porcelain teeth with small platinum hooks so that they could be fastened to a denture base. (Capon, 1927).

In 1838 Elias Wildman produced a translucent porcelain that
would more closely reproduce the colours of natural teeth. Prior to this, dental porcelain was an opaque white material, similar to that then used in industrial ceramics (Clark, 1939).

An American, Charles H. Land conceived the use of platinum foil as a matrix for constructing porcelain restorations. In 1902 he presented a method for constructing an all-porcelain jacket crown, and this method is the one we use today (Clark, 1939).

Since these times, development of dental porcelain has proceeded as an art, based on empirical observation, till today we have porcelains with excellent aesthetic properties. This development has been achieved by the porcelain manufacturing companies, who jealously guard their specific information so as a result, little has been known about this highly specialised industry.

In 1949 vacuum firing of porcelain teeth was introduced by the Dentist's Supply company of New York. This method produced a beautiful, dense and translucent porcelain.

As a result of all these advances, dental porcelain restorations were produced which were aesthetically and biologically acceptable. However, strength of the material remained a problem. Porcelain restorations had to be placed in ideal situations to survive masticatory stresses. There is currently a revival of interest in dental ceramics, with investigations into methods of solving the strength problem of these materials.

The work presented in this thesis is a further investigation
into the method of strengthening dental ceramic materials by ion exchange, first presented by Southan in 1968.

2. **COMPOSITION**

2.1 **Composition of Porcelain**

Modern dental porcelains have evolved from the triaxial whiteware formula, clay/feldspar/quartz, although they are themselves not typical whiteware materials (Southan, 1970a).

Typical hard porcelain for domestic and laboratory ware nearly always has the green (unfired) composition of about 50 per cent kaolin, 25 per cent quartz and 25 per cent feldspar (Salmang 1961, p. 329).

**Kaolin**

Kaolin, which is a finely particled hydrous alumino-silicate \((\text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_2\text{O})\) performs two important functions in ceramic bodies. First its characteristic plasticity, owing to its layer-lattice structure, is basic to many of the forming processes commonly used (Lee 1961, p.11). Secondly, it fuses over a temperature range to become dense and strong without loss of shape (Kingery 1963, p.18).

The kaolin also is directly responsible for the formation of needles of mullite \((3\text{Al}_2\text{O}_3.2\text{SiO}_2)\) during firing of the porcelain article (Salmang 1961, p.335). Kaolin is the only constituent of the green ware with sufficient alumina to develop these crystals (Morey, 1934).
Kaolin content of the porcelain is primarily determined by requirements for forming the article. More difficult forming techniques require increased kaolin content. As feldspar is replaced by kaolin higher temperatures are required for vitrification, and the firing process becomes more difficult and expensive. However, the forming processes become easier and mechanical properties of the ware are improved (Kingery 1963, p.418).

Feldspar and Feldspathoids

Feldspar and nepheline syenite are the commonly used fluxes providing the glassy phase of classical porcelain bodies (Lee 1961, p.16) The amount may be as low as 10 per cent in porous bodies, and much higher in dense and glassy ones. These materials form the bond in ceramics.

Feldspars are solid solutions of anhydrous aluminosilicates containing K⁺, Na⁺, Ca²⁺ and Ba²⁺. As the main constituent of igneous rocks they are abundantly distributed throughout the world (Lee 1961, p.17). Those feldspars of major commercial interest are - potash feldspar (orthoclase and microcline), K₂O.Al₂O₃.6SiO₂; soda feldspar (albite) Na₂O.Al₂O₃.6SiO₂; and lime feldspar (anorthite) CaO.Al₂O₃.2SiO₂. Potash feldspar crystallises in the monoclinic form as orthoclase and in the triclinic form as microcline. Albite and anorthite crystallise in the triclinic...
form (Insley and Frechette 1955, p. 61). The potash feldspars always contain some albite, and the soda feldspars some anorthite.

High grades of feldspars are produced in Europe, especially in Norway and Sweden. With the absence of rich native sources of feldspars in North America, nepheline syenite is widely used. This is an igneous rock resembling granite, and containing little or no free quartz. It is comprised of about 50 per cent albite, 25 per cent microcline, and 25 per cent of the feldspathoid nephelite \((\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)\) (Lee 1961, pp. 16-17).

Because of its high viscosity at the 'melting point', feldspar melts without loss of shape; only on overheating do the edges of a specimen become rounded by flow. The feldspar glass is capable of dissolving appreciable amounts of quartz and clay, and then forms the matrix of the porcelain body (Salmang 1961, p. 173).

**Quartz**

Some form of silica has been almost invariably present in ceramic bodies. In the earliest days it was probably present as a fortuitous impurity. Silica is the principal non-plastic, crystalline portion of the classical ceramics, giving strength to the unfired body.

Pure quartz confers a high degree of translucency on the porcelain, and is for this reason greatly valued
for high quality domestic porcelain (Southan 1970a).

During firing of the ware, the behaviour of silica is characterised by solution effects with other constituents and by its transformations. Solution of the quartz is a slow process. Receiving alkali and probably alumina from the feldspar, quartz grains fuse about their borders, giving a clear solution rim of high silica glass around each grain (Southan, 1970a).

An important property of quartz is its inversion from $\alpha$ (high) to $\beta$ (low) form. This inversion occurs at 573°C and involves a change in crystalline species, with a rapid change in length of about 0.2 per cent. This is a reversible change (Salmang 1961 p.164). This rapid volume change of quartz grains within the porcelain may cause cracking of the glassy matrix as the ware is cooled past the inversion temperature.

2.2 Dental Porcelain

In the evolution of modern dental porcelain from the traditional triaxial whiteware materials, changes have been determined by requirements for forming and firing the article requirements for final properties, and by economic considerations (Southan 1968, p.55).

Dental porcelains are required to be formed only into small and simple shapes, so plasticity of the green ware
is relatively unimportant and drying shrinkage is undesirable. Also, a high degree of translucency is required for dental ceramics. For these reasons a high feldspar - low clay composition is indicated.

Opacification of porcelain is caused by diffuse scattering of light, so that anything which reduces interfaces in a body will increase its translucency. Mullite crystals, being small and with refractive index greatly different from the glassy matrix, will opacify porcelain bodies most efficiently. By increasing the feldspar and decreasing the kaolin content of dental porcelain the mullite phase is reduced, and so translucency is enhanced.

Because the demand for translucency precludes the incorporation of much kaolin, dental porcelain has feldspar as its major ingredient. This was shown by Hodson (1957, 1959b) who examined 12 porcelain powders including high-medium - and low-firing forms of body, opaque, translucent and enamel types. Two of the high-fusing porcelains consisted of raw minerals, while the others contained glassy particles, some associated with mineral grains. Microcline, albite and quartz crystals were identified. Quartz was found only in small quantity (Hodson 1959b). In one low-fusing body porcelain powder she noted needles of mullite in feldspar pseudomorphs. The predominant phase found over all was glassy.
Dental porcelain powders can be supplied in the fritted or unfritted form, or as a mixture of the two forms. Fritting is carried out by melting the raw batch constituents to form a glass which is quenched and finally reduced to the desired particle size by grinding. Fritted porcelain has several advantages over the unfritted type — the fired article has greater homogeneity, higher translucency, a smoother texture and a lower fusing temperature. (Lee 1961, p. 73).

At its firing temperature molten glass attacks, and eventually destroys, any pigment in the material. Since colour matching is important in dental ceramics, low-temperature, short-time firing schedules are desirable. Introducing the pigment at a late stage in the fritting operation means that it will not be subjected to high temperatures for long periods, and so will be more stable in the ware. Colour and translucency in dental ceramics have also been standardised by vacuum-sintering (Gatzka, 1953).

Lee (1961, p. 74) has given typical formulae for compositions of fritted enamel and body porcelain.

<table>
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<tr>
<th>Ingredients</th>
<th>Enamel %</th>
<th>Body %</th>
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<tr>
<td>Feldspar</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>Calcined Kaolin</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Silica</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>
These are apparently representative of American dental porcelain. Further minor constituents which may be added include alumina, tin oxide, zirconium oxide to induce opacity. Borax, boric acid, sodium carbonate, flourspar, lithium carbonate and zinc oxide are used as fluxing materials. The use of these fluxes appears to be unnecessary when a fritted high-albite or nepheline syenite composition is used. Metallic oxides of titanium (TiO₂), iron (Fe₂O₃), copper (CuO), nickel (NiO), cobalt (CoO), uranium (U₃O₈), and manufactured pigments may be used for colouring (Lee 1961, p.72).

As they have little or no dry strength when compacted, fritted porcelain powders may rely on especially selected particle sizes or the inclusion of an organic binder as aids in the forming process. If the particle size distribution is very carefully selected, a binder will not be required.

Although reducing the mullite phase of fired dental porcelain has improved its aesthetic qualities, it has also brought a reduction in strength of the material. In 1965 Hughes and McLean reported the use of 40 to 50 per cent alumina crystals in low-fusing porcelain to produce stronger dental porcelains. This is an example of dispersion strengthening.

.../10
3. INVESTIGATIONS INTO PHYSICAL PROPERTIES OF DENTAL PORCELAIN

(a) Test specimen formation

The nature of porcelain materials is such that, even with extreme care, it is very difficult to eliminate all variation in samples. However, as any test can measure only the properties of that test piece, every effort must be made to produce test samples that are consistent and reproducible. It is desirable also that the test specimen bear some relationship to the practical use of the material, so that the test may simulate practical conditions to some extent.

In the past many investigators in the field of dental ceramics have failed to give much consideration to these requirements in forming their test specimens. Test pieces have been of arbitrary size, with little attempt at standardisation.

Gill, in 1932, gave no method for producing his specimens which measured 13 mm x 10 mm x 4 mm. Felcher, in 1934, used a split iridio-platinum ferrule mould, but gave no dimensions for his specimens. Skinner and Fitzgerald, in 1938, made specimens 3.96 mm x 9.00 mm x 19.88 mm using a mould of removable glass slabs. Condensation of samples was by wet vibration into the mould, and specimens were fired on platinum foil. Sayre, also in 1938, used two types of test piece. Cylindrical specimens 10 mm high x 6 mm diam. were made in a split steel die. Block type specimens 5 mm x 5 mm x 31 mm were made in a glass-lined mould with .../11
removable walls. Both types were fired on platinum foil. Klaffenbach, in 1939, formed flat slab type specimens without describing their size or his method. Sartori (1939) formed rectangular specimens by vibration and spatulation into a mould 7.17 x 10.53 x 20.63 mm. Sacchi and Paffenbarger (1957) made cylindrical specimens in a mould 10 mm high x 6 mm diam. Hodson (1959a) formed discs in a mould 6.5 mm diam. x 3 mm and bars 3/16" x 3/16" x 1/2" in a rubber mould. These were fired on platinum foil and on fine silex. McLean and Hughes (1965) used rod, bar, and disc type specimens. Rods were formed by compaction of powder into a 0.25" diam. steel die under a pressure of 14.5 tons per sq. inch. Bars were made by wet vibration into a split steel mould 30 mm x 5 mm x 5 mm. Discs were made by wet vibration into a circular mould, the dimensions of which were not given. Specimens were fired on 1/8" thick asbestos sheeting impregnated with calcined alumina.

Southan (1968, pp. 173-178) set out specifically to produce test specimens which were of a standardised size and bearing some relationship to the practical use of dental porcelain. He established the volume of a crown build-up for an upper central incisor at 0.36 cc. This was considered typical of the size of a porcelain jacket crown. Three moulds were used, all of this same volume. They were a rectangular block type (A) 6 mm x 6 mm x 10 mm a wafer type (B) 3 mm x 10 mm x 12 mm and a cylindrical type (C) 7 mm high x 8.08 mm diam. Specimens were compacted by wet vibration into the mould.
Southan found that firing specimens on platinum foil caused distortion, due to localised restriction of firing shrinkage by the foil. Coarse silex sprinkled on to a firing tray overcame this problem, but caused the undersurface of the specimen to be pock marked. The most satisfactory support for firing specimens was found to be a pad of levigated alumina powder on a firing tray (Southan 1968, p.182).

(b) Firing

When used in dental practice porcelain powder is mixed with water to form a slip which is condensed and carved into the crown shape on a matrix of platinum foil. The crown build-up, on its matrix, is then placed on a fireclay stand and fired in a small electric furnace.

Thorough drying of the article is essential before firing. The rate of desiccation will be influenced by particle sizes and particle size distribution. In dental ceramics, articles are only of small bulk, so drying is a relatively simple and short process.

With modern dental porcelains, the thermochemical reactions between ingredients are well advanced due to the fritting process, so firing serves basically to fuse the porcelain particles together. Firing cycles are short, and temperatures involved are relatively low.

The usual conditions for firing dental ceramic articles are either atmospheric (air) firing, or low pressure (vacuum) firing. Pressure firing and gas firing have also been used (Lee 1961, p.78).
Southan (1968, p.66) describes two stages in the sintering process:-

(i) the absorbent stage

(ii) the impervious or vitrified stage.

The rate at which sintering takes place will depend on the bulk of the article, the temperature and time of firing, size of powder particles, composition of these particles, and their degree of compaction. Firing past the stage of complete vitrification will only cause deterioration of form, and loss of colour stability.

The dried, unfired article always has a significant proportion of its volume made up of voids, which are spaces between powder particles. If the powder consists of particles of one size, the fractional void space will be about 45 per cent in a well condensed article. Using selected particles of three or more sizes to provide optimal packing, the void space can be reduced to about 25 per cent (Hodson 1959a).

During firing, the article will shrink in volume by an amount similar to the reduction in void space. With air-fired porcelains, shrinkage may range from about 14 to 20 per cent (Lee 1961, p.78). All of the original voids are not removed, so that many bubbles are left inside the porcelain structure.

Vacuum-firing can produce almost complete densification of the porcelain. Consequently, all things being equal, firing shrinkage will be greater. Under either method of firing, the best condensed
articles will shrink least.

Fitzgerald (1936), testing translucent dental porcelains found volumetric firing shrinkages ranging from 31.7 per cent to 33.3 per cent.

Sayre (1938) found volumetric shrinkage of the porcelains he tested ranging from 24.1 to 48.2 per cent. Skinner and Fitzgerald (1938) testing air-fired porcelains, found volumetric shrinkage ranging from 31.7 to 39.5 per cent. Low-fusing porcelains tended to shrink more than high-fusing types. Sartori (1939) reported volumetric firing shrinkage of dental porcelain to be about 34 per cent. Moldal (1939) tested three opaque dental porcelains and reported firing shrinkages ranging from 33.7 to 35.7 per cent. Sacchi and Paffenbarger (1957) found the volumetric shrinkage of low-fusing porcelains (38 per cent) to be similar to that of one high-fusing type (37 per cent). Hodson (1959a) testing low-medium- and high-fusing dental porcelains found volumetric firing shrinkage ranging from 27.6 to 38.1 per cent. Volumetric shrinkage tended to be greatest for low-fusing porcelain and least for the high-fusing type. Southan (1968, p.241), testing a modern vacuum-fired porcelain, and varying his method of condensation of specimens, found mean volumetric shrinkage ranging from 36.0 per cent to 40.5 per cent.

Linear firing shrinkage is approximately one third of the volumetric shrinkage (Sayre, 1938).
(c) **Strength**

In order to produce more aesthetic dental porcelains, the kaolin constituent of these materials has, over the years, been reduced from about 50 per cent in the early opaque materials, to about 3-4 per cent in modern porcelains. This change in composition has reduced markedly the incidence of mullite needles in the fired porcelain structure (see p.3) so that translucency has been greatly increased. However, as mullite needles in the porcelain provide an efficient crack-stopping mechanism, their removal has brought about a deterioration in strength properties. Dental porcelains which have the degree of translucency required to resemble tooth structure will be predominantly glassy in nature, and so will have physical properties which are basically those of a glass. These properties will, of course, be modified by the various crystalline phases dispersed through the glassy matrix.

Much of the experimental work done on dental porcelain has been concerned with strength of the material. Various measures have been used to evaluate strength, namely:

(i) Transverse strength or modulus of rupture

(ii) Compressive strength

(iii) Impact strength

(iv) Fatigue strength.

(i) **Transverse Strength**

The transverse strength or modulus of rupture test has been accepted by most to simulate the forces acting on porcelain crowns
during mastication. A transverse test specimen is made in the shape of a slab or bar, and is tested under a three-point loading system. Load is increased until the specimen breaks.

The first recorded investigation into the transverse strength of dental porcelain after firing was by Fitzgerald in 1936. He tested three translucent porcelains (two high-fusing, and one low-fusing type) and found transverse strengths to be fairly similar. The high-fusing porcelains had transverse strengths of 7,800 and 7,900 p.s.i., while the low-fusing type had a value of 7,200 p.s.i. These specimens were made in a mould 20.34 x 10.31 x 5.082 mm.

Skinner and Fitzgerald (1938) tested high-, medium- and low-fusing porcelains made in a mould 3.96 x 9.00 x 19 mm. Transverse strengths were fairly similar for each type and ranged from 3,700 p.s.i. to 8,300 p.s.i., the mean being 7,200 p.s.i.

Sayre (1938), testing specimens made in a mould 5 x 5 x 31 mm, found transverse strengths ranging from 4,900 to 7,500 p.s.i. He attributed the difference to the degree of compaction of powder before firing.

Moldal (1939), tested three opaque porcelains. The mould used for forming his specimens was similar to that used by Fitzgerald in 1936. Modulus of rupture for these opaque porcelains ranged from 8,300 to 10,400 p.s.i., tending to be a little stronger than the translucent types tested by Fitzgerald.

Sartori (1939), tested specimens produced in a mould 7.17 x 10.53 x 20.63 mm. He found transverse strength to increase from
8,300 p.s.i., after the first firing to 9,200 p.s.i. after the second firing. Strength decreased when the porcelain was fired beyond the stage of complete vitrification, so that after eight firings it was 6,900 p.s.i. After veneer glazing the strength was increased to 10,400 p.s.i. Sartori attributed this increase to the release of stresses in the porcelain by annealing at the time of the glaze firing. However, I feel that a more probable explanation is that the glazed surface was under compression through having a lower coefficient of thermal expansion than the porcelain article.

Seth (1948) tested specimens of dental porcelain and found transverse strengths ranging from 7,100 to 8,300 p.s.i.

Hodson, (1959a) tested porcelain bars made in a rubber mould 3/16" x 3/16" x 1\(\frac{3}{8}\)" long. Using specimens of high-, medium-, and low-firing porcelains with a glaze-fired surface she found transverse strengths ranging from 7,040 p.s.i. to 9,985 p.s.i. Generally the vitreous porcelains were fairly similar in strength as well as structure.

McLean and Hughes (1965) report the modulus of rupture of typical porcelains to range from 3,700 to 12,000 p.s.i. When testing discs of dental porcelain 1 mm. in thickness, they found maximum breaking stress values ranging from 8,029 to 11,313 p.s.i. McLean and Hughes were studying the effect of calcined alumina as a dispersion strengthening agent in dental porcelain. This practice will also increase opacity of the porcelain by increasing the number
of glass/crystal interfaces in the material. However, it was claimed that, by careful selection of the alumina crystal size, test discs could be made of aluminous porcelain which had acceptable translucency and a modulus of rupture greater than 18,500 p.s.i.

Modulus of rupture of a group of 10 aluminous porcelain bars (14,979 ± 876 p.s.i.) which were low-fusing, air-fired with the surfaces ground, was greater than that for a group of 9 non-aluminous dental porcelain specimens of similar type with similar surface treatment (10,291 ± 591 p.s.i.). Tests on rod type specimens showed transverse strengths of glazed aluminous and non-aluminous dental porcelains to be fairly similar. Grinding the surface of the specimen produced a marked decline in strength, of the non-aluminous material, while the aluminous porcelain showed little change.

Southan (1968, pp. 306-7) tested wafer and block type specimen (see p.11). Considering nine different porcelains, he reported transverse strengths ranging from 6,425 to 13,500 p.s.i. Block type specimens tended to have higher modulus of rupture than those of the wafer type. Chemically prestressed specimens were tested, and modulus of rupture figures (Southan 1968, p.312) ranged from 13,975 to 15,560 p.s.i. After chemical prestressing the wafer type specimens matched the block type for strength. Chemically stressed block specimens were equal in strength to dispersion strengthened (aluminous) block pieces. However, chemically strengthened wafer specimens were superior in strength to aluminous wafer specimens.
(ii) Compressive Strength

As porcelain materials are very strong when subjected to compression this property has not been given much consideration in the past. The problems of dental porcelain lie in its tensile strength.

Sacchi and Paffenbarger (1957) carried out compressive strength tests on cylindrical specimens 7 mm high x 4 mm diam. Low- and high-fusing materials were tested and results were identical at 48,000 p.s.i. for each type.

(iii) Impact Strength

There has been quite a deal of disagreement as to the importance of impact strength in dental ceramics. Some workers have claimed that the main forces acting on crowns during mastication are of the impact type, (Skinner and Fitzgerald, 1938, Rodson, 1959a) while others have disagreed (Pitt Roche, 1949).

Fox et al (1960) and Kulp et al (1961) developed an impact test for dental porcelain, involving weights of known hardness dropped down a vertical guide on to conical porcelain specimens. Vacuum-fired samples were found to be more resistant to this test than air-fired porcelain. Air-fired translucent porcelain was weaker than air-fired opaque porcelain.

McLean (1965) reported that aluminous dental porcelains provide a considerable increase in impact resistance over standard porcelains.

Southan (1968, pp. 323-331) devised an impact test method whereby a steel ball was released from a measured height and dropped on to a Brinnell ball, which transmitted the force to the test
specimen. Porcelain dispersion-strengthened with alumina was more resistant than other porcelains when the specimen was thick in cross-section i.e. block mould (A). Chemically pre-stressed block specimens were susceptible to surface chipping under conditions of localised stress. Wafer (B) specimens tended to break at the lower surface. Of these pieces, chemically strengthened ones were the toughest.

(iv) **Fatigue Strength**

It has been recognised for some time that glass suffers from fatigue (Baker and Preston, 1946a). This means that a stress applied which is lower than that required to fracture the material immediately, will produce failure of the material after a period of time. Little work, however, has been done on this property in the field of dental ceramics.

Peet (1970) has shown that fatigue does occur in dental porcelain and that fatigue strength is determined largely by the surface condition of the article. Specimens with ground and annealed surfaces tended to perform better in such a test than freshly ground specimens.
II GLASS

The majority of modern dental porcelains are predominantly glassy in nature, and will have properties which are basically those of glasses. A better understanding of the nature of dental porcelain may be gained by a deeper consideration of the vitreous state.

4. STRUCTURE

(a) Nature of the glassy state

Unlike the majority of solid materials, which are crystalline in nature, glasses fall into the category of non-crystalline solids. This classification describes materials which lack long-range order of atoms periodically located on a regular lattice. Liquids exhibit a similar lack of periodicity, and so Warren (1934, 1937) has described glasses as supercooled liquids, or as amorphous solids.

X-ray diffraction studies on liquids show each atom to be surrounded by about the same number of other atoms to form structural units. These structural units, however, are related to each other in a random manner, so that, although local order exists, there is not the regularly repeating long-range order of crystals. (Warren, 1937).

While glasses have a similar random type of structure, they differ from liquids in that each atom has neighbouring atoms permanently placed at fairly definite distances. In liquids there is continual movement of atoms about other atoms. (Warren 1934).

The structural units for the formation of glasses are polyhedra of certain oxides. These polyhedra link together in a random
network structure. Only small cations, which have a low co-ordination number and high charge, can form glasses (Salmang 1961, p.14). Other cations, while they cannot themselves form glasses, may occupy interstitial spaces between polyhedra of the glassy structure. These can modify the properties of a glass into which they are introduced, and are called network modifying ions. There are, in addition a limited number of oxides which occupy an intermediate group, and may be substituted for true network forming ions in some cases.

The glass-forming materials exhibit sufficient transient bonding in the molten state to produce a highly viscous melt. This high viscosity impedes the atomic rearrangement necessary for crystallisation when the melt is cooled to temperatures at which the free energy of the crystalline phase would be lower than that of the randomly bonded structure. (Warren 1942). So the random liquid-like structure is maintained.

McMillan (1964, p.7) describes glasses as inorganic products of fusion, which have cooled to a rigid condition without crystallising. Ainsworth (1954) regarded a glass simply as a collection of ions, some positively and others negatively charged.

The irregular, three-dimensional glassy network has a more open structure than the corresponding regular crystalline lattice (Fig. 1). This is shown by the permeability of glass to small particles such as sodium ions (Johnson et al 1951).

Structurally, the simplest glass is pure fused (vitreous)
silica. The basic structural unit of fused silica is the silica tetrahedron, SiO$_4$. These tetrahedra are joined together through bridging oxygen atoms. So each silicon atom is bonded tetrahedrally to four oxygens, and each oxygen atom is bonded to two silicons. Part of the oxygens will be shared between two tetrahedral units. This flexible bonding scheme allows the building up of a random non-repeating network (Warren 1942).

If further oxygen atoms are introduced into the vitreous silica system, e.g. as when soda is introduced to form soda-silica glass, the oxygen/silicon ratio will be greater than 2. As each silicon must be bonded tetrahedrally to four oxygen atoms, then not every oxygen can be bonded to two silicons. Some oxygens, then, will be bonded to two silicons, and some will be bonded to one silicon.

Oxygens bonded to only one silicon cannot be bridging atoms, and will form breaks in the strong silicon-oxygen network. The more such breaks there are in the network, the softer will be the glass. In soda-silica glass, the Na$^+$ ions are network modifying ions, situated at random in the interstices of the silicon-oxygen network (Fig. 2) (Warren, 1942).

Zachariasen (1932) considers commercial glasses to be formed as a result of the accommodation of network modifying atoms in the interstices of the silica network. The properties of pure silica are not fundamentally altered by this, but are modified quantitatively.
Fig. 1 - Schematic two-dimensional figures to represent the difference between the regularly repeating structure of a crystal, a, and the random network of a glass, b.
Fig. 2 - Schematic representation in two dimensions of the structure of soda-silica glass. To correspond to two dimensions, the silicons are shown bonded to only three oxygen atoms.
Fig. 2.
(b) Aluminosilicate glasses

Because of the use of feldspars or feldspathoids as raw materials for dental porcelain, the amorphous matrix of the fired ware must be largely aluminosilicate glass. This group of glasses usually has an alumina content of about 20 to 25 per cent. (Skinner and Wilson, 1934). The major ingredient is silica.

While alumina (Al₂O₃) is not itself a glass former, small amounts of Al³⁺ can replace Si⁴⁺ isomorphously in the glassy network. Al³⁺ is acting in this way as an intermediate ion. As the AlO₄ polyhedron is slightly larger than the SiO₄ polyhedron, there will be increased irregularity in the network structure (Salmang 1961, p.15).

The AlO₄ group is the characteristic structural unit of aluminosilicate glasses. The AlO₄ tetrahedron has a negative charge which will neutralise the charge of a univalent cation (network modifying ion) placed interstitially between tetrahedra of the glassy network. (McMillan, 1964, p.14).

So equivalent amounts of Na₂O and Al₂O₃ may be added to silica without producing non-bridging O²⁻ ions. Thus there will be no interruption of continuity of the glassy network structure. The resulting sodium aluminosilicate will have a more stable and glassy structure than the softer sodium silicate glass.

The bond between Na⁺ and surrounding bridging O²⁻ ions in the sodium aluminosilicate will be much weaker than the bond between Na⁺ and the non-bridging O²⁻ of sodium silicates.

.../27
Other network modifying ions, such as K\(^+\), may be involved in the glassy structure in a similar way to Na\(^+\) in the above discussion. Sodium and potassium aluminosilicate glasses may be regarded as three-dimensional networks of SiO\(_4\) and AlO\(_4\) tetrahedra, with alkali ions (Na\(^+\) or K\(^+\)) situated in spaces between the tetrahedra. These alkali ions interact only with bridging O\(^{2-}\) ions, i.e. between Si-Si, Al-Si or Al-Al. So, by attracting electron density away from these binding regions, they will facilitate viscous flow of the glass.

The degree of polarisation of the bridging O\(^{2-}\) ions is related to the size of the alkali ion. The small Li\(^+\) ion exerts greater influence than the Na\(^+\) ion which, in turn, will cause more polarisation than the relatively large K\(^+\) ion.

There exists a definite relationship between field strength of an alkali ion and the major binding forces within the glass, i.e. those of the bridging O\(^{2-}\) ions. Melts of potassium aluminosilicates, then, are more viscous than those of sodium aluminosilicates. Lithium aluminosilicates form melts which are even more fluid. (Southan, 1968, p. 108).

5. THE STRENGTH OF GLASS

(a) Britteness

The concept of brittleness is a complex one, and difficult to define. However, fundamental factors must be involved simultaneously for a material to be brittle. These factors are:-
- a relatively high degree of elasticity
- fair to high tensile strength
- a complete absence of plasticity or of ability to store energy or to dissipate it by plastic flow.

(Preston 1942)

Glasses are excessively brittle materials. Their brittleness is greater than that of almost any other material.

Glasses have been defined over and over again as undercooled, liquids (see p.20). Use of the word "liquid" may tend to imply mobility or fluidity in the material. In fact this is far from so, at least at room temperature. To investigate this thought further, one must consider the property known as flow.

Flow is a response to shearing stresses, and necessitates a finite viscosity. Viscosity is said to become infinite at something like $10^{15}$ poises. If a material has viscosity beyond this level, the flow response will be no longer possible.

In glasses, viscosity cannot be detected and measured anywhere within several hundred degrees of room temperature, because the level is so great. Considering a glass that has been stabilised at room temperature, say $20^\circ C$, calculations show that the viscosity would be of the order of $10^{70}$ poises (Preston, 1942). Viscosity of this order is so great, and so far beyond the level where this property becomes infinite, that it can have no physical meaning. Such a material can distort under stress, and under certain circumstances it may break, but it cannot flow. The material is elastic and in
the case of glass, brittle.

(b) Flaw theory of the strength of glass.

According to calculations based on atomic bonding forces glasses should, theoretically, have strengths about $1 - 10 \times 10^6$ p.s.i. Actual observed strengths, however, do not approach these values in most cases, and are usually of the order of $1 - 100 \times 10^3$ p.s.i. (Kingery 1963, p. 604).

Griffith (1920) assumed that the discrepancy between theoretical strength and strength actually observed experimentally, results from the presence of small cracks or flaws in the material. Strong stress concentrations arise about these flaws when the material is stressed, and this initiates fracture. The theoretical strength will remain the true fracture stress of the material and can actually be reached in small volumes of the specimen, even though the average fracture stress may be low.

As well as the fact that cracks or flaws must be present to account for the observed low fracture stresses of glasses, indications are that the flaws which lead to fracture are those present on the surface of the glass rather than in the interior (Kingery, 1963, p. 606). When the surface of the glass is placed in tension, stresses are concentrated at the tip of the surface crack. The degree of stress concentration will depend on the degree of sharpness of the crack tip. The sharper the tip of the crack, the more effective it will be in concentrating stresses.

Some flaws will be more dangerous than others. The worst flaws
will be those whose position, orientation, and shape cause the greatest amount of stress concentration. On large specimens, then, strength tests measure not the bond strength of the glass, but the effect of the most serious flaw existing in the most highly stressed area.

As a result of Griffith's theory that brittle fracture is initiated at surface flaws, the measured strength of glass will involve a statistical component. Determination of the fracture stress will depend on the probability of the presence of a flaw capable of initiating fracture at a specific applied stress. This statistical component explains the scatter usually found in results for strength of ceramic materials.

(c) Nature and origin of flaws in glass.

Griffith in 1920, observed that freshly drawn fibres of glass possessed remarkable strength. However, touching the fibres with clean fingers, or even merely waiting without touching, caused a marked decline in strength. Griffith concluded from his observations that old fibres had more cracks or flaws than freshly drawn fibres.

More recent investigators have confirmed that fine fibres of glass can have strengths approaching those expected on the grounds of intermolecular bonding forces, because of the absence of surface flaws (Argon et al, 1960). Observed strengths of very fine fibres may be over one million p.s.i. (Anderegg, 1939).

Gurney (1964) classified the sources of weakness in glass...
in the following ways:—

(i) Submicroscopic voids

(ii) Bubbles

(iii) Foreign matter on surface of reheated glass

(iv) Mechanical damage

(v) Effect of moisture.

A further category may well be added to this list, namely

(vi) Effect of intrinsic stresses.

(i) Submicroscopic voids.

Gurney describes submicroscopic voids as spaces in the molecular structure of the glass formed during cooling from the molten state, where equilibrium conditions cannot be achieved by molecular movement. These voids may act as stress concentrators.

Gibbs and Cutler (1951) employ a similar approach, regarding all flaws ultimately as pits or irregularities in the glassy lattice structure. They regard fracture to correspond to deepening of a pit through separation of successive pairs of atoms surrounding the pit.

(ii) Bubbles.

Bubbles in the glass may act as stress concentrators and become sources of weakness (Kingery, 1968, p. 621). Gas-filled bubbles will cause greater stress concentration than empty ones (Gurney, 1964). If bubbles are near the surface,
rapid cooling of their thin walls will cause internal stress, and predispose to cracking. Large bubbles may, of course, weaken a specimen by substantially reducing the amount of glass in a particular cross section.

Shand (1954) regarded internal voids to be seldom significant factors in the breaking of glass.

In certain circumstances bubbles or voids within a glass may act as crack-stopping factors (Keller, 1964). By impeding crack propagation, these voids will strengthen the material. Surface checking will tend to occur rather than complete fracture (Kingery, 1963, p. 621).

(iii) Foreign matter on the surface of reheated glass.

During fire-finishing of glass rods and fibres, impurities may dissolve partially in the surface and form glasses with different physical and chemical properties from the parent glass. Surface roughness as a result of such contamination may also produce weakness by concentrating stresses.

(iv) Mechanical damage.

It is well known that strong glass is greatly weakened by contact with other glass or hard body. This is because such contact causes the surface of the glass to be cracked, scratched, abraded or bruised. However, the damaging agent need not be sharp or even hard for serious flaws to be
produced (Preston, 1942).

A typical scratch on glass does not remove any material and often its existence or nature cannot be determined without etching of the region. The scratch consists of a series of transverse cracks, which form a ladder or "chatter-sleek". The path of the abrasive itself is not a crack, but the transverse cracks along it can severely weaken the glass. The crescent-like chatter cracks represent an intermittent seizing and slipping of the abrasive on the glass surface.

(v) Effect of moisture.

Milligan, in 1929, was the first to suggest that the surrounding medium had some influence on the strength of glass. He found that moistening a freshly cracked piece of glass with water reduced its strength by 20 per cent or more. Baker and Preston (1946) showed that glass rods dried in a desiccator had strength about 15 per cent above wet rods.

Preston (1942) states that when exposed to water, glass spontaneously adsors a moisture film, which breaks up some of the silica bondings in the surface layers of the glass. This produces a weakened surface structure, analogous to a slightly cracked one.

Gurney (1964) explains the process in more detail. Alkali ions in the glass dissolve in the water and are replaced by hydrogen ions. These hydrogen ions, now in the glass, attract
water molecules into the spaces originally occupied by the alkali. The water molecules are too large for the spaces which they then occupy, and so a state of internal stress is set up. This breaks the bonds of the silica network and leads to a general disintegration of the surface.

The weakening effect of moisture on glass is very pronounced at room temperature, but is even more pronounced at elevated temperatures such as those used in autoclaves (Preston, 1942).

In certain situations the presence of moisture may, however, act as a strengthening factor rather than a weakening one. Mould (1960) found that unstressed glass containing pre-existing cracks was strengthened by immersion in water. This process, called aging, operated presumably by rounding the crack tips, so reducing their effectiveness as stress concentrators.

(vi) Effect of intrinsic stresses.

Andrade and Tsien (1937) found cracks in hard glasses, orientated in directions normal to the predominant principal tensions set up during cooling from the molten state. These cracks developed with age of the glass. They were almost completely absent on glass freshly drawn, and frequent on the same glass some hours after drawing.

(d) Static fatigue in glass.

It has been recognised for many years that glass can be
broken by stresses far below its ordinary short-time breaking stress, provided that the load is applied for a sufficiently long time. In contrast to metals, the stress need not fluctuate periodically for this fatigue phenomenon to occur (Orowan, 1944).

Fatigue in glass seems to have been recognised first by champagne producers. They noticed that when bottles were used a second time, the incidence of fracture due to internal pressure was greatly increased.

Murgatroyd (1944) proposed a theory that pockets of "quasi-viscous" material within the elastic glass matrix were responsible for delayed fracture under constant load. This theory relates strength to the applied load, and to time. It would predict delayed fracture in vacuum as well as in air, and we know that this is not so. (Baker and Preston, 1946b).

As well as stress and time, the fatigue failure of glass is related to atmospheric conditions and to temperature. Baker and Preston (1946a) tested rods of glass and porcelain under static loads. They found that all of the glassy materials tested exhibited static fatigue to a marked degree. In the case of rods of soda-lime glass, the 0.01 second strength was 3.1 times the 24 hour strength. For all the glasses tested, the ratio of the 0.1 second strength to the 24 hour strength was between 1.7 and 2.4.

Static fatigue cannot occur in glass without the presence of moisture. Baker and Preston (1946b) found that in vacuum,
thoroughly baked out glass rods had a tensile strength fairly independent of the time of loading. However, glass exposed to moisture rapidly lost its strength under stress. This strength decay appears to be caused by chemical attack in the flaws of the glass by water, and possibly by some gases such as CO₂.

The corrosion of glass by water has been discussed in the previous section (see p.33). Although static fatigue must be closely related to this corrosion process, the dissolution must be of a particular type that will lead to flaw growth and increase the stress concentration at the crack tip. This must continue until the crack is such a size that it will cause fracture as required by the Griffith criterion (Kingery 1963, p.616). Fracture occurs when the applied stress produces a stress at the flaw tip equal to the intrinsic strength of the glass (Ritter, 1968).

For this type of crack growth to occur, the material must be under stress. In fact, etching of the unstressed specimen will tend to round out crack tips and reduce their effectiveness as stress concentration. So for fatigue to occur in glass, there must be the factors of stress and corrosion present simultaneously.

The chemical composition of the glass will have some influence on its susceptibility to stress corrosion. Wiederhorn and Bolz (1970) found that the presence of sodium seemed to be detrimental to the stress corrosion resistance of glass.

The chemical nature of the stress corrosion process is also indicated by its dependence on temperature. Wiederhorn and Bolz (1970) showed that increased temperatures caused stress corrosion
to occur at faster rates. At temperatures above $150^\circ$C, the corrosion rate is so rapid that added stress has but little effect. Below $100^\circ$C, the corrosion rate is too low to be observed in experimental times.

6. **METHODS OF INCREASING THE STRENGTH OF GLASS**

Theoretically, glass should have a strength of several million p.s.i. so that it should stretch to nearly double its length before it breaks (Preston, 1942). However, the strength values found in normal testing of most glass articles are usually no more than one percent of this, that is about 10,000 p.s.i. If the load is applied for any great length of time, the strength will be even less.

Glasses have many desirable qualities, some of which are rigidity, high compressive strength, chemical durability, and high strength-to-weight ratio. In view of such advantages, many efforts have been made to increase the tensile strength of glass, and so make it a more suitable material for wider usage. Methods which have been used to increase the strength of glass include:-

(a) Etching

(b) Toughening or tempering

(c) Dispersion strengthening

(d) Chemical stressing

(a) Etching.

Preston (1942) reported that abnormally high values for strength of glass were obtained after etching the surface deeply with a dilute solution of hydrofluoric acid. He regarded the
glass surface to be "fortified" by the etching process.

Baker and Preston (1946), investigating the effect of water on glass, found that autoclaving resulted in etching of glass surfaces, similar to that caused by hydrofluoric acid. Tests on rods of soda-lime glass showed that their strength could be increased by etching in an autoclave.

Mould (1960) found that the strength of freshly abraded, unstressed glass, increased with "aging" of the specimen in water. This effect was due to etching of the surface by the water.

Lee (1961, p.121) states that when a glass surface is etched with hydrofluoric acid, strength may be increased to nearly 40 times the original value.

The mechanism by which such etching processes increase the strength of glass is quite simple. Part of the surface of the glass is dissolved, so that the original Griffith flaws are removed, or at least their stress-concentrating effects minimised.

The problem with this process as a strengthening method, however, is that the strength increase is not permanent under most conditions. Unless the etched surface is protected from further mechanical or chemical damage, there will very likely be flaws produced in the surface just as dangerous as the original ones.

Bowden and Field (1964) showed also that prolonged etching can eventually weaken a surface. Once reaction products of the etching process settle at points on the surface, preferential etching
...ensues. The unevenness of the resultant surface predisposes to further stress concentration.

(b) Toughening or tempering.

Chill-tempering is the most widely used strengthening process for glassware today. The piece is heated to a temperature somewhat above its annealing range, and then cooled rapidly by means of air jets or oil immersion, or by quenching in a bath of molten salts (Scholes, 1951, p.196). During rapid cooling, the discrepancy between the rates of cooling of the surface and the internal parts of the article causes residual stresses to result. The outer layers of glass cool first while the centre is still hot and therefore soft. When the centre cools and contracts, the outer layers of glass are set in uniform high compression, balanced by internal tension. The whole glass is in a permanent state of stress.

With this residual compressive stress on the surface, an applied stress must first overcome the residual compression before the surface is brought into tension, where failure can occur. With glass tempered in this way, strength increases up to 30,000 p.s.i. could be readily obtained (Nordberg et al 1964).

Although toughened glass has high internal tension, Haward (1949, p.62) shows that fracture still originates from the surface, rather than from internal flaws.

The sum of the surface compressions of toughened glass must be equal to the internal tensions, so the degree of toughening obtained will be governed by the relative rates of cooling of the surface and
the internal glass. In thin sections, the required large differences in cooling rates are not readily produced, so most commercial toughened glass is 3/16" or more in thickness (Haward, 1949, p.63).

Also articles shaped so as to have sharp re-entrant angles do not temper satisfactorily (Nordberg et al, 1964). These two limiting factors restrict the application of the tempering process to some extent.

(c) Dispersion strengthening.

In brittle solids it is characteristic for the radius of a crack tip to remain constant and of molecular dimensions as the crack extends (Cook and Gordon, 1964). So the longer the crack, the less force will be required to propagate it. Once a crack has started, then complete fracture will occur suddenly, often under low stress. As there will always be cracks initiated in glass surfaces, it is desirable to have a mechanism to prevent them spreading catastrophically under low stresses.

In metals, crack propagation is controlled by dislocations in lattice structure, which interrupt the progress of a crack and relieve stress concentration at its tip (Hargreaves, 1966). This mechanism gives the material toughness, which is the ability to absorb the energy of fine cracks that constantly threaten to spread and rupture the material (Fishlock, 1966).

Tough non-ductile materials, such as wood or bone, appear to be similar in that they are not homogeneous. They contain numbers of interfaces, or planes of potential cleavage, which will impede
the progress of a crack by a simple Griffith process (Cook and Gordon, 1964).

In order to increase the strength of porcelain, Batchelor and Dinsdale (1960) introduced crystalline grains of alumina into the material. Strength of the fired body increased progressively with the proportion of added crystalline alumina but only to about 25 to 30 per cent alumina content. Above this level the strength did not improve.

Hasselman and Fulrath (1966) proposed a fracture theory for this type of composite system based on a continuous glass matrix. They proposed that hard crystalline dispersion within the glass matrix will strengthen the composite by limiting the size of Griffith flaws. At low volume fractions of dispersed crystalline phase, the average flaw size is reduced statistically, independently of the size of the dispersed crystals. With high volume fractions of dispersed crystals, average flaw size is restricted by the average distance between dispersed particles in the matrix.

The strengthening effect of a dispersed phase is due to the relationship between the two phases, rather than the strength of the dispersed particles themselves. The resulting composite may be stronger than either of the original components alone. Cook and Gordon (1964) suggest that, to be successful, a composite of this type should have interfaces whose strengths of adhesion are less than the cohesive strength of the solid phases.

McLean and Hughes (1965) state that the thermal coefficient
of expansion of the dispersed phase should be similar to, but not equal to, that of the glass matrix. If there were no differences in thermal expansions, the composite would behave as a homogeneous solid, with the fracture passing indiscriminantly through the glass or the crystalline inclusions. This would defeat the purpose of the exercise.

On the other hand, where the co-efficient of thermal expansion of the glass is higher than that of the crystalline inclusions, the composite tends to crack on cooling (Binns, 1962; Frey and Mackenzie, 1967). So ideally, the dispersed particles should be thermally compatible with the matrix, but be different enough from it for the interface between the two phases to impede the progress of cracks through the composite. Alumina fulfils these requirements in most ceramic materials.

McLean and Hughes (1965) found that the modulus of rupture of dental porcelain could be approximately doubled by using dispersed alumina as a reinforcing phase in the glass matrix. Highest modulus of rupture values were obtained by increasing the fineness of the alumina. In this way a similar volume of alumina would produce more crack-stopping interfaces.

Due to the differences in refractive indexes of alumina and the glass matrix, addition of alumina crystals will increase the opacity of the fired article. Opacity is a feature of all heterogeneous structures and is related to interfaces between
different phases. Although more alumina/glass interfaces will increase strength, they will also increase opacity to a similar extent.

(d) Chemical stressing.

The limitations of thermal tempering as a strengthening mechanism can often be avoided by using the newer methods of chemical strengthening. In this way the composition of the surface is made different from the interior. There are several different ways of achieving this change:

(1) By heating samples of soda-lime-silica glass in atmospheres of sulphur dioxide and air, Boow and Turner (1938) found that a film of sodium sulphate could be formed on the surface. This treatment, which took place about the annealing range of the glass, was found to increase the modulus of rupture by up to 16.9 per cent. The extent of formation of the sodium sulphate film is related to the alkali content of the glass. A disadvantage of this process is that the surface film is water soluble and can be washed off.

Mochel (1966) found that the depth of reaction, and consequently the degree of strengthening achieved, was increased with the presence of alumina in the glass.
(ii) The composition or structure of the outer layers of glass may be chemically changed by high-temperature ion exchange. (Nordberg et al., 1964). In this way an overlay of low expansion glass can be developed over a core of high expansion glass. When the composite cools from above its annealing temperature, its surface will be placed in compression and the interior in tension, resulting in increased strength.

(iii) With glasses of special composition, crystallisation on the surface may be induced by heat treatment. A surface with low expansivity can be developed while the body of the article remains glassy (Shaver, 1964).

(iv) Kistler (1961) reported a strengthening method whereby small monovalent ions in the surface layers of glass are replaced by larger ions, at relatively low temperatures.

Because of the irregular open structure of glasses, it is possible for particles to diffuse through the network. Norton (1953) showed that helium could diffuse through silica glass more rapidly than it would through the more closed structure of crystalline silica. The insertion of network modifying ions into the glassy structure, such as Na ions in
soda glass, tend to plug up the openings in the structure and so reduce penetration.

Johnson et al (1951) used radioactive tracer techniques to study the diffusion of ions in several glasses. They showed that the rate of diffusion is determined by the free energy of activation, and so the degree of penetration of ions into the glass will be governed by the time and temperature of the process. Diffusion coefficients for migration of alkali ions into silicate glass networks were measured quantitatively at temperatures as low as 300°C. The higher the temperature, the more rapid was the diffusion.

Kistler (1961) induced replacement of alkali ions in the surface of glass by exposing that surface to the molten salt of another alkali. Surface compression could be achieved by "stuffing" a larger ion into a site formerly occupied by a smaller ion; for example, substituting potassium ions for sodium ions in the glass surface. Kistler observed maximum stress in the compressed surface of glass discs after such treatment to be 120,000 p.s.i.

Ward et al (1965) treated rods of soda-lime-silica glass by immersion in molten \( \text{KNO}_3 \). They found a maximum strength of about 50,000 p.s.i. for treated
rods, which indicated an additional surface compressive stress of about 33,000 p.s.i. induced by the ion exchange treatment. They showed that the maximum stress figure of 120,000 p.s.i. (Kistler, 1961) was approached only at the extreme surface, where potassium ion concentration approached saturation.

Ward et al (1965) found that depth of penetration of potassium ions into the glass was less than 25 μ in all cases. They suggested that the maximum depth of 50 μ claimed by Stookey et al (1962) would only be produced after prolonged treatment, for example 800 hrs. with KNO₃ at 350°C.

For surface compression to be maintained, it is necessary that this ion exchange treatment take place below the transformation region of the particular glass. Once softening or relaxation of the glassy matrix occurs, all the induced surface compression will be lost. The temperature at which treatment may take place, then, is governed by the transformation region of a particular glass, and will vary from one glass to another.

Of all the chemical strengthening methods mentioned, ion stuffing is the one which is beginning to have the greatest commercial
application (Ritter, 1968). The success of any of these strengthening processes, which rely on the formation of a compressed surface layer, may be attributed to the very high tensile strength of the interior of a glass sample. It has been suggested (Ritter, 1968) that the limiting internal tension for glass is probably in excess of one million p.s.i.
SUMMARY

The development of dental porcelain from traditional triaxial whiteware materials has been discussed. Consideration has been given to the individual ingredients of a modern dental porcelain, and their influence on the quality of the fired article.

Previous investigations into dental ceramic materials have been reviewed, with particular attention to test specimen formation, changes produced on firing, and physical properties of the fired specimens.

Having established that the typical modern dental porcelain is basically a glassy material, the nature of the glassy state is discussed. As dental porcelains fall into the category of aluminosilicates, special attention is given to glasses of this type.

The strength properties of glasses are reviewed and related to the Griffith flaw theory. The nature and origin of flaws in glass have been examined.

Static fatigue in glass is considered, and related to stress corrosion in the presence of moisture.

Methods of increasing the strength of glass are evaluated, namely, etching, tempering, dispersion strengthening and chemical strengthening. The method with most potential in the field of dental ceramics, is considered to be chemical strengthening by low temperature ion exchange. The strength of glass is increased in this way without affecting its optical properties.
PART B

ORIGINAL INVESTIGATION

7. STATEMENT OF PROBLEM - PURPOSE AND SCOPE OF INVESTIGATION

The evolution of dental porcelain over the years has followed a course directed, primarily by aesthetic demands. Changes in composition have made dental porcelains more and more glassy in nature, with physical properties predominantly those of glasses.

The glass-like behaviour of dental porcelain has resulted in a certain lack of confidence in the material among members of the dental profession. In fact, when we consider the insults which a crown in the mouth is subjected to, one may wonder that so many porcelain jacket crowns do survive. The crown is placed into an environment which is continuously moist, and is subjected regularly to the stresses of mastication. In addition there will inevitably be numerous other mechanical and thermal shocks applied to the crown throughout its life. Is it any wonder that a glassy material may fail under such conditions?

For dental porcelain to be a brittle material may not in itself be a disadvantage. In fact, the tendency for porcelain crowns to fracture rather than to distort permanently under stress may be a very desirable feature. The problem lies specifically in the liability of dental porcelain to fracture under relatively low stress in the moist environment of the mouth.

As the performance of dental porcelain jacket crowns may
be regarded, at best, as unpredictable, it has become necessary to improve the strength of the material in some way. Moreover, this strengthening should be achieved in a way that will not compromise to any extent the excellent aesthetic qualities of a good dental porcelain.

Thermal tempering cannot be used to significantly strengthen porcelain jacket crowns, because the thinness of sections in the crown do not allow the required differences in cooling rates to be obtained. Etching is an unacceptable method because aesthetic properties of the porcelain would be affected. Also, any strength increase achieved by etching could not be considered permanent when the crown is placed into function in the mouth. Dispersion strengthening has been used in dental ceramics, and proponents of this method claim a high degree of success. The problem with this process is, however, that the very mechanism which increases the materials resistance to fracture will also increase opacity. This leaves the method of chemical stressing; specifically, surface prestressing by low temperature ion exchange, or ion stuffing.

Southan, in 1968, established that chemical prestressing could be applied effectively to dental porcelain. This was a method that could increase the strength of dental porcelain without any apparent change in the material's desirable optical properties.

The purpose of this research is to determine to what extent chemical stressing may increase the strength of modern dental porcelain, and to establish optimum treatment time and temperature
combinations for selected materials.

An endeavour will be made, wherever possible, to emphasise aspects of the study which apply to the practical use of fused porcelain in dentistry.

Five modern dental porcelains and one commercial glass will be employed in the investigation. Their descriptions, and special designation applied by the author, are listed in Table I.
### TABLE I

**MATERIALS INVESTIGATED**

#### MODERN DENTAL PORCELAINS

<table>
<thead>
<tr>
<th>Manufacturer's Description</th>
<th>Author's Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vita-Vacuum-Keramik 1130°C Dentinmasse Nr. 56</td>
<td>$V_{V_1}$</td>
</tr>
<tr>
<td>Vitadur. 980°C (Aluminous) Dentine powder No. 356</td>
<td>$V_{A_1}$</td>
</tr>
<tr>
<td>De Trey's Aluminous Porcelain 1100°C High-fusing core No. HFC 25</td>
<td>$HFD_{A_0}$</td>
</tr>
<tr>
<td>900°-950°C Core No. C 25</td>
<td>$D_{A_0}$</td>
</tr>
<tr>
<td>900°-950°C Dentine No. D22</td>
<td>$D_{A_1}$</td>
</tr>
</tbody>
</table>

#### COMMERCIAL GLASS

| Thuringian (Normal) Sodium aluminosilicate | $TH_V$ |

* After Southan, 1968
CLASSIFICATION OF DENTAL PORCELAINS

In order to understand the mechanical properties of modern dental porcelains, Southan (1970b), classified all of these materials into two broad groups: those with a disrupted vitreous matrix and those with an intact vitreous matrix.

All quartz-bearing porcelains whose vitreous matrices are rigid at the inversion temperature of quartz (about 573°C) fall into the matrix-disrupted category. As the porcelain is cooled from its firing temperature, the sudden volumetric shrinkage of quartz particles at about 573°C causes microcracking in the glass surrounding these particles. This cracking will occur regardless of the rate of cooling. The resulting disruptions appear usually as semi-lunar cracks in the glass about the quartz grains (Fig. 3).

All other porcelains may be classified as matrix-intact, where no such discontinuities are inherent in the materials structure. This includes the quartz-free materials, such as aluminous dental porcelains. Also included would be quartz-bearing porcelains whose matrices are plastic enough at 573°C to accommodate volumetric changes in the quartz particles.

Of the materials examined in the present study, only the non-aluminous dentine porcelain, V_V, was a matrix-disrupted material. All others were of the matrix-intact type.
Fig. 3 - (a) Thin section of a quartz-bearing modern dental porcelain. Transmitted light. Matrix near quartz grains is disrupted.

(b) Thin section of a modern aluminous dental porcelain. Transmitted light. Matrix remains intact. (Courtesy D.E. Southan).
8. **TEST SPECIMEN FORMATION**

When considering the type of test specimen to be used the aim was to employ a method of manufacture which would produce pieces that were consistent and reproducible as far as possible. A simple, symmetrical shape was indicated to simplify the testing of mechanical properties. It was thought desirable also, to select a specimen whose size would approach the volumes used in dental ceramic practice. This would allow drying periods for test samples to simulate those used in practice, and permit the rapid firing schedules which are employed in the construction of porcelain jacket crowns. Perhaps more importantly, testing procedures on small specimens could simulate the stresses which might be applied to a crown in function.

8.1 **Mould**

The mould selected for specimen formation was identical to the rectangular wafer (B) mould designed by Southan (1968, p. 175). Internal linear dimensions of the mould were:

- **Length**: 12 mm.
- **Breadth**: 10 mm.
- **Height**: 3 mm.

Specimens compacted in this mould would have dimensions 12 x 10 x 3 mm. before firing. Volume of the unfired specimen would be 0.36 ml., which approximates the volume which might be involved in the porcelain build-up for an upper central incisor jacket crown (Southan, 1969).
The mould was constructed precisely from tool steel* in five sections. Side and end sections of the mould could be located accurately into ledges cut in the base. The assembled mould was held firmly in a clamp, with screws tightened against each side and end (Fig. 4).

8.2 Specimen formation

Porcelain powder was placed on a clean watch glass and distilled water added to produce a workable paste. The powder and water mixture was vibrated on a mechanical vibrator and spatulated so as to wet all powder particles and to remove all air bubbles from the mix.

Wet vibration with continual absorption of moisture was selected as the method of condensation. This method has been shown to produce regular fired specimens (Southan, 1968, p. 179), and also simulates the practical use of the material.

The mould in its holder was placed on a mechanical vibrator, and successive increments of carefully mixed paste were added. Vibration of the mould continued for a total time of five minutes. During this time, the flat of a dental cement spatula was vibrated across the surface of the paste in the mould. This vibration caused moisture to be brought to the surface of the mould, where it was absorbed by clean, dry paper tissues. At the end of this process,

---

* Chapman and Goldsmith Pty. Ltd. Engineers,
Bathurst Street, Sydney, 2000, Australia.
Fig. 4 - Mould for test specimen formation.

(a) Diagramatic representation of partly dismantled mould.

(b) Mould assembled in holder.
the mould was slightly overfilled with well compacted porcelain.

Upon removal from the vibrator, the excess porcelain was carefully carved away with a sharp razor blade. The carved surface of the condensed specimen was then whipped with a large squirrel-hair brush.

The filled mould was removed from its holder and placed on a clean glass slab. The long sides of the mould were slid to a position which would support the condensed porcelain specimen, while allowing one of the end sections to be removed. After readjusting the sides, the other end section was removed in a similar fashion. By withdrawing the two side sections of the mould, the compacted specimen was left sitting on the mould base. The base, with the specimen on it, was then carefully placed on its side on the glass slab and the compacted specimen removed from it. This was accomplished by pushing the end of the specimen with one of the detached mould sides (Fig. 5).

With the aid of a cement spatula, the specimen could now be carefully transferred to a firing tray to be dried out and fired. All specimens used in this investigation were prepared in the manner described above.

8.3 Firing

Support of Specimens.

To minimise distortion of specimens caused by uneven firing shrinkage, test samples were supported on a pad of
Fig. 5 - Steps followed in removing the compacted porcelain specimen from the mould.
Fig. 5.
levigated alumina*, which was sprinkled evenly on the firing tray. Southan (1968, p. 182) showed that this method of support would allow uniform firing shrinkage, while producing only minimal interference with the smoothness of the undersurface of the specimen.

In the early stages of the investigation, specimens were fired in small batches of three or four, supported on individual circular firing trays. However, as the work progressed, it was found that a larger, rectangular firing tray could be used to support up to eight specimens simultaneously. Specimens fired in these larger batches could not be distinguished from those fired individually.

Firing schedule.

In order for the muffle to be thoroughly heat soaked, the furnace** was always preheated for at least one hour before use. This preheating was accomplished using a current of 7.5 amperes and with the furnace thermostat set at the recommended firing temperature for the particular porcelain being used.

After thorough preheating, the lift was lowered from the vertical muffle, and condensed porcelain samples on the firing tray,

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* 1557 AB Levigated Alumina Powder, Buehler Ltd.
Metallurgical Apparatus, Evanston, Illinois, U.S.A.

**Model C-3B Dentsply Biomat Furnace
Dentists Supply Company of N.Y. York, Pennsylvania, U.S.A.
were placed on the lower platform to dry for 10 minutes. Following this initial drying, the firing tray was placed in a central position on the upper platform. This position was maintained for a further five minutes to complete drying, and to preheat the article.

The dried specimens, still in the centre of the upper platform, were raised into the muffle, and a partial vacuum of 29 inches mercury induced. Specimens were held in this partial vacuum, at their firing temperature, for a time of four minutes. At this stage the specimens were vitrified throughout while remaining regular in shape, and with no rounding of sharp edges. Macroscopically, the surface of a specimen fired to this extent appeared dense and vitreous, but did not appear glazed. All specimens prepared for this investigation were fired for four minutes.

After the four minute firing cycle, the vacuum was released and the lift automatically lowered. The firing tray was immediately removed from the upper platform, and placed aside for the fired specimens to cool. No special measures were taken to restrict the rate of cooling of newly fired specimens.

Firing schedules for each of the materials used are set out in Table II.

8.4 Surface preparation of specimen.

In order to obtain uniform surfaces on all specimens, the faces and sides of each sample were prepared by abrading longitudinally with grade 220A silicon carbide paper under running water. This preparation was carried out immediately prior to any further surface
treatment. For samples which were to be tested untreated, surface preparation was made immediately before testing.
**TABLE II**

**FIRING SCHEDULES**

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>TEMPERATURE</th>
<th>TIME</th>
</tr>
</thead>
<tbody>
<tr>
<td>VV₁</td>
<td>1090°C</td>
<td>4 mins.</td>
</tr>
<tr>
<td>VA₁</td>
<td>920°C</td>
<td>4 mins.</td>
</tr>
<tr>
<td>HFDA₁</td>
<td>1090°C</td>
<td>4 mins.</td>
</tr>
<tr>
<td>DA₀</td>
<td>930°C</td>
<td>4 mins.</td>
</tr>
<tr>
<td>DA₁</td>
<td>930°C</td>
<td>4 mins.</td>
</tr>
<tr>
<td>TH₁</td>
<td>710°C</td>
<td>4 mins.</td>
</tr>
</tbody>
</table>
9. **THE BEND TEST**

Glassy materials, including the typical modern dental porcelain, are very resistant to compressive stresses, with failure occurring first under tension. Hove and Riley (1965, p. 210) report the compressive strengths of three porcelains to range from 100,000 to 120,000 p.s.i., while tensile strengths for the same materials were only about one tenth of these values. Because of the specific weakness of ceramic materials under tension, investigations into strengths of these materials have been concerned almost exclusively with their tensile strength.

In measuring the tensile strengths of brittle materials, it is often inconvenient to use the direct method of pulling apart a suitably shaped specimen, owing to the difficulty in preparing this type of test piece. Also, precise axiality of loading is required with the direct tensile test so that shear stresses are not added to the system. Whereas ductile materials can correct small misalignments by plastic flow, without significantly affecting the results, brittle materials do not have this capacity.

A number of alternative methods, using specimens of simple shape, are employed to estimate the tensile strengths of brittle materials. Examples of such methods are the bending test, the indentation test, and the diametral compression test. However, where comparisons have been made, these methods have often yielded values for tensile strength which differ considerably from that obtained from the conventional direct tension test (Berenbaum and
Brodie 1959).

In the bend test, a bar-type specimen is bent under the action of a three- or four-point loading system until fracture occurs. The maximum tensile stress at failure is estimated from the applied bending moment, using the simple beam theory.

At the convex surface of the flexed beam, where the maximum tension exists, the material is in a state of pure tension. The material under test must be able to withstand large shear stresses, which occur close to the points of application of the load. Fortunately glasses fail first in tension, so fracture will be caused by the action of this single principal stress alone (Berenbaum and Brodie, 1959). The accuracy of the result depends on failure occurring in the elastic range, and on Hooke's law being obeyed fairly consistently up to the point of fracture (Tweeddale, 1964, p. 221).

In a bend test, stress is not uniform throughout the stressed surface. Fracture will begin at the point of maximum tensile stress which in the case of a three-point loading system, will be directly opposite the point where the load is applied (Ritland, 1955). This point may not, however, be representative of the entire specimen. The tensile strength value obtained by this test will be influenced by the probability that a dangerous Griffith flaw exists at the point of maximum tension. By using a four-point loading system, a more uniform tensile stress on the convex surface of the specimen will result. This will allow more
representative and consistent strength values to be obtained (Duckworth, 1951).

Because of the importance of surface imperfections in glassy materials, the measured values of breaking strength usually show a large variation. Berenbaum and Brodie (1959) showed the bend test to be more sensitive to changes in surface condition than other tests for tensile strength. Because of the wide spread of results, it is important that large groups of samples be tested, and that statistical analyses be made before conclusions are drawn from experimental work.

The fraction of the surface area of a specimen which is under the maximum tensile stress will vary from one testing method to another. It will be least for the three-point bending test, while in the axial tension test it will equal the entire surface area of the specimen. For this reason the data taken by one testing system should not be compared directly with those of another system. For example, tensile strength values obtained from the direct tension test are considerably lower than those obtained from the bend test, often only about half the latter (Milligan, 1953).

The strength value determined by the bend test will be the transverse strength, or modulus of rupture. It is known that the modulus of rupture is not itself a true stress (Roark, 1965, p. 35) but is used for the purposes of comparison. The formula can
be used to predict the strength of a similar beam of the same material.

The conventional equation for deriving the modulus of rupture is:

\[ C_t = \frac{M}{Z} \quad (1) \]

where \( C_t \) = maximum tensile stress in the bottom fibres

\( M \) = bending moment at the point of fracture

\( Z \) = modulus of section of the test piece.

(Duckworth, 1951, Tweeddale, 1964, p. 221)

Several assumptions are made in deriving this equation, namely:

1) The beam is of homogeneous material which has the same modulus of elasticity in tension and compression.

2) The beam is straight or nearly so.

3) The cross section is uniform.

4) The beam has at least one longitudinal plane of symmetry.

5) All loads and reactions are perpendicular to the axis of the beam and lie in the same plane, which is a longitudinal plane of symmetry.

6) The beam is long in proportion to its depth.

7) The beam is not disproportionately wide (Roark, 1965, p. 96)

For precise ceramic work, the modulus of rupture equation may become:
\[ C_t = \frac{3W}{2bd} \cdot \frac{1}{d} \]  

1 = length between the transverse supports 

b = breadth of the specimen 

d = depth of the specimen

(Duckworth 1951, Black, 1936)

Most accurate results are obtained from bars of rectangular section (Milligan, 1953; Tweeddale, 1964, p. 221).

It has been shown that modulus of rupture increases as the span/depth \((S/d)\) ratio of the specimen decreases below about 10:1 (Milligan, 1953). This variation is slight unless the \(S/d\) ratio is much below 10:1. For a 2:1 ratio, the true modulus of rupture is 80 per cent of that calculated by the simple bending formula. At \(S/d\) ratios below about 1.5:1 the stress distribution changes radically and the ratio of calculated stress to the true modulus of rupture increases rapidly as \(S/d\) becomes still smaller (Roark, 1965, p. 130). In such beams of small \(S/d\) ratio, the shear stresses are likely to be high, and the resulting deflection due to shear may not be negligible.

Because the stress is greatest at the surface, the bend test is particularly sensitive to the state of the specimen surface. Berenbaum and Brodie (1959) predict that the bend test will best demonstrate the effect of modified surface layers in thin specimens.
THE MODULUS OF RUPTURE OF VARIOUS MATERIALS

MATERIALS AND METHODS

All tests for transverse strength were performed on a Hounsfield Tensometer*. As the $g/d$ ratio for the specimens used was relatively small (approximately 3:1) a three-point loading system was chosen so as to minimise the shear stresses in the testing system. It was realised that calculations based on formula (2) would not give the exact true modulus of rupture, but as results were to be used primarily for the purposes of comparison, their accuracy was considered to be adequate.

The compression attachment was assembled into the machine, and within this system, one compression die and a Brinell ball (3 mm. diam.) bolster opposed each other.

Attached directly to the compression die was an assembly for supporting the test specimen. This assembly consisted of two hardened steel supporting rods (0.0913 in. diam. and 7/16 inch. long) set in a brass pad 1" x 7/16". The supporting rods were set parallel to one another, and 0.25 inches apart at their centres. The soft brass pad served to improve the uniformity of load distribution where the supporting rods contacted the test specimen.

The Brinell ball served as the loading head, and was directly opposite the supporting assembly, centred in mid-span.

* Hounsfield Tensometer, Type W. Tensometer Ltd.,

81 Morland Road, Croydon, Surrey, U.K.
This loading system is illustrated in Figure 6.

Samples of $V_{v1}$, $VA_{v1}$, $HFDA_{v0}$, $DA_{v0}$, $DA_{v1}$ and $TH_v$ were prepared in the manner described in section 7. Firing was carried out for 4 minutes at the various temperatures set out in Table II. For each material, a group of 10 specimens was prepared and tested. The only exception was the $TH_v$ group, which consisted of 5 samples only.

As the bend test is especially sensitive to changes in surface characteristics of the test pieces, all specimens were abraded longitudinally with grade 220A Silicon Carbide paper under running water before testing (see p.61). This surface preparation was aimed at producing uniform surface characteristics for all specimens tested.

Each specimen was thoroughly moistened with water immediately before testing. Not only does this procedure eliminate differences caused by variations in relative humidity during testing, but it promotes a testing environment which simulates the severe conditions of the mouth.

In all tests in this section, a 250 lb. beam was used, and movement of the load towards the specimen occurred at the rate of $1/64"$ per minute. Using the conventional equation for modulus of rupture, the rate of tensile loading at the convex surface of the specimen was calculated to approach 6,000 lb./sq.in./min.
Fig. 6 - Three-point loading system - photoelastic analysis. A two-dimensional representation of the distribution and intensity of stress in a glass test piece, when force is applied to the loading head. (Courtesy D.E. Southan).
RESULTS

THE MODULUS OF RUPTURE OF VARIOUS MATERIALS.

Table III shows the modulus of rupture values for the six groups of samples tested. It is interesting to note that the non-aluminous dentine porcelain, $V_{v_1}$ showed a higher transverse strength than either of the aluminous dentine materials, $V_{A_{v_1}}$ (at $>99.9$ per cent level of confidence) or $D_{A_{v_1}}$ (at $>99$ per cent but $<99.9$ per cent level of confidence).

The high-fusing aluminous core material, $HFDA_{v_o}$, was very much stronger than $V_{v_1}$ or any of the other materials tested, $D_{A_{v_o}}$ a lower-fusing aluminous core material, was shown to be stronger than $V_{v_1}$ but not highly significantly so (at $>98$ per cent but $<99$ per cent level of confidence). $D_{A_{v_o}}$ was definitely weaker than $HFDA_{v_o}$.

Modulus of rupture of the sodium aluminosilicate glass, $TH_v$, was not significantly different from that of $V_{v_1}$. 

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### Table III

**Modulus of Rupture of Various Materials**

<table>
<thead>
<tr>
<th>Porcelain</th>
<th>Number of Specimens</th>
<th>Modulus of Rupture</th>
<th></th>
<th></th>
<th>Kg/cm²</th>
<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>p.s.i.</td>
<td>f.s.d.*</td>
<td></td>
<td>p.s.i.</td>
<td>f.s.d.*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
<td>s.d.</td>
<td></td>
<td>Mean</td>
<td>s.d.</td>
</tr>
<tr>
<td>$V_{v1}$</td>
<td>10</td>
<td>7,947.5</td>
<td>753</td>
<td>598</td>
<td>555.4</td>
<td>53</td>
<td>38</td>
</tr>
<tr>
<td>$V_{av1}$</td>
<td>10</td>
<td>5,556.6</td>
<td>727</td>
<td>520</td>
<td>389.0</td>
<td>51</td>
<td>36</td>
</tr>
<tr>
<td>HA$\cdot$</td>
<td>10</td>
<td>14,839.3</td>
<td>1,793</td>
<td>1,282</td>
<td>982.7</td>
<td>126</td>
<td>90</td>
</tr>
<tr>
<td>DA$\cdot$</td>
<td>10</td>
<td>9,104.1</td>
<td>1,078</td>
<td>771</td>
<td>637.3</td>
<td>76</td>
<td>54</td>
</tr>
<tr>
<td>DA$\cdot$</td>
<td>10</td>
<td>6,610.9</td>
<td>669</td>
<td>478</td>
<td>462.8</td>
<td>47</td>
<td>34</td>
</tr>
<tr>
<td>TH$\cdot$</td>
<td>5</td>
<td>8,050.6</td>
<td>1,501</td>
<td>1,863</td>
<td>563.6</td>
<td>105</td>
<td>130</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean
CONCLUSIONS

The aluminous dentine porcelains tested (VA_v1 and DA_v1) were significantly weaker than the non-aluminous dentine material, V_v1.

The aluminous core material, DA_v0, was definitely stronger than the aluminous dentine porcelains, but only stronger than the non-aluminous dentine porcelain at >98 per cent but <99 per cent level of confidence.

The high-fusing aluminous core material was much stronger than any of the other porcelains investigated.
DISCUSSION

Some very interesting comparisons can be drawn between the various materials tested. Perhaps the most striking of these would be between the two aluminous dentine porcelains and the non-aluminous dentine type.

The reason for introducing alumina crystals into dental porcelain originally, was to increase the strength of the material. The fact that neither of the aluminous dentine porcelains (\(VA_{V1}\) or \(DA_{V1}\)) was stronger than the non-aluminous dentine type \(V_{V1}\) indicates that the alumina crystal content of \(VA_{V1}\) and \(DA_{V1}\) is inadequate to produce any significant increase in strength. Certainly the macroscopic appearance of specimens of \(DA_{V1}\) and \(VA_{V1}\), particularly the latter, did not indicate any great loss of translucency through addition of alumina crystal. The translucency of \(VA_{V1}\) appeared to be at least equal to that of \(V_{V1}\). Southan (1968, p. 221) showed that \(DA_{V1}\) had a moderate content of alumina grains, about \(10-35 \mu\) in diameter. The glassy phase in the porcelain was predominant.

To understand why \(V_{V1}\) was, in fact, significantly stronger than either of the aluminous dentine porcelains, we must consider the basic classification into matrix-disrupted or matrix-intact types. \(V_{V1}\) is a matrix-disrupted porcelain, having micro-cracks around the quartz grains within it. It is reasonable that these cracks, being planes of weakness within the material, will act as
crack-stopping factors, and in this way strengthen the porcelain. The aluminous dentine materials, having no quartz content, and very little alumina crystal content, will have little benefit from such crack-stopping mechanisms. A crack in such a material would have little difficulty in passing completely through the glass without meeting any obstruction.

The high-fusing aluminous core material, HFDA\textsubscript{\textit{VO}}, has a very high alumina crystal content, so that this porcelain appears completely opaque. The main reason for its extremely high modulus of rupture may be the increased stiffness of the material, resulting from a very intimate chemical bond between the glass matrix and the many alumina crystal inclusions. It appears that this bond is achieved during manufacture of the porcelain, by heating the glass/alumina mixture over long periods at high temperatures. The large number of glass/crystal interfaces in HFDA\textsubscript{\textit{VO}} may also contribute to its great strength by acting as crack stoppers. It is possible however, that with a good chemical bond between glass and crystal, the crack-stopping effect of this interface may diminish.

While the lower-fusing core, DA\textsubscript{\textit{VO}}, appears to have as much alumina content as HFDA\textsubscript{\textit{VO}}, its lower strength may be attributed to an inferior bond between the glass matrix and the alumina crystal inclusions. In its manufacture, DA\textsubscript{\textit{VO}} is evidently not treated at as high a temperature or for as long a time as HFDA\textsubscript{\textit{VO}}.

If there is anything to be gained by using an aluminous core in the construction of a porcelain jacket crown, it appears
that one should select the high-fusing types. Even here, however, we must have reservations, simply because the core material rarely constitutes the full thickness of the jacket crown. More work is required to examine the behaviour of laminates of core, dentine and enamel materials.
10. **LOW TEMPERATURE ION EXCHANGE**

**THE EFFECT THAT VARIOUS TIME/TEMPERATURE COMBINATIONS FOR ION EXCHANGE HAVE ON MODULUS OF RUPTURE**

In 1968, Southan (p. 233) undertook a semi-quantitative spectrographic analysis for sodium and potassium on four dental porcelain powders, one of which was \( V_1 \). All of the samples studied showed sodium and potassium to be present in similar amounts, although sodium tended to predominate in all the materials. Southan concluded from these results that the vitreous component of these dental porcelains represented a sodium potassium aluminosilicate glass. This is a reasonable conclusion, considering the raw materials from which dental porcelain is made.

In view of the type of glass involved, it seemed reasonable to expect that a surface compressive stress could be induced by replacing sodium ions in the surface glass, with larger potassium ions. Southan (1968, p. 310) showed that it was possible to increase the strength of dental porcelain by inducing surface compression in this way. The method used for this process was to immerse the fired porcelain specimen (or crown) in molten Potassium Nitrate for a period of time.

The aim of the present experimental work was to determine to what extent dental porcelain could be strengthened, using low-temperature ionic exchange, and to develop optimum time/temperature combinations for the treatment of specific dental porcelains.

Four factors were considered to be of primary importance in relation to the ionic exchange process. These factors are:-
(i) Temperature of treatment

(ii) Time of treatment

(iii) Transformation region of the glass

(iv) Chemical composition of the glass.

(i) **Temperature of treatment.**

It is easy to understand a bath of molten potassium nitrate as an environment saturated with potassium ions. When a porcelain specimen is placed into this environment it is surrounded by potential replacements for its own network-modifying ions. Energy, supplied in the form of heat, allows an interchange of ions to take place between the surface glass and the surrounding salt. The result will be an increase in the potassium content of the surface glass, and compression of this zone by the mechanism previously outlined (see p. 45). The rate of diffusion of potassium ions, and the depth of penetration of these ions into the glass, will be governed by the temperature at which the treatment takes place.

(ii) **Time of treatment.**

The length of time over which the ionic exchange process is performed will influence the extent to which the glassy surface can be compressed. Considering treatment at a specific temperature; the longer the time of treatment, the more energy has been supplied. The ion exchange reaction, then, will have proceeded further, evidenced by a greater degree of penetration of potassium ions into the glass surface.

It will be evident that treatment at a low temperature for a long time may produce the same degree of surface compression as a
higher temperature for a shorter time. The important factor here is
the energy of activation for the reaction to take place, and this is
determined by both temperature and time.

(iii) Transformation region of the glass.

The transformation region of a glass may be defined as the
temperature at which all stresses in the glass are released in a
relatively short time, usually considered to be within 15 minutes. At
these temperatures the glass has a viscosity of the order of $10^{13}$ poises,
which is low enough to allow stresses to be released within this short
time (Jones, 1948-49). As the name implies, this should not be
interpreted as a specific, well-defined temperature point. Even at
temperatures considerably below the transformation region, stresses in
the glass may still be released, but at a very slow rate. As the
transformation region is approached, the rate of stress release is
increased. At temperatures above the transformation region, of course,
no stresses can exist in the glass. This phenomenon may be understood,
perhaps, as a softening of the glassy matrix. The transformation region
will vary from one glass to another, depending on its chemical
composition.

Success of the ion exchange process for strengthening glass
depends on compressive stresses being set up in the glassy surface. As
the treatment temperature is raised close to the transformation region,
the surface compression will start to be released by softening of the
glassy matrix, so defeating the purpose of the treatment. If the
temperature of treatment is too close to the transformation region, or if the treatment time is too long, the rate of release of stresses by relaxation of the matrix may be greater than the rate of induction of surface compression. Such a situation must be avoided by keeping treatment temperatures well below the transformation region and restricting the time of treatment. It will be realised that once surface stresses have been released due to relaxation with overheating, the surface will be resistant to further chemical stressing, as it is already saturated with potassium ions.

It will be obvious that all three factors considered above (temperature, time and transformation region) must be intimately related in producing an optimal programme for chemical strengthening. Due to differing transformation regions, optimum time/temperature combinations will vary from one glass to another.

(iv) Chemical composition of the glass.

The ion exchange process is effective for most dental porcelains because, being sodium-potassium aluminosilicate glasses, there are sodium ions available in the matrix to be exchanged for larger potassium ions. If the glass was only a potassium aluminosilicate, then this process would not be effective. On the other hand, in the case of a purely sodium aluminosilicate glass, a greater degree of surface compression might be expected.
MATERIALS AND METHODS

Groups of prepared samples of $V_{V1}$, $VA_{V1}$, $HFDA_{V0}$, $DA_{V0}$, $DA_{V1}$ and $TH_{v}$ were treated by immersion in molten potassium nitrate of analytical quality.

Temperatures were chosen, varying from 400$^\circ$C to 600$^\circ$C and groups of specimens were immersed in the molten salt for times ranging from 1 hour to 96 hours. Times longer than 96 hours were not considered because unless the extra strength gain was extremely great, such lengthy treatments would not be feasible in dental practice.

For heating specimens in the ion-exchange treatment, a Jelenko inlay furnace*, which had a photo-electric cell temperature control, was used. The potassium nitrate was placed in a ceramic crucible and the porcelain specimens placed on the crystals. This crucible was then placed in the furnace, which had been preheated to the desired treatment temperature.

Immediately following placement of the crucible into the furnace, there was a fall in temperature. Treatment time was measured from the time that the selected temperature was regained. The time lapse between placement of the crucible into the furnace, and the selected temperature being regained, was noted. This time was usually about 10 minutes.

* Model LFA furnace, J.F. Jelenko and Co. Inc.

170 Petersville Road, New Rochelle, New York, 10801.
### TABLE IV

RELATIONSHIP BETWEEN TRANSFORMATION REGIONS AND TREATMENT TEMPERATURES AND TIMES USED FOR PORCELAIN SPECIMENS.

<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>TRANSFORMATION REGION</th>
<th>TEMPERATURES USED FOR TREATMENT</th>
<th>TREATMENT TIMES USED (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{v1}$</td>
<td>ca 700°C*</td>
<td>400°C, 500°C, 600°C</td>
<td>1, 6, 18, 48, 96, 1, 6, 18, 24, 48, 96, 1, 3, 4.5, 6, 12, 18</td>
</tr>
<tr>
<td>$VA_{v1}$</td>
<td>ca 635°C*</td>
<td>400°C, 500°C, 600°C</td>
<td>1, 6, 18, 24, 48, 96, 1, 6, 18, 24, 48, 96, 1, 3, 6</td>
</tr>
<tr>
<td>HF$VA_{v0}$</td>
<td>ca 705°C*</td>
<td>400°C, 500°C, 600°C</td>
<td>1, 6, 24, 48, 96, 1, 6, 18, 24, 48, 96, 1, 3, 6, 12, 24, 48, 96</td>
</tr>
<tr>
<td>$DA_{v0}$</td>
<td>ca 620°C*</td>
<td>400°C, 500°C</td>
<td>1, 6, 18, 24, 48, 96, 1, 6, 18, 24, 48, 96</td>
</tr>
<tr>
<td>$DA_{v1}$</td>
<td>ca 620°C*</td>
<td>400°C, 500°C</td>
<td>1, 6, 18, 24, 48, 96, 1, 6, 18, 24, 48, 96</td>
</tr>
<tr>
<td>$TH_{v}$</td>
<td>ca 535°C*</td>
<td>400°C, 500°C</td>
<td>1, 6, 18, 24, 48, 96, 1, 3, 6, 18, 24, 48, 96</td>
</tr>
</tbody>
</table>

* As determined by Southan - personal communication.
** As supplied by Garsco Pty. Ltd., 386a Eastern Valley Way, East Roseville, N.S.W. Australia.
Upon completion of the treatment time, the crucible was removed from the furnace. The specimens were removed from the molten salt with tweezers, and placed on a metal tray to cool. After cooling to room temperature, the treated specimens were thoroughly washed in water to remove any crystallised salt. These specimens were then tested for transverse strength as outlined previously.

Table IV shows the materials treated, the transformation region for each material, and the temperatures and times used in the ion exchange treatment.

A control group of 10 $V_{v1}$ specimens was placed in the inlay furnace on a pad of asbestos at 500$^\circ$C, using dry heat only for 24 hours. These specimens were then cooled and tested in the normal way.
RESULTS

$V_{v1}$ - Tables VI, VII, VIII and Fig. 7.

After only one hour of ionic exchange treatment, the conventional dentine porcelain ($V_{v1}$) was significantly stronger than the untreated samples. This was so for all three temperatures used: $400^\circ\text{C}$, $500^\circ\text{C}$ and $600^\circ\text{C}$ (at $>99.9$ per cent level of confidence in each case).

At 1 hour, the $500^\circ\text{C}$ and $600^\circ\text{C}$ samples had moduli of rupture which were not significantly different from one another, as seen in Tables VI and VII. The $400^\circ\text{C}$ samples at this time were weaker than the $500^\circ\text{C}$ samples (at $>99$ per cent but $<99.9$ per cent level of confidence) but less significantly weaker than the $600^\circ\text{C}$ samples (at $>95$ per cent but $<98$ per cent level of confidence).

Table V shows that, treating at $400^\circ\text{C}$ the modulus of rupture increases gradually and uniformly after 1 hour, to reach a mean value of 14,419.0 p.s.i. after 96 hours.

At $500^\circ\text{C}$, the modulus of rupture reaches its highest value after 18 hours. From this time until 96 hours, the strength of $V_{v1}$ remained consistently high. Modulus of rupture after 96 hours tended to be lower than that for 18 hours but the difference was not significant ( $>80$ per cent but $<90$ per cent level of confidence).

Treatment at $600^\circ\text{C}$ resulted in a dramatic increase in modulus of rupture, reaching a peak at 4.5 hours. Further treatment at this temperature produced a noticeable deterioration in strength due presumably to the release of surface compressive stresses by

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softening of the glassy matrix.

Maximum strength increase of \( V_{V_1} \) was reached after 18 hours treatment at 500°C. Modulus of rupture after 4.5 hours at 600°C was not significantly lower than this value.

Results for the control group of \( V_{V_1} \), treated in dry heat only, are shown in Table B. The modulus of rupture for this group was not significantly different from that for untreated specimens of \( V_{V_1} \) ( > 70 per cent but < 80 per cent level of confidence).

**TABLE V**

**MODULUS OF RUPTURE**

\( (V_{V_1}) \) treated in dry heat only at 500°C 24 hrs.

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>NO. OF SPECIMENS</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>p.s.i.</td>
<td>Kg/cm²</td>
<td>p.s.i.</td>
</tr>
<tr>
<td>10</td>
<td>8,653.3</td>
<td>605.7</td>
<td>1,522</td>
</tr>
</tbody>
</table>
### TABLE VI

**MODULUS OF RUPTURE**

$(V_{v1})$ immersed in molten $\text{KNO}_3$ at $400^\circ\text{C}$

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>$n^{**}$</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p.s.i.</td>
<td>Kg/cm²</td>
<td>p.s.i.</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>7,947.5</td>
<td>556.4</td>
<td>753</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>10,438.2</td>
<td>730.7</td>
<td>639</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>12,171.7</td>
<td>852.0</td>
<td>960</td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>13,726.9</td>
<td>960.9</td>
<td>1,253</td>
</tr>
<tr>
<td>48</td>
<td>10</td>
<td>14,521.3</td>
<td>1,016.5</td>
<td>1,659</td>
</tr>
<tr>
<td>96</td>
<td>10</td>
<td>14,419.0</td>
<td>1,009.3</td>
<td>1,575</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean

$n^{**}$ number of specimens
TABLE VII

MODULUS OF RUPTURE

(\( V_{V_1} \)) immersed in molten \( \text{KNO}_3 \) at 500\(^\circ\)C

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p.s.i.</td>
<td>Kg/cm(^2)</td>
<td>p.s.i.</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>7,947.5</td>
<td>556.4</td>
<td>753</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>11,833.0</td>
<td>828.3</td>
<td>1,116</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>13,468.2</td>
<td>942.8</td>
<td>1,407</td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>16,917.1</td>
<td>1,184.2</td>
<td>943</td>
</tr>
<tr>
<td>24</td>
<td>10</td>
<td>15,980.7</td>
<td>1,118.7</td>
<td>1,253</td>
</tr>
<tr>
<td>48</td>
<td>10</td>
<td>16,397.7</td>
<td>1,147.9</td>
<td>1,499</td>
</tr>
<tr>
<td>96</td>
<td>10</td>
<td>16,157.3</td>
<td>1,131.0</td>
<td>908</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean.

n** number of specimens.
TABLE VIII

MODULUS OF RUPTURE

($V_{v1}$) immersed in molten KNO$_3$ at 600°C

The effect treatment time has on modulus of rupture.

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p.s.i.</td>
<td>Kg/cm$^2$</td>
<td>p.s.i.</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>7,947.5</td>
<td>556.4</td>
<td>753</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>11,889.5</td>
<td>832.2</td>
<td>1,775</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>15,430.1</td>
<td>1,080.1</td>
<td>1,423</td>
</tr>
<tr>
<td>4.5</td>
<td>10</td>
<td>16,873.4</td>
<td>1,181.1</td>
<td>644</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>15,751.6</td>
<td>1,102.6</td>
<td>944</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>14,194.4</td>
<td>993.6</td>
<td>672</td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>13,242.0</td>
<td>926.9</td>
<td>1,017</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean

n** number of specimens.
Fig. 7 - Transverse strengths of a quartz-bearing dental porcelain (\(V_{v1}\)) after various chemical treatments.

- represents 95 per cent confidence limits for the true mean.
VA_{1} - Tables IX, X and Fig. 8.

The aluminous dentine porcelain VA_{1}, proved to be very susceptible to strengthening by low temperature ion exchange. At each of the temperatures used (400°C, 500°C and 600°C) a highly significant increase in strength over untreated samples was produced after only one hour of treatment (at > 99.9 per cent level of confidence in each case). At this stage the 500°C group was significantly stronger than the 400°C group (at > 99 per cent but < 99.9 per cent level of confidence).

At 400°C, as shown in Table IX, strength after 6 hours of treatment had increased beyond the 1 hour level, but this increase was not highly significant (at > 95 per cent but < 98 per cent level of confidence). When treatment at 400°C continued longer than 6 hours strength remained virtually constant, at least until 96 hours.

Table X shows that treatment at 500°C produced an even rate of strength increase from 1 hour to 96 hours of treatment. Maximum strength gain for this material was achieved after 96 hours of treatment at 500°C. Strength at this time was significantly higher than that after 24 hours at 500°C (at > 99 per cent but < 99.9 per cent level of confidence).

At 600°C, as shown in Table XI, the highest strength is achieved after 1 hour of treatment. Further treatment at this temperature causes a quite rapid deterioration in strength.
TABLE IX

MODULUS OF RUPTURE

(\(V_{A_{v_{1}}}\)) immersed in molten KNO\(_3\) at 400\(^{\circ}\)C

The effect treatment time has on modulus of rupture.

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p.s.i.   Kg/cm(^2)</td>
<td>p.s.i. Kg/cm(^2)</td>
<td>p.s.i. Kg/cm(^2)</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>5,556.6   389.0</td>
<td>727</td>
<td>51</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>11,673.0  817.1</td>
<td>1,934</td>
<td>135</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>13,491.9  944.4</td>
<td>1,418</td>
<td>99</td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>14,294.8  1,000.7</td>
<td>1,859</td>
<td>130</td>
</tr>
<tr>
<td>24</td>
<td>10</td>
<td>13,742.8  962.0</td>
<td>1,898</td>
<td>133</td>
</tr>
<tr>
<td>48</td>
<td>10</td>
<td>13,854.8  969.9</td>
<td>1,181</td>
<td>83</td>
</tr>
<tr>
<td>96</td>
<td>10</td>
<td>13,798.3  965.9</td>
<td>1,956</td>
<td>137</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean

n** number of specimens.
TABLE X
MODULUS OF RUPTURE

(\(VA_{V_1}\)) immersed in molten KNO\(_3\) at 500\(^\circ\)C

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>p.s.i.</td>
<td>Kg/cm(^2)</td>
<td>p.s.i.</td>
<td>Kg/cm(^2)</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>5,556.6</td>
<td>389.0</td>
<td>727</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>14,577.9</td>
<td>1,020.5</td>
<td>1,560</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>15,162.4</td>
<td>1,061.3</td>
<td>1,875</td>
</tr>
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<td>10</td>
<td>15,815.5</td>
<td>1,107.1</td>
<td>1,950</td>
</tr>
<tr>
<td>24</td>
<td>10</td>
<td>17,044.2</td>
<td>1,193.1</td>
<td>2,308</td>
</tr>
<tr>
<td>48</td>
<td>10</td>
<td>18,402.8</td>
<td>1,288.2</td>
<td>2,430</td>
</tr>
<tr>
<td>96</td>
<td>10</td>
<td>19,730.3</td>
<td>1,381.1</td>
<td>1,132</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean

n** number of specimens.
TABLE XI

MODULUS OF RUPTURE

(V4) immersed in molten KNO₃ at 600°C

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p.s.i.   Kg/cm²</td>
<td>p.s.i.   Kg/cm²</td>
<td>p.s.i. Kg/cm²</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>5,556.6  389.0</td>
<td>727      51</td>
<td>520 36</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>15,195.7 1,063.7</td>
<td>1,713     120</td>
<td>1,225 86</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>13,507.4 945.5</td>
<td>1,047     73</td>
<td>749 52</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>11,041.3 772.9</td>
<td>977      68</td>
<td>699 49</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean.

n** number of specimens.
Fig. 8. - Transverse strength of an aluminous 'body' dental porcelain ($\Delta V_{y_1}$) after various chemical treatments. 
- represents 95 per cent confidence limits 
  for the true mean.
HFDA\textsubscript{\textit{vo}} - Tables XII, XIII, XIV and Fig. 9.

The high fusing aluminous core material (HFDA\textsubscript{\textit{vo}}), when treated in molten KNO\textsubscript{3} for 1 hour at 500\textdegree{}C or 600\textdegree{}C, became highly significantly stronger than the untreated specimens (at $>99.9$ per cent level of confidence in each case). Strengths of 500\textdegree{}C and 600\textdegree{}C samples at this stage were not significantly different from one another.

Treatment at 400\textdegree{}C, as shown in Table XII, produced after 1 hour, an increase in strength over the untreated samples. This increase, however, was not a highly significant one (at $>95$ per cent but $<98$ per cent level of confidence). When treatment continued at 400\textdegree{}C, strength increased to a mean of 21,751.1 p.s.i. at 6 hours. With further treatment after 6 hours, strength remained fairly constant, with only a slight tendency to increase, up to 96 hours.

At 500\textdegree{}C, as Table XIII shows, strength increased slowly after 1 hour of treatment, to reach a mean of 30,187.4 p.s.i. at 18 hours. This value was equivalent to the best strength value obtained for HFDA\textsubscript{\textit{vo}}. Continuing treatment for longer than 18 hours produced no significant change in strength, up to 96 hours.

Table XIV shows strength to increase rapidly for the first 3 hours of treatment at 600\textdegree{}C. Further treatment at this temperature resulted in an apparent strength increase at 6 hours, but this was not a significant gain. Treatment after 6 hours caused a gradual deterioration in transverse strength. After 96 hours, strength was highly significantly lower than at 6 hours. (at $>99.9$ per cent level of confidence).
### TABLE XII

MODULUS OF RUPTURE

*(HFDA\(_4\)) immersed in molten KNO\(_3\) at 400°C*

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p.s.i.</td>
<td>Kg/cm(^2)</td>
<td>p.s.i.</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>14,039.3</td>
<td>982.7</td>
<td>1,793</td>
</tr>
<tr>
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<td>10</td>
<td>16,371.1</td>
<td>1,146.0</td>
<td>2,056</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>21,751.1</td>
<td>1,522.6</td>
<td>2,065</td>
</tr>
<tr>
<td>24</td>
<td>10</td>
<td>21,610.8</td>
<td>1,512.8</td>
<td>2,609</td>
</tr>
<tr>
<td>48</td>
<td>10</td>
<td>22,148.4</td>
<td>1,550.4</td>
<td>2,718</td>
</tr>
<tr>
<td>96</td>
<td>10</td>
<td>25,167.4</td>
<td>1,761.7</td>
<td>3,266</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean.

n** number of specimens.
### TABLE XIII

**MODULUS OF RUPTURE**

*(HFDA<sub>v</sub>) immersed in molten KNO<sub>3</sub> at 500°C*

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p.s.i.</td>
<td>Kg/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>p.s.i.</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>14,039.3</td>
<td>982.7</td>
<td>1,793</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>24,294.9</td>
<td>1,700.7</td>
<td>2,264</td>
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<tr>
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<td>10</td>
<td>27,647.0</td>
<td>1,935.3</td>
<td>2,733</td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>30,187.4</td>
<td>2,113.1</td>
<td>3,554</td>
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<tr>
<td>24</td>
<td>10</td>
<td>28,743.8</td>
<td>2,012.1</td>
<td>2,950</td>
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<tr>
<td>48</td>
<td>10</td>
<td>30,372.1</td>
<td>2,126.0</td>
<td>1,956</td>
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<td>10</td>
<td>30,683.0</td>
<td>2,147.8</td>
<td>3,162</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean.

n** number of specimens.
--- 99 ---

**TABLE XIV**

**MODULUS OF RUPTURE**

$(HYDA_{V_o})$ immersed in molten KNO$_3$ at 600ºC

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n**</td>
<td>p.s.i.</td>
<td>Kg/cm$^2$</td>
<td>p.s.i.</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>14,039.3</td>
<td>982.7</td>
<td>1,793</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>24,806.8</td>
<td>1,736.5</td>
<td>3,249</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>27,497.6</td>
<td>1,924.9</td>
<td>1,427</td>
</tr>
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<td>10</td>
<td>28,412.2</td>
<td>1,988.8</td>
<td>1,973</td>
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<tr>
<td>12</td>
<td>10</td>
<td>27,737.4</td>
<td>1,941.6</td>
<td>1,944</td>
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<tr>
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<td>10</td>
<td>27,076.6</td>
<td>1,895.4</td>
<td>2,064</td>
</tr>
<tr>
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<td>10</td>
<td>26,049.3</td>
<td>1,823.4</td>
<td>2,807</td>
</tr>
<tr>
<td>96</td>
<td>10</td>
<td>25,133.7</td>
<td>1,759.4</td>
<td>1,022</td>
</tr>
</tbody>
</table>

* For calculation of 95% confidence limits for the true mean.

n** number of specimens.
Fig. 9 - Transverse strengths of an aluminous high-fusing core dental porcelain ($HFDA_{V_o}$) after various chemical treatments. 

represents 95 per cent confidence limits 
for the true mean.
DAV₀ - Tables XV, XVI and Fig. 10.

The aluminous core porcelain DAV₀ was peculiar in that, with chemical pre-stressing, strength values tended to become unpredictable. This material showed a tendency toward wide scattering of results, with coefficients of variation ranging up to 40 per cent (after treatment at 500°C for 24 hours). Results from the other materials with similar transformation regions indicate that such a treatment could not be considered a particularly severe one.

Treatment at 400°C (Table XV) produced a steadily increasing strength, up to a mean maximum of 19,356 p.s.i. at 48 hours. Transverse strength after 96 hours at 400°C, however, was not significantly lower than the 48 hour level.

Table XVI shows that, when treating in KNO₃ at 500°C maximum strength is reached at 6 hours. As treatment proceeds beyond this time, there is an apparent tendency for strength to deteriorate. However, this could not be regarded as a significant strength decrease, as the strength after 96 hours is not significantly lower than that at 6 hours. (at <70 per cent level of confidence).
TABLE XV
MODULUS OF RUPTURE

\((\text{DA}_v)\) immersed in molten \(\text{KNO}_3\) at 400\(^{\circ}\)C

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>(n^{**})</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>(*f.s.d.) (95%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td>p.s.i.</td>
<td>Kg/cm(^2)</td>
<td>p.s.i.</td>
</tr>
<tr>
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<td>10</td>
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<td>637.3</td>
<td>1,078</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>13,088.4</td>
<td>916.2</td>
<td>1,631</td>
</tr>
<tr>
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<td>10</td>
<td>15,257.2</td>
<td>1,068.0</td>
<td>2,125</td>
</tr>
<tr>
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<td>10</td>
<td>14,904.2</td>
<td>1,043.3</td>
<td>3,496</td>
</tr>
<tr>
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<td>10</td>
<td>16,564.6</td>
<td>1,159.6</td>
<td>1,965</td>
</tr>
<tr>
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<td>10</td>
<td>19,356.1</td>
<td>1,354.9</td>
<td>2,980</td>
</tr>
<tr>
<td>96</td>
<td>10</td>
<td>18,743.0</td>
<td>1,312.0</td>
<td>3,061</td>
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</tbody>
</table>

\(^*\) For calculation of 95\% Confidence limits for the true mean.

\(^{**}\) number of specimens.
TABLE XVI

MODULUS OF RUPTURE

(\(DAv_0\)) immersed in molten KNO_3 at 500°C

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>±f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
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<td>p.s.i.</td>
<td>Kg/cm²</td>
<td>p.s.i.</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>9,104.1</td>
<td>637.3</td>
<td>1,078</td>
</tr>
<tr>
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<td>10</td>
<td>12,022.1</td>
<td>841.5</td>
<td>2,602</td>
</tr>
<tr>
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<td>10</td>
<td>16,635.8</td>
<td>1,164.5</td>
<td>2,648</td>
</tr>
<tr>
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<td>10</td>
<td>16,159.9</td>
<td>1,131.2</td>
<td>5,785</td>
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<td>10</td>
<td>13,622.5</td>
<td>953.6</td>
<td>5,493</td>
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<tr>
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<td>10</td>
<td>15,358.9</td>
<td>1,075.1</td>
<td>4,684</td>
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<tr>
<td>96</td>
<td>10</td>
<td>14,903.6</td>
<td>1,043.3</td>
<td>3,800</td>
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</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean.

n** number of specimens.
Fig. 10 - Transverse strengths of an aluminous core dental porcelain (DA$\gamma_o$) after various chemical treatments.  
- represents 95 per cent confidence limits for the true mean.
DA\textsubscript{v$_1$} - Tables XVII, XVIII and Fig. 11.

Samples of aluminous dentine porcelain DA\textsubscript{v$_1$}, underwent dramatic increase in strength with low temperature ionic exchange treatment.

Treating in molten KNO\textsubscript{3} at 400\degree C, as shown in Table XVII, produced a significant strength increase over the untreated level, in only 1 hour. (at $> 99.9$ per cent level of confidence). With further treatment at this temperature, a mean transverse strength of 18,280.7 p.s.i. was achieved at 6 hours. Beyond 6 hours of treatment, strength remained fairly constant up to 96 hours. At 96 hours, strength was not significantly greater than at 6 hours. (at $> 60$ per cent but $< 70$ per cent level of confidence).

Table XVIII shows that treatment at 500\degree C for 1 hour resulted in strength significantly higher than that of untreated samples (at $> 99.9$ per cent level of confidence). Further treatment at 500\degree C, produced a significant strength increase at 6 hours, over the 1 hour (at $> 99$ per cent but $< 99.9$ per cent level of confidence).

From 6 hours to 48 hours there was no significant change in strength. However, when treatment extended beyond 48 hours, strength did deteriorate. Modulus of rupture at 96 hours was significantly lower than that at 48 hours (at $> 99.9$ per cent level of confidence).

It is interesting to note the similarity between the 400\degree C and the 500\degree C curves for DA\textsubscript{v$_1$}, from 6 hours to 96 hours. (Fig. 11). For example, at 18 hours there is no significant difference in strength between the 400\degree C group and the 500\degree C group (at $> 30$ per cent but $< 40$ per cent level of confidence).
TABLE XVII

MODULUS OF RUPTURE

(DA\textsubscript{v1}) immersed in molten KNO\textsubscript{3} at 400\textdegree C

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
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<tbody>
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<td>Kg/cm\textsuperscript{2}</td>
<td>p.s.i.</td>
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<td>462.8</td>
<td>669</td>
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<td>10</td>
<td>12,567.8</td>
<td>879.8</td>
<td>1,518</td>
</tr>
<tr>
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<td>10</td>
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<td>1,279.7</td>
<td>2,477</td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>19,630.2</td>
<td>1,374.1</td>
<td>988</td>
</tr>
<tr>
<td>24</td>
<td>10</td>
<td>16,996.1</td>
<td>1,189.7</td>
<td>3,097</td>
</tr>
<tr>
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<td>10</td>
<td>19,891.4</td>
<td>1,392.4</td>
<td>1,861</td>
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<tr>
<td>96</td>
<td>10</td>
<td>19,575.9</td>
<td>1,370.3</td>
<td>2,625</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean.

n** number of specimens.
TABLE XVIII

MODULUS OF RUPTURE

(DA,1) immersed in molten KNO₃ at 500°C

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
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</thead>
<tbody>
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<td></td>
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<td>Kg/cm²</td>
<td>p.s.i.</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>6,610.9</td>
<td>462.8</td>
<td>669</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>16,495.4</td>
<td>1,154.7</td>
<td>2,371</td>
</tr>
<tr>
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<td>10</td>
<td>19,928.4</td>
<td>1,395.0</td>
<td>2,620</td>
</tr>
<tr>
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<td>10</td>
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<td>1,412.3</td>
<td>2,919</td>
</tr>
<tr>
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<td>1,486.0</td>
<td>3,829</td>
</tr>
<tr>
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<td>10</td>
<td>20,919.9</td>
<td>1,464.4</td>
<td>1,178</td>
</tr>
<tr>
<td>96</td>
<td>10</td>
<td>17,819.2</td>
<td>1,247.3</td>
<td>1,936</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean.

n** number of specimens.
Fig. 11 - Transverse strengths of an aluminous 'body' dental porcelain (DAυ₁) after various chemical treatments. 

represents 95 per cent confidence limits for the true mean.
THγ - Tables XIX, XX and Fig. 12.

For the commercial sodium aluminosilicate glass THγ, five specimens were used in each group, instead of the usual ten.

When treated in molten KNO₃ at 400°C, as shown in Table XIX, transverse strength after 1 hour was significantly higher than the untreated level (at > 99.9 per cent level of confidence). As treatment continued for longer than 1 hour there was a fairly gradual tendency for strength to increase. Maximum strength increase for this material at 400°C, was reached after 96 hours of ion exchange treatment.

Table XX shows that treatment at 500°C produced a dramatic strength increase after only 1 hour. The strength at 1 hour was highly significantly greater than the untreated level (at > 99.9 per cent level of confidence). Continuing treatment at this temperature beyond 1 hour resulted in a constant strength level for as long as 96 hours, with no significant change in that time.


TABLE XIX

MODULUS OF RUPTURE

\( (TH_v) \) immersed in molten \( \text{KNO}_3 \) at \( 400^\circ \text{C} \)

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th><em>f.s.d.</em> (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p.s.i. Kg/cm²</td>
<td>p.s.i. Kg/cm²</td>
<td>p.s.i. Kg/cm²</td>
</tr>
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<td>5</td>
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<td>1,501 105</td>
<td>1,863 130</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>13,153.4 920.7</td>
<td>1,584 111</td>
<td>1,966 138</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>15,625.2 1,093.8</td>
<td>2,066 145</td>
<td>2,564 179</td>
</tr>
<tr>
<td>18</td>
<td>5</td>
<td>17,276.4 1,209.3</td>
<td>3,896 273</td>
<td>4,835 338</td>
</tr>
<tr>
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<td>5</td>
<td>16,022.0 1,121.5</td>
<td>1,914 134</td>
<td>2,375 166</td>
</tr>
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<td>5</td>
<td>18,335.8 1,283.5</td>
<td>1,948 136</td>
<td>2,417 169</td>
</tr>
<tr>
<td>96</td>
<td>5</td>
<td>18,826.2 1,317.8</td>
<td>2,404 168</td>
<td>2,983 209</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean.

n** number of specimens.
TABLE XX

MODULUS OF RUPTURE

(Te) immersed in molten KNO₃ at 500°C

The effect treatment time has on modulus of rupture

<table>
<thead>
<tr>
<th>TIME (hrs)</th>
<th>n**</th>
<th>TRANSVERSE STRENGTH</th>
<th>STANDARD DEVIATION</th>
<th>*f.s.d. (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p.s.i.   Kg/cm²</td>
<td>p.s.i.   Kg/cm²</td>
<td>p.s.i.      Kg/cm²</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
<td>8,050.6  563.6</td>
<td>1,501     105</td>
<td>1,863      130</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>18,501.2 1,295.1</td>
<td>2,376     166</td>
<td>2,949      206</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>18,679.6 1,307.6</td>
<td>2,876     201</td>
<td>3,569      250</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>20,239.6 1,416.8</td>
<td>3,004     210</td>
<td>3,728      261</td>
</tr>
<tr>
<td>18</td>
<td>5</td>
<td>18,457.4 1,292.0</td>
<td>2,307     161</td>
<td>2,863      200</td>
</tr>
<tr>
<td>24</td>
<td>5</td>
<td>20,173.4 1,412.1</td>
<td>4,434     310</td>
<td>5,503      385</td>
</tr>
<tr>
<td>48</td>
<td>5</td>
<td>18,917.0 1,324.2</td>
<td>2,756     193</td>
<td>3,420      239</td>
</tr>
<tr>
<td>96</td>
<td>5</td>
<td>20,474.4 1,433.2</td>
<td>1,803     126</td>
<td>2,238      157</td>
</tr>
</tbody>
</table>

* For calculation of 95% Confidence limits for the true mean.

n** number of specimens.
Fig 12 - Transverse strengths of an aluminosilicate glass (TH) after various chemical treatments. It represents 95 per cent confidence limits for the true mean.
Fig. 12.
Fig. 13 - Comparisons between untreated strengths and maximum strengths achieved by chemically treating various porcelains. 

represents 95 per cent confidence limits for the true mean.
CONCLUSIONS

Table XXI shows the maximum transverse strength attained for each material after chemical prestressing in molten KNO₃. For each material tested, mean transverse strength after chemical prestressing was at least double the untreated level. The aluminous dentine porcelains, VAᵥ₁ and DAᵥ₁, had their moduli of rupture more than trebled by ionic exchange treatment.

The high-fusing aluminous core material, HFDAᵥ₀, was by far the strongest of the untreated porcelains, and continued to be the strongest following chemical prestressing.

Maximum transverse strength for the sodium alumino-silicate glass (THᵥ) after ion exchange treatment was not significantly different from that of either of the aluminous dentine porcelains, VAᵥ₁ or DAᵥ₁.

When considering optimum temperature/time combinations for ion exchange treatment in practice, one must consider factors other than just the maximum strength attainable. An important consideration must be the convenience of treatment schedule. Another might be the influence that stress-zone thickness may have on serviceability of the article.

If, for example, the strength after 18 hours of treatment is not significantly higher than that after 6 hrs. then the shorter treatment would probably be preferred. It would also be desirable to avoid inconvenient treatment times, such as 12 hrs.
In view of these considerations, Table XXII has been prepared to show what have been considered optimal treatment schedules for each material, and to present transverse strengths attained after such treatments.
### TABLE XXI

**MODULUS OF RUPTURE**

The effect that chemical stressing in molten KNO₃ has on modulus of rupture

<table>
<thead>
<tr>
<th></th>
<th>UNTREATED TRANSVERSE STRENGTH</th>
<th>TREATMENT</th>
<th>MAXIMUM STRESSED TRANSVERSE STRENGTH</th>
<th>FACTOR BY WHICH MATERIAL IS STRENGTHENED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>p.s.i.</td>
<td>Kg/cm²</td>
<td>TEMP.</td>
<td>TIME</td>
</tr>
<tr>
<td><strong>Vᵥ₁</strong></td>
<td>7,947.5</td>
<td>556.4</td>
<td>500°C</td>
<td>18 hrs.</td>
</tr>
<tr>
<td></td>
<td>(538)</td>
<td>(38)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Vₐᵥ₁</strong></td>
<td>5,556.6</td>
<td>389.0</td>
<td>500°C</td>
<td>96 hrs.</td>
</tr>
<tr>
<td></td>
<td>(520)</td>
<td>(36)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>HFDₐᵥₒ</strong></td>
<td>14,039.3</td>
<td>982.7</td>
<td>500°C</td>
<td>96 hrs.</td>
</tr>
<tr>
<td></td>
<td>(1,282)</td>
<td>(90)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Dₐᵥₒ</strong></td>
<td>9,104.1</td>
<td>637.3</td>
<td>400°C</td>
<td>48 hrs.</td>
</tr>
<tr>
<td></td>
<td>(771)</td>
<td>(54)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Dₐᵥ₁</strong></td>
<td>6,610.9</td>
<td>462.8</td>
<td>500°C</td>
<td>24 hrs.</td>
</tr>
<tr>
<td></td>
<td>(478)</td>
<td>(34)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tᵥᵥ</strong></td>
<td>8,050.6</td>
<td>563.6</td>
<td>500°C</td>
<td>6 hrs.</td>
</tr>
<tr>
<td></td>
<td>(1,863)</td>
<td>(130)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

f.s.d. (95%) in brackets.

* Each group of Thᵥ consisted of 5 specimens only. All other materials contained 10 specimens per group.
### TABLE XXII

**Modulus of Rupture**

Optimal treatment time/temperature combinations for various materials.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>NO. OF SPEC.</th>
<th>UNTREATED TRANSVERSE STRENGTH p.s.i.</th>
<th>Kg/cm²</th>
<th>TREATMENT TEMP.</th>
<th>TIME</th>
<th>TREATED TRANSVERSE STRENGTH p.s.i.</th>
<th>Kg/cm²</th>
<th>FACTOR BY WHICH MATERIAL IS STRENGTHENED</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{V1}$</td>
<td>10</td>
<td>7,947.5</td>
<td>556.4</td>
<td>600°C</td>
<td>4.5 hrs.</td>
<td>16,673.4</td>
<td>1,181.1</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(539)</td>
<td>(38)</td>
<td></td>
<td></td>
<td>(660)</td>
<td>(32)</td>
<td></td>
</tr>
<tr>
<td>$VA_{V1}$</td>
<td>10</td>
<td>5,556.6</td>
<td>389.0</td>
<td>500°C</td>
<td>6 hrs.</td>
<td>15,162.4</td>
<td>1,061.3</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(520)</td>
<td>(36)</td>
<td></td>
<td></td>
<td>(1,341)</td>
<td>(94)</td>
<td></td>
</tr>
<tr>
<td>$NDA_{V1}$</td>
<td>10</td>
<td>14,039.3</td>
<td>982.7</td>
<td>600°C</td>
<td>6 hrs.</td>
<td>28,412.2</td>
<td>1,986.8</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1,282)</td>
<td>(90)</td>
<td></td>
<td></td>
<td>(1,614)</td>
<td>(99)</td>
<td></td>
</tr>
<tr>
<td>$DA_{V1}$</td>
<td>10</td>
<td>9,104.1</td>
<td>637.3</td>
<td>500°C</td>
<td>6 hrs.</td>
<td>16,635.8</td>
<td>1,164.5</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(771)</td>
<td>(54)</td>
<td></td>
<td></td>
<td>(1,893)</td>
<td>(133)</td>
<td></td>
</tr>
<tr>
<td>$DA_{V1}$</td>
<td>10</td>
<td>6,610.9</td>
<td>462.8</td>
<td>500°C</td>
<td>6 hrs.</td>
<td>19,928.4</td>
<td>1,395.0</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(478)</td>
<td>(34)</td>
<td></td>
<td></td>
<td>(1,873)</td>
<td>(131)</td>
<td></td>
</tr>
<tr>
<td>$TH_{V}$</td>
<td>5</td>
<td>8,050.6</td>
<td>569.6</td>
<td>500°C</td>
<td>6 hrs.</td>
<td>20,239.6</td>
<td>1,416.8</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1,053)</td>
<td>(130)</td>
<td></td>
<td></td>
<td>(3,728)</td>
<td>(261)</td>
<td></td>
</tr>
</tbody>
</table>

f.s.d. (95%) in brackets.
DISCUSSION

With all of the materials tested, the most rapid rate of strength increase tended to occur early in the ionic exchange treatment. The first hour of treatment resulted, almost invariably, in significant strength increases over untreated levels, even at the lowest temperature used (400°C). This early dramatic strengthening appears to be related to an early pre-stressing of the very surface of the glass rather than to depth of ionic crowding. The exact relationship however, may not be a simple one.

The degree of ion exchange occurring at the surface of the glass will be governed by the amount of energy supplied in the form of heat. It has been shown that alkali ion exchange in a glass follows Fick's diffusion law (Nordberg et al, 1964). This means that while ionic exchange at the surface will occur rapidly, a considerably greater amount of energy is required to involve deeper layers of glass. If the strengthening effect of the ion exchange treatment were dependent only on the depth of reaction, then the above explanation would perhaps be sufficient. However, this is probably not so.

As surface flaws are principal factors in limiting the strength of glass it is interesting to consider the effect that surface prestressing might have on these flaws. The dangerous part of a surface flaw is its apex, from where the crack may propagate. If the zone of surface compression, induced by ionic exchange is wide enough to include the apices of a fair proportion of the Griffith flaws on the surface of the
glass, the weakening effect of these flaws may be negated, and a
significant increase in strength produced. It is possible that a
critical depth of stress-zone may exist, which will include a large
proportion of the dangerous surface flaws. If this zone is narrow, it
could possibly correspond to the depth of penetration reached early in
the treatment, evidenced by the early dramatic strength increase. If
this is so, subsequent strength increases following further treatment
may result from compression of deeper flaws, and from stiffening of the
glass.

It must be emphasized that the above discussion is only surmise.
Much more work is required to examine the relationship between a stressed
surface and the flaws in that surface.

Results showed some obvious differences between various porcelains
in their susceptibility to strengthening by ionic exchange. The non-
aluminous dentine porcelain (V_v1), for example, was significantly stronger
than either of the aluminous dentine materials (VA_v1 or DA_v1) in the
untreated condition. After ionic exchange treatment however, both
aluminous porcelains were significantly stronger than the non-aluminous
type.

The most obvious difference between V_v1 and the aluminous
dentine materials lies in the character of their glassy matrices; V_v1
being a matrix-disrupted material, while VA_v1 and DA_v1 are matrix-
intact types. The zone of surface compression produced by chemical
pre-stressing must be balanced by a similar amount of internal tension

.../120
While under normal conditions a disrupted matrix may provide a porcelain with a crack-stopping mechanism, the same matrix might be less able to withstand internal tension than one that is intact. If this be so, then a disrupted matrix would limit the surface compression attainable. These factors could influence the measured strengths before and after treatment.

If the ionic exchange strengthening process is to be used in practice, then there is a definite indication for constructing jacket crowns from aluminous porcelains. Most benefit gained by this, however, would probably be due to the absence of quartz which would produce disruptions in the glassy matrix, rather than to the inclusion of alumina in the porcelain.

The aluminous core material $DA_{vO}$, appeared to have promising possibilities when tested in the untreated form, however, the unpredictability of its strength after chemical treatment proved somewhat disconcerting. It appears that the alumina crystals in this material are added late in the fritting process so bonding between alumina crystals and the glassy phase is relatively weak. Firing of the porcelain crown involves only relatively low temperatures, and short times, so the alumina/glass interfaces remain regions of weakness. These weak bonds may limit the strengthening attainable by ionic exchange in a similar way to the matrix-disrupting cracks of $V_{v1}$.

In choosing optimal time/temperature combinations for chemical pre-stressing of each material, consideration was given to practical aspects as well as to the amount of strengthening attainable. There
would be little point in attaining tremendous increases if this required a treatment schedule which was totally impractical. Our aim is to arrive at a method for strengthening porcelain crowns rather than specimens of porcelain in the laboratory. I feel that treatment schedules have been presented which are convenient enough to be used routinely by most dentists.

It will be noted that the optimal treatment schedule suggested for the high-fusing core material \( \text{HFDA}_v \) is different from that shared by all of the other aluminous porcelains. \( \text{HFDA}_v \) will, of course, be used in conjunction with dentine and enamel porcelains rather than by itself. As such, the core porcelain must be chemically treated using the schedule required by the dentine or enamel materials. Wherever laminates of different porcelains are to be treated, the time and temperature of treatment should be those which suit the material of lowest transformation region. This will avoid significant release of stresses through relaxation of the matrix.

When choosing a chemical strengthening treatment schedule it may be important to consider the influence that depth of surface stress-zone might have on durability of the glass. Indications are that, beyond a critical depth, increased penetration of reaction does not necessarily result in greater strengthening. However, depth of stress-zone may affect serviceability. This will probably depend on whether ion stuffing imparts significantly greater durability to the glass, and whether penetration of the surface stress-zone results in release of surface...
compression in the region of damage. These questions open up a field for further investigation which could be most satisfying and rewarding for the profession.
11. **SUMMARY**

The strengthening effect of chemically pre-stressing dental porcelains has been studied.

Representatives from quartz-bearing (matrix-disrupted) and aluminous (matrix-intact) brands were examined.

Chemical treatments involved immersing the fired porcelains in molten potassium nitrate for various times at selected temperatures. Two optimal treatments, which might be used in the manufacture of porcelain jacket crowns, have been suggested. The optimal treatment to be selected is dictated by the porcelains used in the manufacture of the crown. All materials were strengthened by at least a factor of 2. There were some whose strength was trebled. Possible explanations for this behaviour were discussed.
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