

ION EXCHANGE STRENGTHENING OF A LEUCITE-REINFORCED
DENTAL CERAMIC

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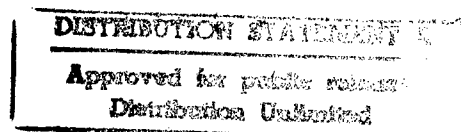
Jose J. Villalobos, B.A., B.S., D.D.S.

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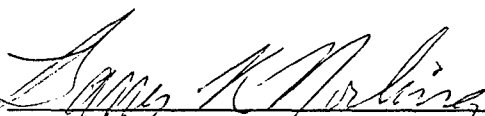


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ION EXCHANGE STRENGTHENING OF A LEUCITE-REINFORCED CERAMIC

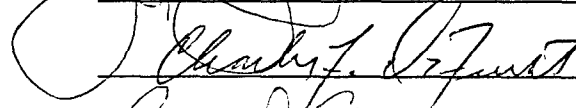
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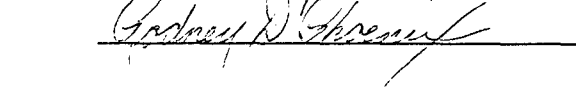
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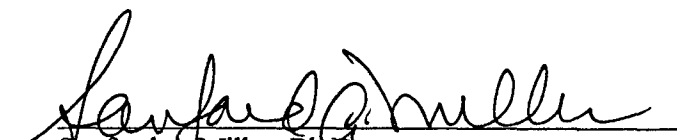






17 Jan 97
Date

APPROVED:



Sanford A. Miller, Ph.D.
Professor and Dean

ION EXCHANGE STRENGTHENING OF A LEUCITE-REINFORCED DENTAL CERAMIC

Jose J. Villalobos, M.S.

The University of Texas Graduate School of Biomedical Sciences
at San Antonio

Supervising Professor: Barry K. Norling, Ph.D.

Demand for improved dental esthetics has led to an increased use of ceramics in dentistry, specifically all-ceramic restorations. Unfortunately, the brittle characteristics of dental ceramics remain an area of concern and limit their applications. Metal-ceramic restorations have proven successful, but problems associated with the use of metal substructures exist. Numerous all-ceramic systems have been introduced, however strengths equivalent to metal-ceramic restorations have not been obtained. As a result, strengthening techniques are being actively investigated.

A popular method for strengthening glass and ceramic materials is through creation of residual stress in the form of a surface compressive layer. This can be accomplished by overglazing, tempering, or chemical treatment via ion exchange. Traditional ion exchange involves the replacement of small sodium ions present in the glass, by larger potassium ions applied to the surface. Crowding of atoms occurs in the surface microstructure while the bulk

material remains unchanged. Flexural strength of the ceramic increases as a result of this induced surface compression.

Successful strengthening of conventional feldspathic porcelains by means of potassium for sodium ion exchange is well documented. Ion exchange strengthening of feldspathic porcelains used with metal-ceramic restorations, however, is of questionable value. Although metal substructures compromise esthetics by altering natural light transmission, they provide excellent protection against crack propagating tensile forces.

Leucite-reinforced all-ceramic restorations are increasing in popularity due to improved translucency, color control and strength. The high potassium content characteristic of leucite-reinforced ceramics led to the hypothesis tested in this investigation, that rubidium-for-potassium exchange will yield higher flexural strength than conventional potassium-for-sodium ion exchange. The purpose of this investigation was to determine the effect of five ion exchange treatments on the biaxial flexural strength of a leucite-reinforced dental ceramic. The glass transition temperature (T_g) of the ceramic was determined. A range of temperatures, relative to T_g , was employed to determine optimal conditions for treatment.

One hundred sixty disks of a high leucite porcelain (Optec HSP, Jeneric/Pentron) were prepared according to the manufacturer's directions. The disks were lapped to provide parallel faces. Subsequently, the specimens were finished and randomly divided into 32 groups ($n=5$). Fourteen groups were treated using conventional potassium-for-sodium ion exchange (Tuf-Coat, GC International) and 14 groups were treated using a rubidium nitrate paste. Optimal treatment temperatures for both ions were identified using 15° C temperature increments over a range of 250° C - 510° C. All groups were treated for 30 minutes.

Following identification of optimal treatment temperatures, consecutive ion exchange treatment was performed on additional groups using the determined temperatures. A final group was treated with a 50-50 mixture (by weight) of both agents. An untreated group of specimens served as a control group. All specimens were loaded to fracture using a pin-on-three-ball fixture at a crosshead speed of 0.5 mm/minute.

Among the rubidium exchanged groups, the peak strength value was 194.1 ± 10.9 MPa at 465°C (an increase of 57.7% over the control group). For potassium, the peak was 170.3 ± 13.5 MPa at 405°C (38.5% increase). Consecutive treatment with both ions yielded a strength increase of 64%, with values of 202.5 ± 17.4 (potassium followed by rubidium) and 202.3 ± 21.1 MPa (rubidium followed by potassium). A mixture of both agents yielded a mean strength value of 204.4 ± 12.9 MPa at 429°C (66.1% increase).

Statistical analysis and evaluation of the data revealed that ion exchange with rubidium nitrate yielded significantly higher flexural strength values than potassium exchange at similar treatment conditions (Student Newman-Keuls analysis, $p < 0.05$). Consecutive treatments with potassium and rubidium, as well as a mixture of the two did not significantly increase strength over the use of rubidium alone. Ion exchange produced no visible change in appearance of the ceramic.

According to the results of this investigation, rubidium exchange provides more effective strengthening than conventional potassium exchange of leucite-reinforced dental ceramic. Strengthening is highly dependent on the temperature of the treatment. The internal surfaces of dental restorations are subject to high tensile forces which can lead to failure. Ion exchange treatment of leucite-reinforced restorations, particularly the internal surfaces, significantly improves strength without changing the appearance of the ceramic. Further

research to evaluate clinical pre-cementation surface preparation procedures, and their effects on ion exchange treated surfaces, are needed in order to fully exploit the advantages of ion exchange strengthening.

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I. INTRODUCTION

During the early 1970's, tremendous interest in metal-ceramic restorations produced rapid advancements. Base metal (nickel-chromium) alloys were introduced and palladium-silver systems quickly followed. Popularity grew as improvements were made and by 1974, metal-ceramic restorations accounted for 90 percent of all fixed prostheses fabricated in the United States (Jones, 1985). During the same period, ion exchange strengthening was first applied to dental porcelains, but drew limited attention.

Although metal-ceramic systems fulfill the physical requirements for single and multiple-unit restorations, metal substructures significantly alter light transmission, decreasing translucency and compromising esthetics. In an attempt to overcome this difficulty, a number of all-ceramic restorative systems have been introduced. Unfortunately, all-ceramic restorations are more susceptible to fracture. Therefore, techniques for strengthening all-ceramic systems while maintaining their optical properties are extremely desirable.

Alumina-reinforced materials (*e.g.*, In-Ceram, Vitadur N core; Vita Zahnfabrik, Bad Sackingen, Germany) exhibit the highest fracture toughness values among all-ceramic systems currently available. They are, however, the least translucent (Seghi *et al.*, 1995). In order to achieve acceptable esthetic results, the highly opaque core materials must be veneered with weaker translucent porcelains which limit load capacity. Because they are used in such thin cross sections, core materials may contribute only moderately to strength (Southan, 1987a; Hondrum, 1992). The quality of the core-veneer interface, a potential source of failure, also is critical to the success of layered restorations (Kelly *et al.*, 1995; Carrier *et al.*, 1995).

Leucite-reinforced dental ceramics are becoming increasingly popular. They are available as conventional sintered powder systems, or in ingot form for heat-pressing using the lost wax technique. Leucite-reinforced restorations are composed of a single material requiring no separate core. Consequently, strength values can surpass those of layered structures (Seghi *et al.*, 1995). Nevertheless, excellent translucency and color control are their principal advantages.

Ion exchange has no visible effects on dental ceramics and can enhance the strength of leucite-reinforced materials without affecting their desirable optical properties. Traditional ion exchange involves substitution of larger potassium ions for smaller sodium ions at elevated temperatures. Residual compressive stresses develop within the exchanged surface upon cooling that must be exceeded for cracks to propagate from the surface of the ceramic material. Conventional feldspathic porcelains can be strengthened significantly using this process (Seghi *et al.*, 1990; Anusavice *et al.*, 1991). When applied to leucite-reinforced ceramic, however, only modest increases in strength result (Anusavice *et al.*, 1992).

Leucite-reinforced ceramics display higher potassium contents than conventional feldspathic porcelains. High potassium content already present in certain dental porcelains is thought to reduce the driving force for potassium-for-sodium exchange (Piddock *et al.*, 1991). Thus, substitution of a larger monovalent ion for the potassium ion already present in leucite-reinforced material, is the logical solution.

Kistler (1962), first demonstrated the use of rubidium for substitution of smaller monovalent ions in industrial glasses. Denry *et al.* (1993), demonstrated the use of rubidium for potassium exchange in a conventional feldspathic porcelain. The greater volume of rubidium ion (33%) relative to potassium ion, and the fact that feldspathic porcelains often

contain twice as much potassium as sodium, made rubidium a logical choice (Denry *et al.*, 1993). In fact, the investigators, obtained a maximum flexural strength increase of 82% using rubidium compared to 50% using potassium at the same time/temperature parameters.

If mobile ions are available for substitution in both the glass and crystalline phases, the high leucite content (and an attendant high potassium content) in leucite-reinforced ceramic should facilitate ion exchange with rubidium. Consequently, the objectives of this investigation were to evaluate the relative changes in flexural strength of a leucite-reinforced dental ceramic following treatment with potassium and rubidium ion exchange. This study addressed the following questions:

- 1) Does the high potassium content characteristic of a leucite-reinforced dental ceramic allow for significant strength increase with rubidium exchange relative to potassium exchange?
- 2) What is the optimal treatment temperature yielding the maximum strength in a leucite-reinforced ceramic treated with potassium exchange?
- 3) What is the optimal treatment temperature yielding the maximum strength in a leucite-reinforced ceramic treated with rubidium exchange?
- 4) What is the effect of subsequent ion exchange treatment using a) potassium exchange followed by rubidium exchange, and b) rubidium exchange followed by potassium exchange?
- 5) What is the effect of ion exchange treatment using a 50-50 mixture of potassium and rubidium on a leucite-reinforced ceramic?

II. LITERATURE REVIEW

A. The Chemistry of Dental Porcelain

The development of porcelain by Chinese ceramists dates back as early as 1000 A.D. (Jones, 1985). In the seventeenth century, European artisans were repeatedly unsuccessful in imitating the Chinese porcelain after numerous attempts. In 1717, a Jesuit priest named d'Entrecolles gained the trust of Chinese ceramists, and learned their secrets. Shortly thereafter, d'Entrecolles returned to Europe with the secrets of this material. Sixty years later, porcelain was used for the first time as a dental restorative material (Jones, 1985).

True porcelains are described as scattered islands of undissolved minerals in a sea of non-crystalline glass. This is the general character of porcelains used for denture teeth and pontics, also classified as high- and medium-fusing porcelains (Lacy, 1977). Because fusion of true porcelain to metal is fraught with problems, development of lower-fusing porcelains emerged that were formulated specifically for this purpose.

Dental porcelain contains a minimum of approximately 60 percent SiO_2 (McLean, 1979). Because of the close relationship to glass, an understanding of the nature of glass is essential.

1. The Nature of Glass

Fused silica (SiO_2) is chemically the most elementary glass, and the basic glass-forming material of dental interest (Lacy, 1977). As SiO_2 melts, its crystalline structure breaks down into long polymer-like chains resulting in a very viscous liquid. When cooled below the melting point, the entangled polymers are unable to reorient into their crystalline positions, subsequently freezing in an amorphous, "liquid" configuration. The resulting glass,

known as a "supercooled" liquid, is homogeneous in composition with no fixed melting point (Lacy, 1977).

Fused silica is a strong solvent for other oxides. The effect of adding Na_2O , extra oxygen balanced electrically by Na^+ cations, results in breakdown of the Si-O polymer chains. This has very important effects on the physical and chemical properties of the glass. Addition of Na_2O reduces the thermal energy needed to break down the molecular structure of silica, resulting in a reduction in melting temperature. The coefficient of thermal expansion is increased by loosening of the atomic structure and the addition of large cations. Shortening of the Si-O polymer chains also increases the fluidity of the liquid (Lacy, 1977).

Commonly used glass modifying oxides, known also as fluxes, include Na_2O , K_2O , Li_2O , MgO and CaO . A limit exists on how much modifying oxide can be added to the glass without inducing detrimental effects. As polymer chains are broken down, mobility of the molecules increases, thereby making crystallization more likely (Lacy, 1977). A return towards a crystalline state is termed devitrification.

Metal-ceramic technology requires dental porcelains with high thermal expansion coefficients for compatibility with specially formulated metal alloys. This is attainable by adding large quantities of modifying oxides to the porcelain formulation. Low-fusing, highly fluxed porcelains are relatively unstable, requiring careful control during manufacture and use to prevent crystallization. Crystallized glass exhibits poor optical properties and loss of surface glaze. Devitrification can occur as a result of prolonged heating or "too many bakes," allowing molecules to assume their lowest energy or crystalline arrangement (Lacy, 1977). Contaminants in the porcelain can also induce crystallization by acting as nuclei upon which silicate crystals can grow (Lacy, 1977). Stability of dental

porcelain is dependent on the Si-O covalent bond. Excessive reduction of these bonds can lead to problems.

2. Dental Porcelain Composition

Potassium and sodium feldspar are naturally occurring minerals composed of potash (K_2O), soda (Na_2O), alumina (Al_2O_3), and silica (SiO_2). Feldspar (75 - 85%) is the primary ingredient used in the preparation of many dental porcelains. When potassium feldspar is mixed with various metal oxides and fired at high temperatures ($1150^\circ C - 1530^\circ C$), it can form the crystalline mineral leucite and a glass phase. Leucite is a potassium-aluminum-silicate mineral with a high coefficient of thermal expansion (Anusavice, 1996)..

Quartz (12 - 22%), a high-fusion material, consisting of pure SiO_2 , contributes stability during heating by providing a framework for the other ingredients (Craig, 1993). It helps prevent slumping and also acts to strengthen the porcelain (Naylor, 1992).

Kaolin (3 - 5%), a clay produced in nature by the weathering of feldspar, is found as a residue deposited along the banks and bottoms of streams. Pure kaolin is an almost white powder with the formula of $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (Craig, 1993). Historically, this material was used as a binder, added to help form a workable mass during molding. Kaolin imparts opacity to porcelain and is consequently used in limited quantities if at all (Phillips, 1982; Naylor, 1992).

Dental porcelain with specific properties can be made by the careful addition of modifying oxides as previously mentioned. Once formulated, the mixture is heated to temperatures well above those used in the dental laboratory. The melt is quenched in cold water, immediately breaking up the glass into fragments called "frit" (McLean, 1979).

Fritting, the process of blending, melting and quenching, can be repeated several times to ensure homogeneity in the glass. The frit is then ground to specific particle sizes ranging from 2 to 75 microns in different porcelains as established by the manufacturer (Binns, 1983).

The colorless ground frit is further prepared into a multitude of colors and opacities according to the designated role for that particular material. This is accomplished by the addition of metallic oxides that act as pigments and opacifying agents. Metallic pigments include titanium oxide for yellow-brown shades, manganese oxide for lavender, iron oxide for brown and red, cobalt oxide for blue and copper or chromium oxide for green (Craig, 1993). Opacifying agents consist of metal oxides ground to very fine particle size (<5 microns). These materials screen out the underlying surface color of metal-ceramic restorations. Commonly used opacifying agents include: cerium oxide, titanium oxide, zirconium oxide and tin oxide (McLean, 1979; Craig, 1993).

In the dental laboratory, complete fusion of the glass frit is neither accomplished nor desired. The bottled glass powder is molded, compacted, dried, then reheated under vacuum. The fusion temperatures used (871° - $1,066^{\circ}$ C) are much lower than those used for the original glass melt. The particles soften and coalesce at all points of contact without any further chemical change (Lacy, 1977). This process is known as condensation and sintering. The final product depends on the quality and quantity of ingredients, as well as the particle size and firing conditions chosen (Claus, 1989).

3. Classification of Dental Porcelain

Dental porcelains are traditionally classified according to their fusion temperatures (Anusavice, 1996):

1) High-fusing porcelains fuse at a temperature of 1,300° C (2,372° F). These materials are used almost exclusively by manufacturers in the fabrication of porcelain denture teeth.

2) Medium-fusing porcelains have fusion temperatures ranging from 1,101° to 1,300° C (2,013° to 2,072° F). Medium-fusing porcelains are used by manufacturers to fabricate pontic facings (*e.g.*, Trupontics), as well as denture teeth.

3) Low-fusing porcelains have fusion temperatures ranging from 850° to 1,100° C (1,562° to 2,012° F). Due to the popularity of metal-ceramic restorations, low-fusing porcelains represent the most widely used class of dental porcelain.

4) Ultra-low fusing porcelains display fusion ranges below 850° C (1562° F). They are formulated specifically for use with titanium and specialized Type IV gold alloys.

Low-fusing dental porcelains are not true porcelains, but a variety of powdered and fused glass. These materials, more appropriately referred to as dental glasses, represent a variety of nearly homogeneous glasses with profound tendencies to react chemically with other metallic oxides (McLean, 1979). These reactions greatly modify the appearance and behavior of low-fusing porcelains. The modified silica glass can be transformed into a material which, when layered with other similar glasses, looks very much like the true dental porcelains that were used for many years (Lacy, 1977).

The development of new dental ceramic systems, along with alternative methods of fabrication, has made classification difficult. Classification of dental ceramics according to fusion temperature alone is inadequate. Besides fusion temperature, dental ceramics can be categorized according to type, usage, processing methods, and substructure material.

B. Strength Limiting Factors

To better understand techniques for strengthening dental ceramics, a discussion of factors which limit the strength of glass and ceramic materials is helpful.

1. Fracture Mechanics of Ceramic Materials

The importance of surface condition on practical strength is widely accepted. This concept was referred to by Preston (1933) in a statement: "We do not measure the strength of glass, we measure the weakness of the surface." Griffith (1920) postulated the existence of minute cracks and scratches, submicroscopic in size, on the surface of glass. These surface defects, termed "Griffith flaws," act as stress concentration centers when the glass is subjected to tensile loading. Fracture occurs when the critical breaking stress, concentrated at the flaw tip, is exceeded, resulting in crack propagation (Stookey, 1965).

Brittle fracture involves both crack formation and crack propagation. The longer the crack, the less energy is required to continue its growth, making it self propagating (McLean and Hughes, 1965). Compressive forces tend to approximate the edges of surface cracks, explaining the characteristic high strength of ceramic materials seen in compression. Tensile forces open crack sites, explaining ceramics' characteristic weakness in tension.

The theoretical strength of glass is calculated to be 1×10^3 to 3×10^3 kg/mm² (Sugerman, 1967). Surface flaws (or microcracks) are responsible for the discrepancies between observed and theoretical strengths (Kingery, 1976). In actuality, observed strengths are 1/100 to 1/1000 the theoretical strength values for bulk glasses (Jones, 1983). Experimental glass specimens prepared in a controlled laboratory setting illustrate this point. Surface flaws may be removed from glass fibers by repeated dipping in a variety of acids. Glass fibers treated in this manner exhibit tensile strengths approaching 2×10^6 psi, or 13,847

MPa (Nordberg *et al.*, 1964; Stookey, 1965). Simply touching the prepared surface with one's fingers reduces strength from 10^6 to 10^5 if no strengthening measures are taken (Kingery, 1976). Ceramic materials in everyday use have, in general, 1/10 of the strength of similar materials prepared in controlled settings (Jones, 1983).

There are many potential causes of microcracks in dental ceramic restorations. Mismatches in coefficients of thermal expansion between veneer and core porcelains can produce such difficulties. Heat generation during grinding and adjustment also can lead to microcrack formation and propagation. Heat concentration during grinding procedures often creates differences in expansion in different areas of the porcelain. Microcracks resulting from excessive heat generation are more detrimental than the surface changes (scratches) produced by grinding (Riley, 1977). Certain factors leading to microcrack formation in dental restorations may be unavoidable, such as simple handling, as previously mentioned. The most significant unavoidable factor, however, is the destructive, repetitive masticatory force that occurs in the harsh environment of the oral cavity (Riley, 1977).

2. Dental Porcelain Bulk Texture Limitations

Griffith (1920) postulated that surface flaws are more important than internal flaws. Nevertheless, internal flaws which occur during fabrication also limit the strength of dental restorations (Jones, 1983).

The bulk texture of dental porcelain is characterized by imperfections between interfaces of the original frit particles. These imperfections may result from incomplete fusion during sintering. Thermal stresses also can create internal flaws, causing fused particles to separate at their interface during cooling. The sizes and shapes of frit particles also can be a factor. Rounded particles exhibit better packing densities than angular grains (McLean,

1979). Smaller particles may lead to smaller flaws and a reduction in their total number due to more rapid and efficient sintering. Firing time and temperature parameters also can affect the sizes of internal flaws (Jones, 1983).

The presence of porosity in dental porcelain generally is believed to reduce strength. A tenfold reduction in porosity due to vacuum firing, surprisingly showed no significant effect on strength (Jones, 1983). This was thought to be due to the spherical type of porosity associated with glassy feldspathic porcelains. Irregular, nonspherical porosity, however, may facilitate crack initiation when subjected to critical stresses. Aluminous porcelains, unlike feldspathic porcelains, exhibit an inverse relationship between porosity and strength. This may be due to irregularly shaped porosity often seen in many pure oxide ceramic systems (Jones, 1983).

A more significant effect of porosity in dental porcelain is a highly undesirable increase in opacity. The introduction of vacuum firing in 1940 largely overcame this feature of sintered dental porcelain.

Porosity is most detrimental if present at the surface, if irregularly shaped, or, if seen at the metal-ceramic interface (Jones, 1983). Southan (1977) summarized the strength phenomenon by saying, "the observed strength of dental porcelain is principally determined by the presence of surface flaws, whose effect overshadows other variables present."

3. Fatigue

Dental ceramics, like other materials, are subject to fatigue. Fatigue refers to the degradation of strength over time. Two types of loading conditions can lead to fatigue: 1) cyclic (repetitive) loading and 2) static loading, which may be potentiated by the presence of a chemically active agent such as water. In the oral environment, there is a combination of

both conditions (Reid *et al.*, 1990). The progressive loss of strength that accompanies cyclic loading is due to the gradual propagation of one or more pre-existing cracks. Strength of the material falls as the crack-free section of the ceramic decreases in area (Reid *et al.*, 1990).

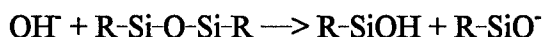
The presence of water is known to enhance this process (Charles, 1958; Zijlstra and Burggraaf, 1968; Kingery *et al.*, 1975). In some cases, the strengths of ceramic materials may depend more on the chemical environments to which they are exposed rather than their surface flaws (Wiederhorn, 1968). The effects of environmental moisture can be illustrated experimentally. Identical glass rods, for example, are three times stronger when tested in a vacuum environment rather than when tested in moist air (Hallig, 1962).

Dental ceramics also are susceptible to crack growth enhanced by moisture (Jones, 1983; Morena *et al.*, 1986; Anusavice and Lee, 1989; Fairhurst *et al.*, 1993). Feldspathic and aluminous porcelain samples have been shown to exhibit a 27% reduction in strength when tested while submerged in water (Sherrill and O'Brian, 1974). Clinically, crowns must function in the presence of moisture, externally from saliva and internally from a cementing agent. An apparent time factor seems to be involved in the fracture process of porcelain jacket crowns (Southan, 1983). Lehman (1967) observed that after two years of clinical service, approximately 5% of porcelain jacket crowns failed. This time-dependent reduction in strength, aided by the combined influence of water and stress, is termed "static fatigue".

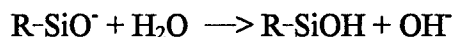
The mechanism for static fatigue, also known as stress corrosion, is believed to be a chemical reaction between water molecules and glass surfaces (Charles, 1958). The reaction rate is greatest at crack tips, where the stresses are highest. The absorbed moisture lowers the energy required for crack propagation (Hasselman, 1968). The pre-existing flaws

grow to critical dimensions. Since stress concentration increases with length, crack propagation continues until the load is removed or fracture occurs (Kingery *et al.*, 1975).

In 1972, Weiderhorn hypothesized that stress corrosion was the result of hydroxyl ions, attacking Si-O bonds:



The silonate groups, which are highly basic, are hydrolyzed by water to form silanol groups and hydroxyl ions:



Weiderhorn supported his hypothesis with data indicating an increase in crack velocity with increasing hydroxyl ion concentration.

The degree to which static fatigue proceeds depends on the glass composition, temperature, humidity, time allowed and nature of the surface damage (Charles, 1958; Weiderhorn, 1972). Concentration of reactants also plays a role, as well as the structural state of the glass (Charles 1958). Glass has lower density or "expanded" structure at elevated temperatures. An expanded structure also results when a large number of metal cations such as Na^+ are present. This behavior is characteristic of highly fluxed, low-fusing dental porcelains commonly used today. Charles (1958) concluded that stress corrosion of an expanded glass structure proceeded faster than corrosion of a compacted glass structure, even though external conditions and glass compositions were identical.

Temperature is believed to play a role in the stress corrosion process. The temperature range encountered in the oral environment is sufficiently elevated to promote this process. Surface flaws undergo slow crack growth when subjected to forces of mastication along with the wide range of temperature fluctuation seen in the oral cavity (Ritter *et al.*, 1985; Morena *et al.*, 1986).

Various dental porcelains are influenced by loading rates. In general, glass materials loaded at rapid rates require higher forces for fracture. Static or slow loading of glass materials cause fracture at stresses lower than expected. Porcelain specimens were tested using a slow bend test at a speed of 0.01 cm per minute, and again dynamically at a constant rate of 800 cm per minute. The modulus of rupture values were between 43 and 97% higher when the rate was increased to 800 cm per minute (Jones, 1972). Dental porcelain subjected to rapid or short-term loading is stronger than porcelain placed under slow or long-term loading conditions (Jones, 1983).

Static loading is a detrimental form of stress to dental ceramic restorations. Ill-fitting restorations forced to place are in a constant state of stress. Constant stress, enhanced by moisture in the oral environment, will lead to early failure at stresses much lower than the reported tensile strengths of the porcelains utilized (Riley, 1977). Subcritical crack growth parameters for three different dental ceramics using a dynamic fatigue (constant stressing rate) method were obtained by Morena *et al.* (1986). Feldspathic and aluminous porcelains along with a fine-grain polycrystalline core material (Cerestore) were tested in distilled water at 37°C. The feldspathic porcelain was also tested in artificial saliva. Considerable differences in crack growth values were found. Feldspathic porcelain exhibited the lowest value while the fine-grain polycrystalline exhibited the highest value. Lifetime prediction curves, constructed

from crack growth values and inert strengths, showed fatigue failure within 5 years was a good possibility for feldspathic porcelain at stress levels consistent with the oral environment. Little likelihood of failure was predicted for the fine-grain ceramic. The low value for feldspathic porcelain, the most adversely affected by water, was comparable to that of silicate glass.

Silicate glass is known to be among the most fatigue susceptible glasses (Morena, 1986). Similarities between silicate glass and feldspathic porcelain suggest that the mechanical properties of feldspathic porcelain are controlled largely by the glass matrix and not by the crystalline phase (Morena, 1986). High values obtained for the fine-grain ceramic suggest this material should be relatively unaffected by the oral environment, except at high stresses maintained for long duration. This data was consistent with previous data of fine-grain, $\alpha\text{-Al}_2\text{O}_3$ ceramics (Pletka and Weiderhorn, 1982). In terms of resistance to subcritical crack growth, aluminous porcelain was positioned between feldspathic porcelain and the fine-grain ceramic. Despite a glassy content comparable to feldspathic porcelain (30-40%), crack growth value was much higher than feldspathic porcelain. This indicated direct interaction occurring between cracks and dispersed alumina phase (Morena *et al.*, 1986).

Certain oxides present within the glass decrease the incidence of static fatigue. Incorporation of tin into the glass, for example, can cause the material to be less prone to static fatigue (Jones, 1983).

The use of a thin chemical barrier to prevent moisture from reaching fracture initiating surface microcracks, was investigated by Rosenstiel *et al.* (1993). A fluorsilane agent, commercially used as a water repellent, was chosen due to its ability to form a strong bond with glass. The fluorsilane coat was seen to effectively reduce stress corrosion in soda-

lime glass. When tested on feldspathic porcelain, strength increased significantly from 56 to 71 MPa. Unfortunately, the fluorochemical was deemed extremely toxic by the manufacturer, and withdrawn. Thin-film coating, however, may be a practical method of increasing the longevity of ceramic restorations.

C. Strengthening Methods

Strengthening mechanisms are designed to resist initiation and propagation of surface flaws. Southan once stated, "any strengthening process must either remove flaws, stiffen the material or protect its surface from moisture contamination (1977). There are three basic methods by which the strength of dental ceramics can be improved:

- 1) A porcelain surface can be protected from destructive tensile forces by fusing onto a ductile metal substrate.
- 2) Mechanical properties of the porcelain bulk itself may be improved by incorporation of a crystalline ceramic into its' glassy matrix.
- 3) The ceramic can be strengthened by development of compressive stresses at the surface (Jones, 1983).

1. Fusion of Porcelain to Metals

All-ceramic crowns predominantly fail from tensile stresses occurring on their internal surfaces, that propagate surface flaws through the restoration (McLean, 1979). Propagation of such flaws can be prevented by fusion of the porcelain to an oxide-coated metal surface. The metal at the internal surface distributes stresses and provides rigid support (Yamamoto, 1985).

Fusion of ceramics to metal has been used in industrial manufacturing processes for centuries (Jones, 1983). In 1886, Charles Land first introduced the use of fused porcelain for dental restorations. Land's patented method utilizes a burnished platinum foil matrix to which the porcelain is fused (Jones, 1985). A significant development in dental ceramic to metal bonding occurred in 1956, with the fusion of porcelain to gold alloy (Brecker, 1956). Crowns and fixed partial dentures were fabricated with the esthetics of porcelain and the strength of the gold alloy. Difficulties with these early alloys however, soon rendered them obsolete. Differences in coefficient of thermal expansion between metal alloy and ceramic was a major obstacle. In 1962, Weinstein et al., patented a gold alloy formulation and a feldspathic porcelain designed for porcelain-fused-to metal restorations.

Porcelain systems containing at least 11% K_2O , produce high-expansion suitable for metal-ceramic bonding when subjected to heat treatments of 700 to 1200°C. High thermal expansion is the result of leucite crystallization which is controlled by K_2O content, temperature and treatment time (Jones, 1991). The amount of leucite formation is also affected by the cooling rate of the fired porcelain (Mackert and Evans, 1991). Current porcelain systems rely upon this leucite phase to provide the thermal expansion necessary for compatibility with metal-ceramic alloys (Mackert *et al.*, 1994).

Metal-ceramic systems depend on a strong bond between the metal and fused ceramic. This bond is thought to be largely mechanical in nature however, other mechanisms besides mechanical interlocking may be involved such as van der Waals forces, compression, and chemical bonding. (McLean, 1979; Bagby *et al.*, 1990).

1) Mechanical Interlocking - According to McLean (1979), a roughened alloy surface produced by sandblasting provides an easily wettable surface which will assist in

mechanical retention. Besides increasing surface area, the roughened surface provides irregularities into which porcelain can flow (Dykema *et al.*, 1986). Excessive surface roughness however, may compromise adhesion if voids occur at the interface (Craig, 1993). The effect of surface roughness reported in the literature is difficult to interpret. The degree of surface roughness is not defined and is only sparsely used in the dental laboratory (Bagby *et al.*, 1990).

2) Van der Waal forces or "wetting bonds", involve surface tension of porcelain in the liquid state, as well as contact angle. Wettability of the liquid porcelain can be measured by its contact angle. A contact angle greater than 90 degrees indicates a lack of wetting and, consequently, lack of adhesion (Dykema *et al.*, 1986). This surface energy approach considers adhesion in wetting to be a source of bonding (O'Brien, 1977).

3) External surface compression - Thermal expansion of the veneered porcelain must be slightly less than that of the metal alloy. Porcelains formulated for metal-ceramics have typical coefficients of thermal expansion between 13.0 and $14.0 \times 10^{-6} / ^\circ\text{C}$ and metals between 13.5 and $14.5 \times 10^{-6} / ^\circ\text{C}$. During cooling, the porcelain is held in a state of compression as shrinkage of the metal occurs.

4) Chemical bonding - The chemical bond involves an intermediate oxide layer present at the porcelain-metal interface. Porcelain at the interface partially dissolves and is saturated with the metal oxide. The metal oxide is saturated with metal. As a result, a continuous structure is formed from the porcelain through the oxide layer to the metal, chemically bonding the porcelain to the metal (Bagby *et al.*, 1990).

Metal-ceramic restorations have been accepted almost universally. The excellent fit, strength and improved esthetics of metal-ceramic restorations have made them

the most commonly used complete coverage dental restoration (Christensen, 1986). Although a metal substructure seems to adequately strengthen, there are disadvantages to metal-ceramic restorations.

Human enamel transmits up to 70% light, whereas dentin varies between 20 to 40% (McLean, 1979). Metal substructures markedly diminish light transmission resulting in loss of translucency found in natural teeth. In addition, the underlying metal color often penetrates the porcelain, lowering the value of the restoration and making it appear grayer than the surrounding teeth (Wall and Cipra, 1992). Opaque porcelains are used to mask the metal coping; however, they are highly reflective causing a less than natural appearance (McLean, 1979). In an attempt to avoid this reflection, metal-ceramic restorations are often overcontoured during fabrication. Overcontouring, especially in the cervical region of the restoration, interferes with natural cleansing, leading to poor gingival health.

Metal-ceramic restorations require significant removal of tooth structure. Inadequate preparation due to overly conservative tooth reduction is a common problem. Highly esthetic, natural looking, and properly contoured metal-ceramic restorations require adequate space for restorative materials. This often necessitates intentional devitalization of teeth. Esthetic metal-ceramic restorations are difficult to achieve. Strict attention to detail is required during both clinical and laboratory phases of restorative procedures.

2. Dispersion Strengthening

The mechanical properties of feldspathic porcelain were significantly improved by McLean and Hughes in 1965. Addition of 40 to 50% alumina to a low-fusing glass produced a glass-crystal composite with twice the flexural strength of feldspathic porcelain. Theoretically, the energy required for crack propagation through both phases is thought to be

higher than that required to fracture the weaker glass phase alone (McLean and Hughes, 1965). The reinforced material, designed for use as a core replacing the metal substructure, is veneered with a thermal expansion-matched porcelain. Alumina-reinforced porcelain has been used for the fabrication of porcelain jacket all-ceramic crowns for the last 30 years.

Properties of multiphase ceramic materials have been studied by several investigators. Binns (1962) demonstrated the presence of internal stresses resulting from differences in thermal expansion of dispersed alumina and zirconia in a glass. He stated that strength of crystal-glass solids are dependent on the interaction between the two phases. In his work, the properties of the glass matrix were modified by the presence of crystalline grains. Strength and elasticity of the glass increased considerably when interaction took place with an included phase having high modulus of elasticity. Binns found the modulus of elasticity increase was independent of grain size of the included phase.

Hasselman and Fulrath (1966) observed that crack propagation took place preferentially through the glass matrix, and that alumina spheres offered considerable resistance to crack propagation. Their proposed fracture theory hypothesized that hard crystalline dispersions present within glass will limit the size of Griffith flaws and strengthen the composite. The flaw size of glass was calculated, using Griffith theory, to be approximately 50 microns. For a high strength ceramic (such as alumina) flaw size would be only a few microns.

The effect of a dispersed alumina phase on glass was investigated quantitatively. The volume fraction of alumina within the glass was varied and a range of particle sizes were used. At low volume, flaw size was statistically reduced independent of

particle size. At high volume, flaw size was governed by the distance between particles dispersed in the matrix. Therefore, strength should be a function of volume fraction of dispersed phase at lower volumes, and dependent on both volume and particle size of dispersed phase at high volume fractions.

According to Jones (1982), the wide deviation in coefficient of thermal expansion between a quartz crystalline phase and feldspathic glass explains the lower strength observed when these materials are present. The coefficient of thermal expansion of dispersed alumina, on the other hand, is only slightly higher than the glass. This allows the crystals to remain in intimate contact with the glass. Upon cooling, the glass is placed into compression, increasing the strength of the glass-alumina composite.

a. Leucite-Reinforced Feldspathic Porcelain

Alumina particles strengthen dental porcelain; however, they also increase opacity limiting their use to core materials. Research has concentrated on the development of high-strength ceramic restorations that allow light transmission similar to the human tooth. This has led to the development of a new class of dispersion strengthened systems known as leucite-reinforced feldspathic porcelain. This material has a typical crystalline content of 45%, with a grain size less than 5 microns (Katz, 1989). Addition of a crystalline phase with high modulus of elasticity results in a glass with considerable increase in strength and elasticity. The high strength crystals probably bear a greater proportion of an applied load and act as a reinforcing phase.

As in alumina-reinforced porcelain, differences in thermal expansion coefficient between the glass and crystalline phases also play a role in leucite-reinforced ceramics. The dispersed leucite crystalline phase, with thermal expansion slightly greater than the glass, will place the glass matrix in compression upon cooling (Jones, 1982; Dong et al., 1989). The uneven stress distribution between the two phases may be responsible for the increased strength observed in these materials.

Despite a high crystalline content, the material retains its translucency due to the close match between the refractive index of leucite and that of the glass matrix (Hondrum, 1992). Excellent translucency and color control are major advantages of these systems allowing high potential for creating very esthetic restorations.

3. Surface Compression

It is essentially impossible to prevent surface abrasion and crack development in ceramic restorations while in service. The employment of processes which will prevent these surface defects from becoming sources of restoration failures is highly desirable. The most effective methods for strengthening glasses and ceramics currently involve introducing a compressive layer at the surface (Olcott, 1963; Stookey, 1965). For breakage to occur, applied tensile stresses must first overcome the surface compressive stresses (Stookey, 1965). Various physical and chemical methods for achieving compressive surface layers are available. These methods, used in the glass and ceramic industry, are currently being investigated for application into dental ceramic materials.

a) Thermal Tempering

Thermal tempering, perhaps the most familiar method for introducing surface compression, dates back to the seventeenth century (Olcott, 1963). The best known application for this technique is in the production of automotive glass. Thermal tempering involves heating a glass to a temperature just below its glass transition temperature, then rapidly cooling it using air jets or a liquid medium. The rapidly cooled surface freezes in a low-density state, characteristic of high temperature, while the slower cooling interior densifies before freezing. The shrinking interior pulls on the exterior surface placing it into compression, while the interior develops a compensating tension (Stookey, 1965; and Olcott, 1963).

Strengthening by thermal tempering has certain limitations. Simple shapes are required such that uniform stress distributions can occur. In industry, for example, windows and automotive glass are successfully strengthened by this technique. Glass objects must also have a minimum thickness and minimal wall thickness variation (Nordberg *et al.*, 1964; Zijlstra and Burggraaf, 1968). Thermal tempering has been applied to dental ceramic materials with reported increases in flexural strength of 158% (Anusavice and Hojjatie, 1991). Dental restorations, however, are characterized by complex shapes, sharp angles and varying thickness. Strengthening of dental ceramics by means of thermal tempering involve challenges which must be overcome.

b) Glazing and Lamination

Lamination, or glazing, with low expansion glass is routinely used in industry. Surface compression is obtained by coating a glass or ceramic object with a thin layer of a glass having lower thermal expansion. During cooling, the low-expansion glass coat shrinks less than the substrate and is consequently placed in compression (Eppler, 1983).

Optimum results can be obtained when coefficients of thermal expansion between glass and surface coat differ as much as possible.

Silicate glass tends to increase in volume as a result of moisture absorption. Expansion of glass decreases the compression of the glaze, transforming the surface stress into tension. After sufficient time, the ceramic will then tend to craze (Kingery *et al.*, 1975). Delayed crazing-type failures occur while in service and have been observed on overglazed ceramic crowns some years after functioning in the mouth (Jones, 1983).

In dentistry, the benefit of applying a low-fusing glass coat or "overglaze" is controversial. Some investigators feel dental ceramic restorations are better fabricated without the use of overglazes, especially since self-glazing can be accomplished satisfactorily. According to McLean (1979), overglazes are difficult to apply evenly, detailed surface characteristics are difficult to obtain, they produce too high a gloss and they eventually erode, leaving a rough surface.

c) Ion Exchange

Ion exchange, a well-established technique used in the glass and ceramics industry, involves ion substitution between the glass surface and an applied reagent while maintaining electrical neutrality. A surface compression later results, which strengthens the ceramic by opposing crack propagation. This technique differs from physical strengthening methods because the chemical composition at the surface differs from the interior bulk after treatment (Nordberg *et al.*, 1964).

i) Ion Exchange Above Glass Transition Temperature

An early unconventional method of ion exchange, which has not found much commercial application, involves substituting the monovalent ions present in the

glass for smaller ions provided by a lithium salt bath (Hood and Stookey, 1957). This technique differs from subsequent techniques in that: 1) ion exchange is conducted at temperatures above the transition temperature of the glass, and 2) a large ion is replaced by a smaller ion. Strengthening ultimately occurs because a surface with lower thermal expansion than the interior glass results after treatment, placing the surface in compression during cooling. The high temperatures (above glass transition) and the associated risk of deformation, limit application of this technique.

ii) Ion Exchange Below Glass Transition Temperature

Kistlers' (1962) ion exchange technique involves the substitution of monovalent alkali ions (sodium) occupying spaces or "holes" in the irregular silicate network by larger ions (potassium) provided by a molten salt bath. At temperatures approximating 400° C, the monovalent ions from both salt bath and glass become mobile. Ion exchange occurs by an inward flow of potassium ions down a concentration gradient which provides the driving force. At this low treatment temperature the glass' rigidity is maintained, therefore, residual stress induced from crowding in the surface microstructure is not lost due to structural relaxation. Because Kistler's method is executed at temperatures below glass transition, the risk of viscous deformation associated with higher temperatures is eliminated (Kistler, 1962; Nordberg *et al.*, 1964; Stookey, 1965).

D. Ion Exchange and Dental Ceramics

Ion exchange strengthening was first applied to dental ceramics by Southan in 1970. Southan found, by means of semi-quantitative spectrographic analysis, that sodium and potassium ions were present in comparable amounts in two popular brands of dental

porcelain. Flexural strength increases of approximately 122% were obtained by immersion of abraded porcelain specimens into molten potassium nitrate at 475° C for 19 hours (Southan, 1970). The strength increase obtained by Southan, although impressive, was marred by the excessive amount of treatment time required.

Dunn *et al.* (1977), investigated a variety of time-temperature parameters in an attempt to obtain adequate strengthening in a reasonable period of time. Ceramco body porcelain and a potassium nitrate molten salt bath were utilized. Temperatures from 375° C to 475° C, and treatment times from 30 minutes to 9 hours were tested. High temperatures yielded fast diffusion rates, therefore, greater strengths were achieved quickly. Strengthening, however, dropped after prolonged treatment at these higher temperatures. Strength values significantly decreased at 475° C, as the glass transition temperature of the porcelain was approached. The optimum treatment temperature, for the particular brand of porcelain used, was 400° C. Maximum strength was achieved in four hours, however, adequate strength almost twice that of untreated samples was obtained in one hour.

Compressive stress generated by ion exchange predominates at lower treatment temperatures and/or shorter treatment time, while stress relaxation occurs at higher temperature and/or longer treatment time, reducing the degree of surface compression obtained (Dunn *et al.*). Stress relaxation occurring within the glass microstructure acts as a competing mechanism to compressive strength produced by ion exchange. The low viscosity associated with high temperature allows rearrangement of the surface microstructure in order to accommodate larger ions.

As illustrated in the previous study, surface compressive stress generated by ion exchange is diffusion controlled. Other studies investigating ion exchange and diffusion

kinetics support this hypothesis. White and Seghi (1992), also evaluated time and temperature variables associated with ion exchange. Temperature was varied by 50° C increments from 300° C to 600° C. The glass transition temperatures (T_g) coincided with temperatures in which strength began to drop. Glass transition temperature (T_g) is defined as that temperature at which there is an abrupt increase in the thermal expansion coefficient. It is characteristic of each particular ceramic and indicates increased molecular mobility (Anusavice, 1996). Residual compressive stress generated within the ceramic surface is controlled by the opposing phenomena of diffusion and relaxation, which is directly effected by the selected temperature (White and Seghi, 1992). The authors suggested precise control of temperature was more critical than control of time..

Although ion exchange strengthening of dental porcelain has proven effective, the technique has yet to be utilized in a broad-scale manner by the dental community. The excessive time requirement reported may be a reason, another may be hazards associated with use of molten salts. A commercial product which minimizes these difficulties was introduced in 1985 (Tuf-Coat, GC International, Tokyo, Japan). GC Tuf-Coat is a potassium-silicate solution, as revealed by energy dispersive x-ray analysis (Wassenaar, 1990). The product is painted on the completed ceramic restoration, dried, then heat-treated. A conventional porcelain oven, already present in most dental labs and many dental offices, is the only equipment required. The time/temperature parameters recommended by the manufacturer produced maximum flexural strengths in various porcelains, when tested by an outside source (Seghi and White, 1992).

Introduction of the potassium-based ion exchange product by GC sparked a great deal of interest, and many studies resulted. One study applied this product to seven different

feldspathic porcelains (Seghi *et al.*, 1990). Specimens were dried at 150° C for 20 minutes then heat-treated for 30 minutes at 450° C, as recommended by the manufacturer. Flexural strength significantly increased in all porcelains tested with strength increases ranging from 20% to 83%. The variable range of strength increases obtained were attributed to differences in glass transition temperatures (T_g), which in turn were attributed to differing chemical compositions among the porcelains tested. It is interesting to note that Will-Ceram, a low sodium porcelain, yielded the highest strength improvement, illustrating once again that factors other than ion concentration within the chemical composition play a role in this process.

The compressive layer thickness is thought to be important in limiting crack propagation. The depth must extend beyond the surface flaws in order to be effective. Dunn *et al.* (1977) advocated a minimum thickness of 50 microns was needed. Electron probe microanalysis after potassium for sodium exchange, revealed ion penetration of 30 to 100 microns (Piddock *et al.*, 1991; Anusavice *et al.*, 1992). Although the compressive layer thickness is related to the depth of ion penetration, it is not necessarily identical with it (Kingery *et al.*, 1975). Greater ion penetration is possible with higher temperatures closer to the T_g , but not without risk of stress relaxation.

2. Effect of Surface Insult on Ion Exchange Treated Porcelain

Surface defects, in the form of scratches and abrasion, on both chemically treated and untreated porcelains were investigated (Southan, 1987b). Controlled scratches, 30 to 40 microns deep, were shown to severely decrease strength on untreated tensile surfaces. Chemically treated samples with identical scratches also experienced strength reduction. However, this group was over three times stronger than the comparably damaged

untreated group. Treated samples abraded to a depth of 60 to 74 microns, using 220 grit silicon carbide paper, were still stronger than non-abraded untreated controls, revealing that the weakening effect of grinding ion exchange treated samples to these depths, is only marginal (Southan, 1987b).

A more recent study found grinding to a depth of 50 microns, on ion exchange-treated specimens, had no significant effect on strength (Anusavice *et al.*, 1994). However, grinding to depths of 100 to 250 microns resulted in significant reduction in strength. The compressive stress layer thickness typically obtained by ion exchange appears adequate, however, its thin nature may be a limitation of this technique especially if procedures which greatly alter the surface become necessary.

Certain clinical procedures may compromise a chemically treated surface. Grinding the internal surface during fitting of restorations may decrease the strength if the abrasion exceeds the stress layer thickness. Air abrasion, used to divest, clean and roughen a surface to enhance retention, not only introduces surface flaws, but can also reduce the compressive stress layer. Additional heat-treatments such as staining and glazing may anneal out any residual stress, diminishing the strength of the treated porcelain. These problems can be avoided by completing any surface altering procedures, such as fitting, staining and glazing, prior to ion exchange treatment (Giordano *et al.*, 1994). Ion exchange should be the final procedure prior to actual cementation of the dental restoration.

Cementation of most all-ceramic restorations is accomplished using resin based systems. Acid etching followed by silination of the fit surface just prior to cementation is standard procedure. In industry, acid-etching has been utilized to remove surface flaws in order to obtain higher strength properties in glass (Stookey, 1965). Anusavice *et al.* (1994),

studied the effect of etching with 1.23% acidulated fluoride gel on a chemically strengthened ceramic surface. Acid-etch treatment times of 30 minutes, 60 minutes and 300 minutes were utilized. Etching in excess of 60 minutes was shown to significantly decrease the effect produced by ion exchange.

Acid-etching dissolves a portion of the surface glass and may compromise strengthening obtained by ion exchange. The depth of surface penetration, or etch, will depend on several factors including the acid concentration and length of application. Clinical cementation of all-ceramic restorations call for much shorter etching time. Acid-etching associated with clinical precementation procedures, and its effect on ion exchange treated surfaces, should be investigated.

2. The Internal Tensile Surface

The internal or "fit" surface of the restoration, has long been implicated as the site of major tensile forces most likely to cause failure (Southan, 1972; Southan, 1977; McLean, 1979; Marquis, 1985). More recently, fracture surface analysis of clinically failed all-ceramic restorations reveals that failure often occurs from the internal surface, due to internal surface flaws (Kelly *et al.*, 1989; Kelly *et al.*, 1990). Finite-element-stress analysis reveals that the occlusal region of the internal surface is subject to the highest tensile stress (Anusavice *et al.*, 1992).

The nature of occlusal forces, stress location and distribution, must be considered when applying ion exchange clinically. For example, the external surface of an all-ceramic restoration is subject mainly to compressive stresses intraorally. The benefit of ion exchange treatment on this surface would not be dramatic. This was demonstrated by Piddock *et al.* (1991). In this investigation, improved strength was only measured when the porcelain disk

specimens used were loaded to failure with the ion exchange treated surface in tension (facing downward). Ion exchange of the opposite surface placed in compression during loading (facing upward), had no beneficial effect on strength. Ion exchange treatment of the internal surface, however, would be beneficial due to high tensile stresses experienced in this area. The ability to treat the internal surface and margin of all-ceramic restorations, those surfaces experiencing the highest tensile stresses, represents the greatest potential advantage of ion exchange strengthening.

Various feldspathic porcelains are known to be conducive to ion exchange with significant flexural strength increases reported (Seghi *et al.*, 1990; Piddock *et al.*, 1991; Anusavice *et al.*, 1992). The majority of dental ceramics investigated, however, are intended for use with metal-ceramic systems. Ion exchange strengthening of metal-ceramic restorations is of questionable value since the metal substrate provides the best known protection against tensile failure from internal sources. Ion exchange strengthening studies should therefore emphasize non-metal systems. Not only does the ceramic composition of all-ceramic systems differ from those designed for fusion with metal, there are also differences among the various all-ceramic systems available. Different treatment parameters and/or ionic species for substitution are required in order to achieve optimal strengthening.

Potassium-for-sodium exchange of leucite-reinforced ceramic has yielded relatively low increases in flexural strength, as previously mentioned (Anusavice *et al.*, 1992). This may be due to the high potassium content already present in these materials. In order to induce effective surface compression in this high potassium ceramic, the need for a monovalent ion larger than potassium seems logical.

Ion exchange using a rubidium salt has been demonstrated in industrial glass (Kistler, 1961). Rubidium-for-potassium ion exchange was applied to Ceramco II, conventional feldspathic porcelain, yielding flexural strength increases of up to 82% (Denry *et al.*, 1993). Rubidium-for-potassium ion exchange of leucite-reinforced ceramics may lead to significant strengthening and should be investigated.

E. Experimental Objectives

The objectives of this investigation are:

- 1) To evaluate the relative changes in flexural strength of a leucite-reinforced ceramic following treatment with potassium and rubidium ion exchange.
- 2) To determine the optimal treatment temperatures for both potassium ion exchange and rubidium ion exchange.
- 3) To investigate the effect of the following consecutive ion exchange treatments: a) potassium followed by rubidium, and b) rubidium followed by potassium ion exchange.
- 4) To investigate the effect of treatment with a 50-50 mixture of both potassium and rubidium ion exchange agents.

III. Materials and Methods

A. Experimental Plan

1. Materials

The dental ceramic selected for this investigation was Optec HSP (Jeneric/Pentron, Wallingford, CT) a leucite-reinforced feldspathic porcelain used for fabricating all-ceramic dental restorations. Optec HSP was the first leucite-reinforced porcelain introduced. Other systems, now available on the market, are similar in composition. Optec HSP porcelain is filled with 50.6% leucite particles by weight, which are less than 5 microns in size. The restorations are fabricated on foil matrices or refractory dies using traditional condensation and sintering techniques.

a. Fabrication of Specimens

One-hundred sixty disks of Optec HSP porcelain (shade A3, Lot # MO832), 12 mm in diameter and 1 mm thick, were prepared (Plate 1). A cylindrical plastic mold approximately 15 mm in diameter and 2 mm in depth was used to form the porcelain disks prior to firing. The disks were fired once under vacuum at a heating rate of 55° C/min to a temperature of 1016° C, as recommended by the manufacturer. The resultant specimens were individually wet-ground to parallel sides and desired thickness using 60, 180, 240, 320, 400, and 600 grit silicon carbide abrasive paper and a hand-lapping fixture (Model 150, South Bay Technology Inc., San Clemente, CA) on a rotary lapping table. Each disk was finished to 600 grit on the test surface and 180 grit on the loading surface. The prepared specimens were randomly divided into 32 groups (n=5).

b. Ion Exchange Agents Investigated

Two chemical agents were evaluated. Tuf-Coat (GC International Corp., Tokyo, Japan), the first commercially available ion exchange agent, strengthens feldspathic porcelain via a $\text{Na}^+ - \text{K}^+$ process. Energy dispersive x-ray analysis suggests Tuf-Coat is a potassium silicate solution (Wassenaar, 1990). The potassium-based paste was developed for final treatment of glazed porcelain surfaces. It allows a simple, time efficient method of ion exchange strengthening compared to 4 - 24 hour molten salt bath immersion, as used in the past.

The second agent evaluated for ion exchange was rubidium nitrate (Alfa Aesar Chemicals, Ward Hill, MA). In the 1880's, rubidium was used therapeutically (as a bromide salt) for treatment of epilepsy, syphilis and cardiac conditions. In cardiac patients an incidental finding of subjective well-being demonstrated rubidium's mood altering effect (Linter, 1985). Rubidium exerts biologic and pharmacological effects similar to those of classic antidepressant drugs. Administered orally as rubidium chloride, it appears to be nontoxic and therapeutically effective in several types of depressive disorders. The therapeutic role of rubidium in clinical psychiatry, however, requires further investigation to understand its mode of action (Williams, 1987).

2. Methods

a. Part 1:

Fourteen groups of specimens were treated with Tuf-Coat ion exchange agent. In addition to the manufacturer's recommended heat treatment of 450°C , ion exchange using various temperatures ranging from 250°C - 510°C were employed as shown in Table 1. The rubidium nitrate crystals were finely ground and mixed with distilled water to form a paste (Denry et al., 1993). Fourteen additional groups were treated with rubidium

nitrate using the same temperature range. Treatment duration was held constant at 30 minutes for all groups. Thirty minutes is feasible, both clinically and in the laboratory.

Flexural strength vs temperature data was collected, plotted then analyzed using two dimensional curve fitting (TableCurve 2D, Jandel Scientific, San Rafael, CA). Treatment temperatures yielding maximum flexural strength increases were identified for both potassium and rubidium exchange (Figure 1).

b. Part 2:

The specimens were then subjected to consecutive treatments with both chemical agents at the optimal temperatures taken from the fitted curve (Figure 1). The first group was treated with Tuf-Coat at 420°C subsequently followed by rubidium nitrate at 437°C. The second group was treated with rubidium nitrate at 437°C followed by Tuf-Coat at 420°C. Both chemical agents were mixed together in equal amounts by weight then used to treat a third group at 429°C (the average of both optimal temperatures). A group of specimens was left untreated and served as a control. To evaluate for possible residual stress induced during surface grinding and finishing, a group was annealed following surface preparation by heat treatment at 540°C for 15 minutes.

c. Ion Exchange Agent Application

Ion exchange was carried out by applying a uniform 0.25 mm layer of ion exchange paste to the 600 grit finished surface. To control the thickness, each disk was stabilized on soft putty (Ticene) and positioned in a recessed channel machined into an aluminum block. The treatment surface was positioned parallel to and 0.25 mm below the surface of the block using a 0.25 mm feeler gauge. The slurry agent was deposited on the disk until flush with the top of the block. All coated specimens were then placed on a tray in

groups of five and dried in a small furnace (Jelenko Accu-Therm II 1000, Armonk, NY) at 150°C for 20 minutes. Upon drying, the disks were transferred immediately to a porcelain oven (Programat P95, Ivoclar, Amherst, NY) for 30 minute heat treatments at the various temperatures. Specimens were removed from the oven after heat treatment, and fast-cooled in ambient air. When cool, the slurry residue was removed with a brush, and each disc was rinsed with running water for 30 seconds. All specimens were stored at ambient conditions prior to being tested.

3. Biaxial Flexural Strength Analyses

Biaxial flexural strength was determined on all 32 groups using a pin-on-three ball fixture (Wachtman *et al.*, 1972). Disk specimens were positioned with the treated side facing downward (in tension) and loaded to failure using a universal testing machine (Instron Model 1125, Instron Corp., Canton, MA). The load was applied centrally using a flat ended indenter at a crosshead speed of 0.5 mm per minute. Polyethylene film, 0.1mm thick, was placed between the disk and loading piston of the test fixture to obtain uniform loading at the contact area. Failure stress, σ , was calculated for all specimens using the following equations developed by Marshall (1980):

$$\sigma = \frac{AP}{t^2}$$

and

$$A = \frac{3}{4} \pi \left[2(1 + \nu) \ln \frac{a}{r_0^*} + \frac{(1 - \nu)(2a^2 - r_0^{*2})}{2b^2} + (1 + \nu) \right]$$

where P is the applied load at failure, ν (Poisson's ratio) is 0.28 (Ban and Anusavice, 1990), a is the radius of the support circle, b is the radius of the disk specimen, t is the thickness of the

disk specimen and r_0 is the radius of the piston at the surface of contact. For small r_0 values, such as used in this investigation, $r_0^* = (1.6 r_0^2 + t^2)^{1/2} - 0.675t$.

4. Qualitative Analyses

Qualitative analysis of the relative changes in potassium, sodium and rubidium concentration after ion exchange treatment was accomplished using energy dispersive x-ray spectroscopy (EDS) analysis. An Amray 1610T scanning electron microscope (Amray, Bedford, MA), coupled to a Noran 5500 energy dispersive spectrometer (Tracor Northern, Middleton, WI) was used. Representative disk fragments from all test groups and the control group were carbon coated and analyzed.

Plate 1. Porcelain Disks Loaded to Failure Using a Pin-On-Three-Ball
Fixture at a Crosshead Speed of 0.05 mm/min

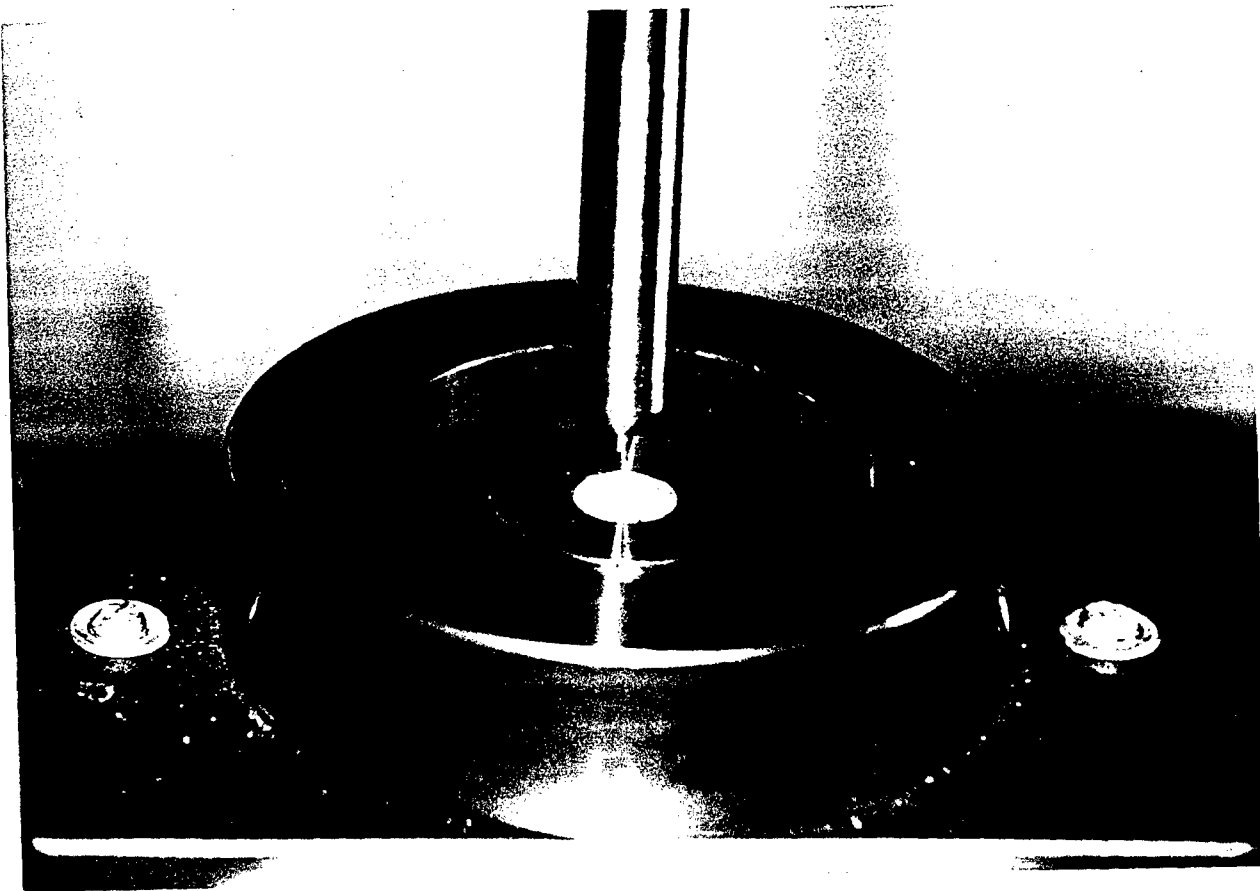


Plate 2. Representative Specimen Fractured Under Biaxial Flexure
Conditions Allowing Maximum Tensile Stresses Within the
Central Loading Area

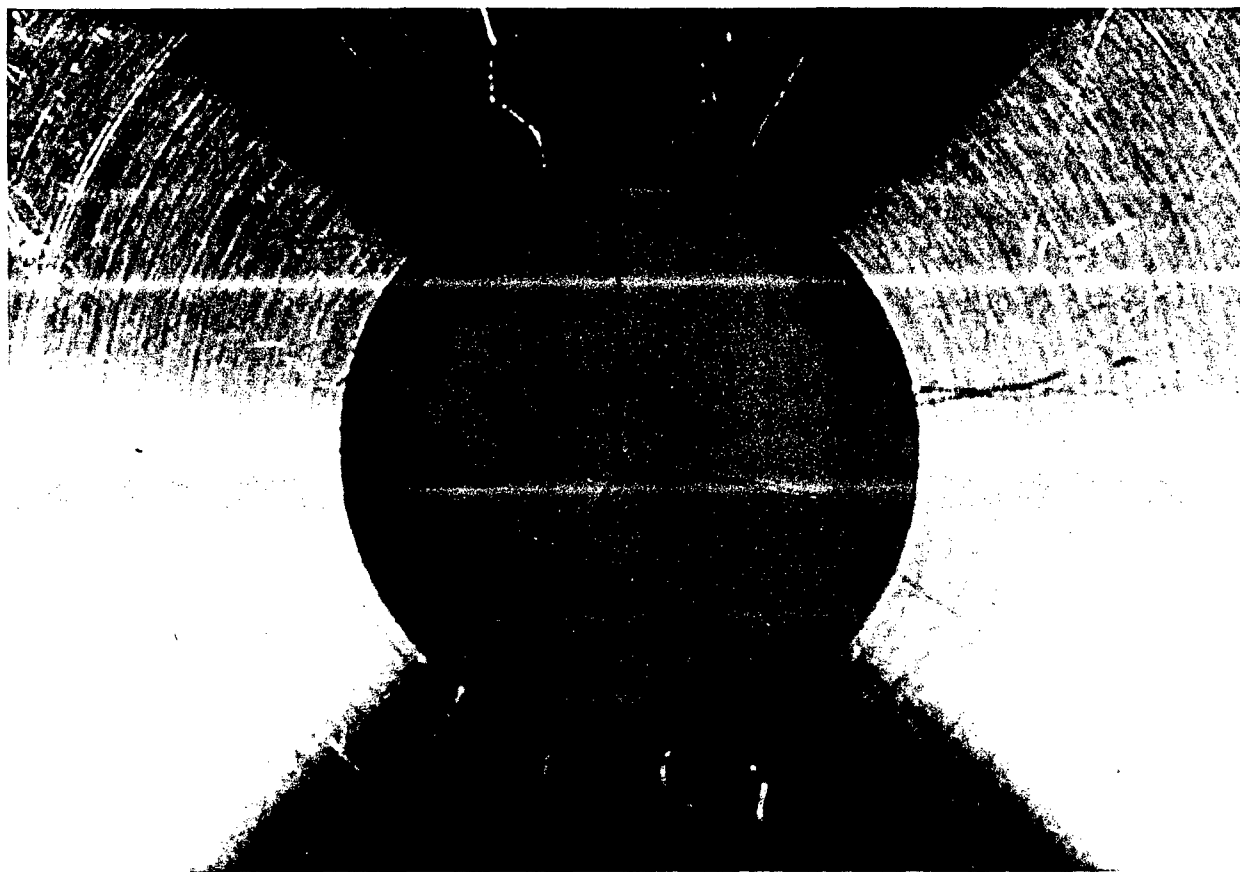


Plate 3. Leucite-Reinforced Porcelain, Hand-Lapping Fixture and Finished
Disk Specimens





Plate 4. Potassium Salt (Tuf-Coat) (A) and Rubidium Nitrate Paste (B)
Applied to Porcelain Disk Specimens Prior to Heat Treatment

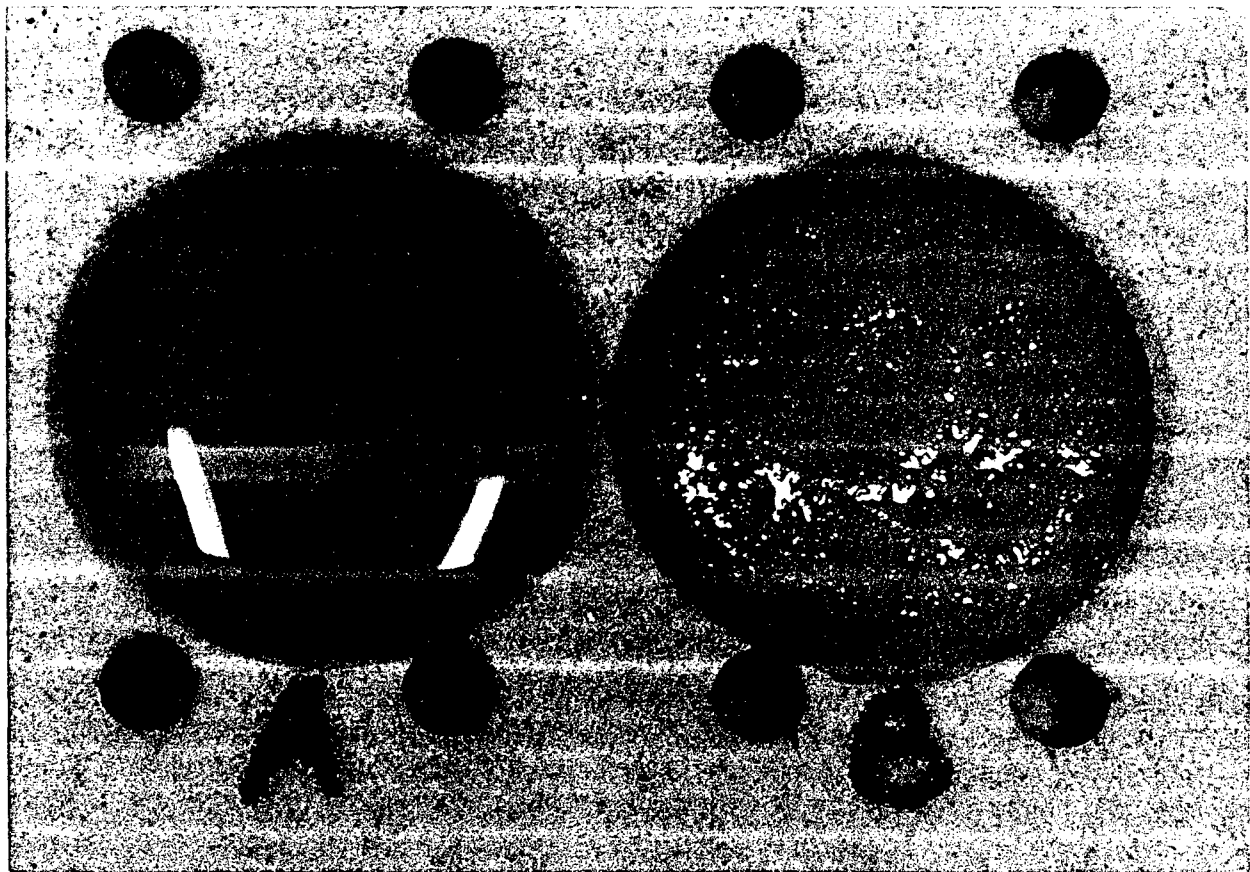


Plate 5. Potassium Salt (Tuf-Coat) (A) and Rubidium Nitrate Paste (B)

Dried for 20 minutes at 150° C

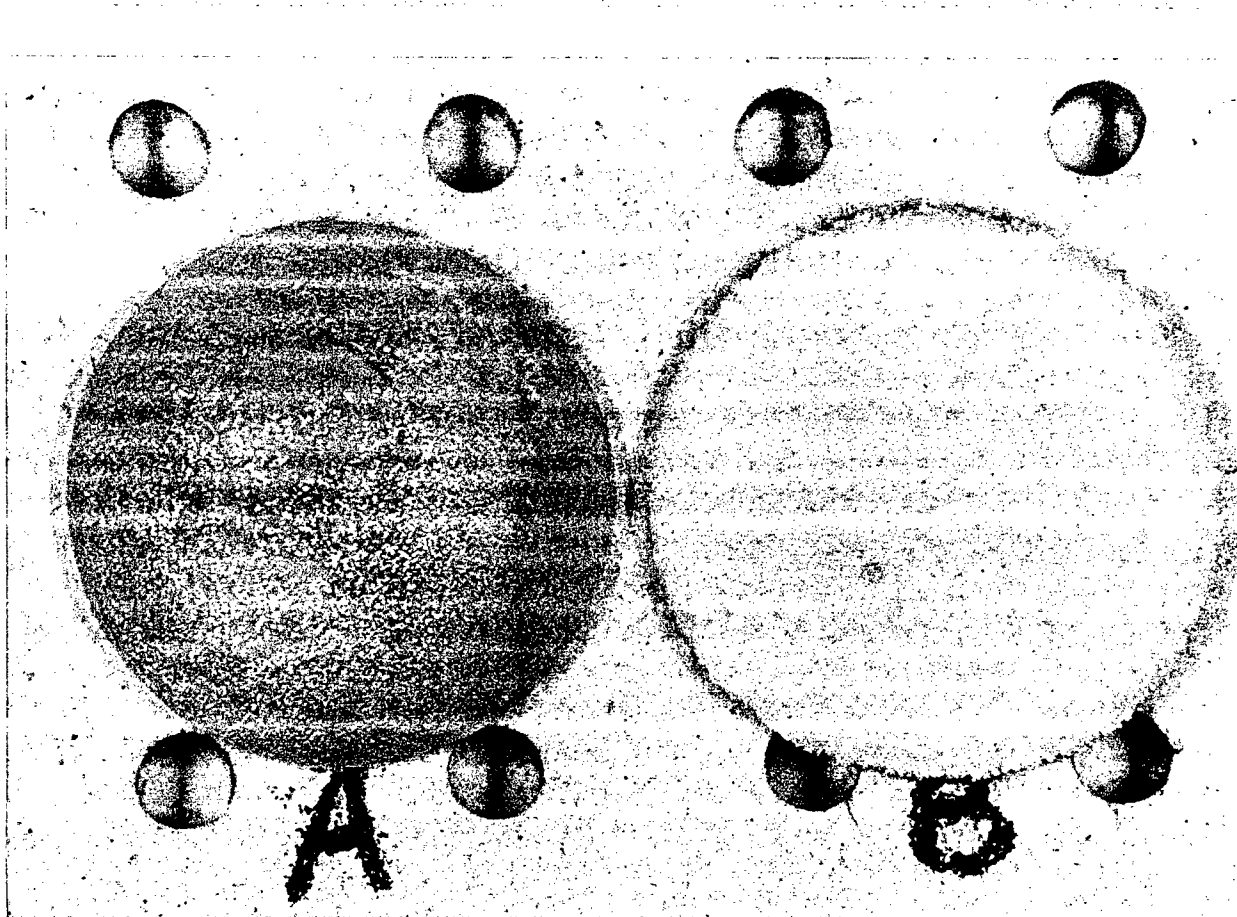


Plate 6. Potassium Salt (Tuf-Coat) (A) and Rubidium Nitrate Paste (B)
After Heat Treatment (Ion Exchange) for 30 minutes at 437° C

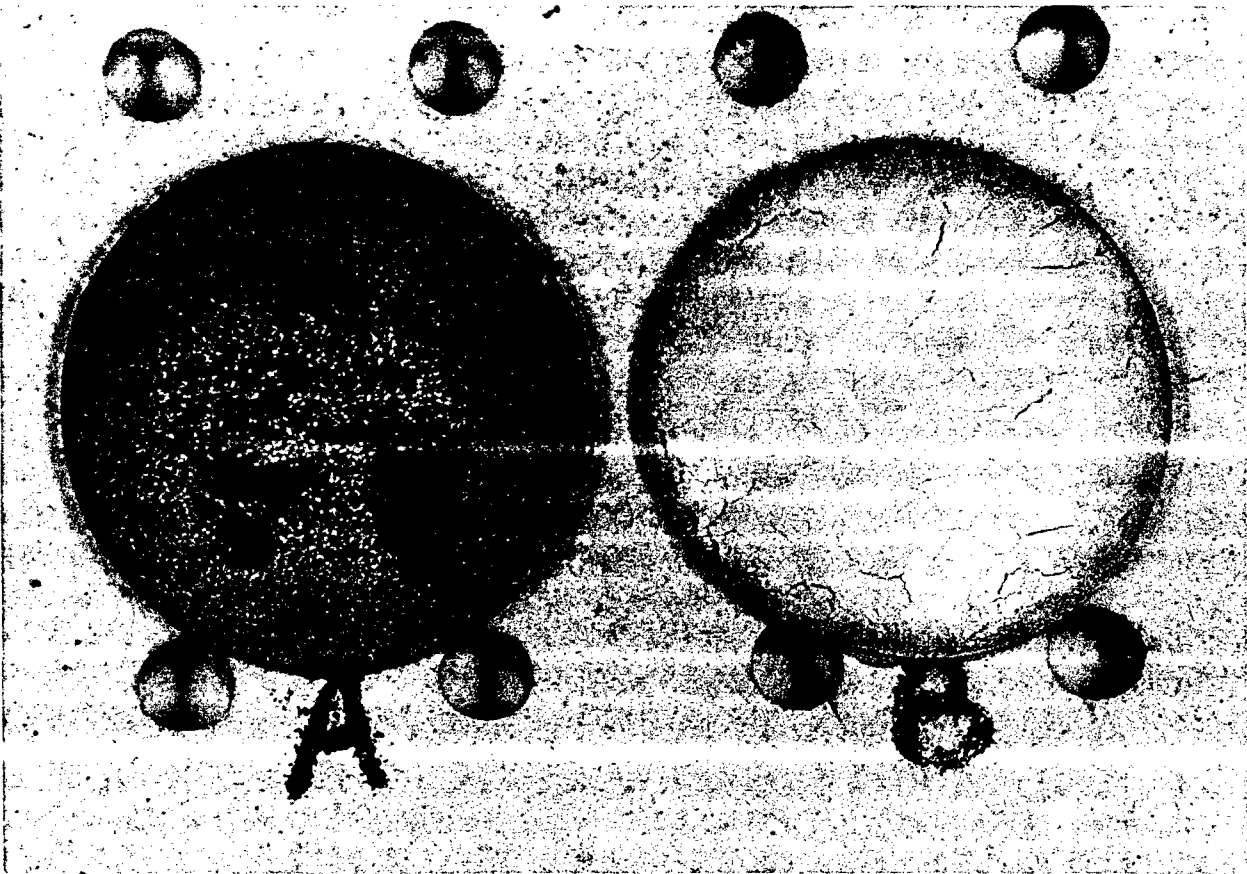
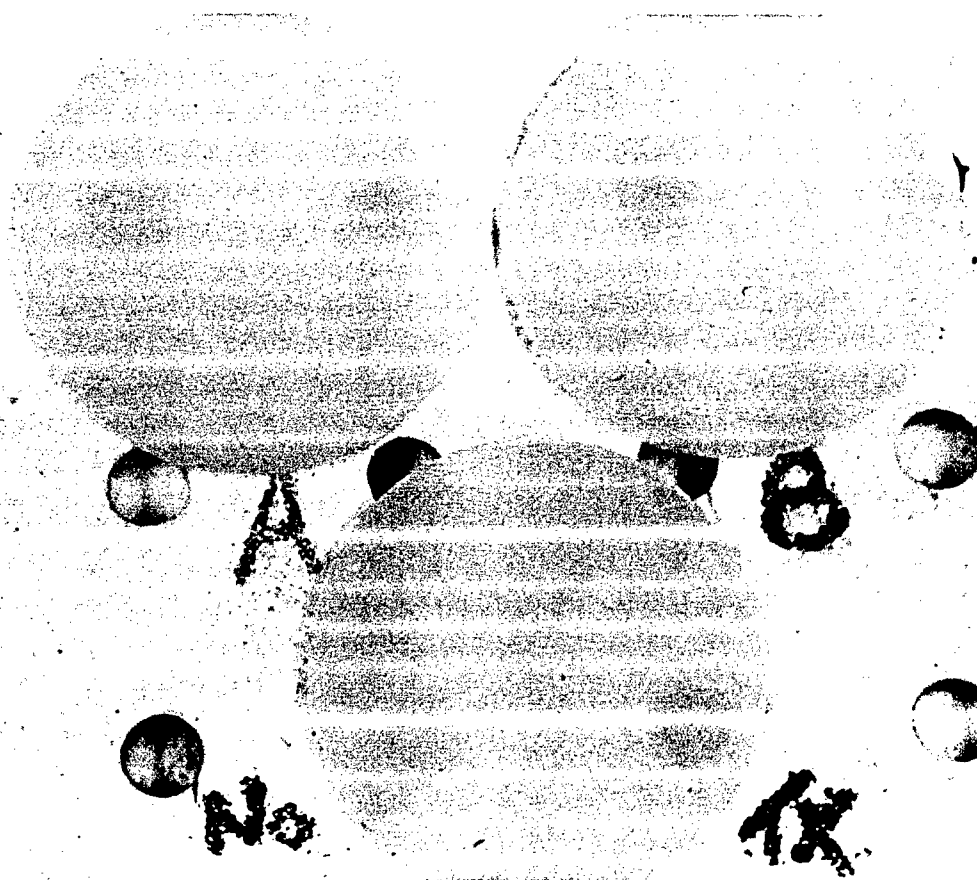


Plate 7. Potassium (A) and Rubidium (B) Ion Exchange Treated Specimens
(Residue Removed) Along With Untreated Specimen





IV. RESULTS

Data were collected and organized according to ion exchange agent and treatment temperature. For both ions tested, a gradual increase in mean biaxial flexural strength reached a peak at a temperature specific for that particular ion, then dropped rapidly as the glass transition temperature was approached. Non-linear two-dimensional curve fitting indicated that curves for both potassium and rubidium were fit with an asymmetric double sigmoidal peak equation of the form:

$$y = a + \frac{b}{1 + \exp\left(-\frac{x - c + \frac{d}{2}}{e}\right)} \left[1 - \frac{1}{1 + \exp\left(-\frac{x - c - \frac{d}{2}}{f}\right)} \right]$$

where $a = 122, 123$; $b = 118, 106$; $c = 467, 437$; $d = 0.00, 103$; $e = 117, 70.6$ and $f = 20.8, 20.9$ for potassium and rubidium, respectively. The respective r^2 and Fstat values are 0.949, 0.963 and 33.6, 47.4 (Figure 1).

The glass transition curve and temperature (T_g), 513°C , was obtained from one disk from the initial batch of specimens using differential scanning calorimetry (DSC V4.OB DuPont 2000), (Figure 2).

Qualitative analysis results are displayed in Figure 3,4 and 5. The concentration profiles of sodium and potassium show a slight inverse relationship, with potassium increasing

and sodium decreasing after treatment with the potassium-based paste (Figure 3). In the rubidium ion exchanged specimen (Figure 4), marked decreases in concentrations for potassium and sodium are seen. Because spectral deconvolution was not performed, the concentration profile for rubidium cannot be discerned due to overlap between the rubidium, aluminum and silicon peaks (Figure 4). In the specimen treated with a mixture of both ions (Figure 5), potassium is also greatly reduced. The high sodium peak suggests that ion exchange with sodium did not occur to any notable extent.

Modulus of rupture, mean and standard deviation values for each group as well as percentage change in strength, relative to control specimens, are listed in Tables 1 and 2. An analysis of variance (ANOVA) was followed by a Student Newman-Keuls test. Results are summarized in Table 2. Vertical lines connect subgroup means that were not significantly different at the $p < 0.05$ level.

The treatment temperatures yielding maximum flexural strengths over the untreated controls were 405° C for the potassium-based slurry (38.5% increase), and 465° C for rubidium nitrate (57.7% increase). In contrast, the optimal temperatures taken from the fitted curve (Figure 1) were 420° C for potassium and 465° C for rubidium nitrate. Consecutive treatment with both slurries yielded a strength increase of 64% regardless of order. Treatment with a mixture of both chemical agents yielded the highest strength increase of 66.1%, although this was not significantly different from any of the treatments involving the rubidium ion at $p < 0.05$. Visual examination of ion exchange treated specimens revealed no apparent changes when compared with untreated specimens.

Table 1. Effect Of Treatment Temperature On Flexural Strength (Modulus of Rupture), MPa

Temp (°C)	K ⁺ Exchange MOR* (SD)	Rb ⁺ Exchange MOR* (SD)	% Change w/ K-Silicate	% Change w/ RbNO ₃
control	123.0 (5.2)**	123.0 (5.2)**	-	-
250	141.0 (8.5)	137.3 (10.0)	14.6	11.6
300	144.3 (7.8)	147.1 (6.0)	17.3	19.6
345	151.9 (8.6)	158.2 (13.3)	23.5	28.6
360	151.9 (16.4)	166.6 (11.3)	23.5	35.4
375	154.6 (15.9)	172.9 (14.7)	25.7	40.6
390	160.3 (14.9)	177.2 (10.2)	30.1	44.1
405	170.3 (13.5)	186.8 (4.9)	38.5	51.9
420	165.0 (11.6)	184.3 (15.3)	34.1	49.8
435	158.6 (13.1)	187.0 (12.2)	28.9	52.0
450	162.0 (9.9)	183.0 (11.7)	31.7	48.8
465	153.5 (9.6)	194.1 (10.9)	24.8	57.7
480	142.8 (7.5)	167.6 (20.1)	16.1	36.3
510	130.6 (7.3)	148.5 (10.6)	6.2	20.7

*Modulus of rupture, mean and standard deviations. **

Untreated control group (for comparison).

Table 2. Flexural Strength As A Function Of Treatment

Surface Treatment	Heat Treatment (° C)	Flexural Strength (MPa)	% Increase vs Control
uncoated	none	123.0 (5.24)	0
K-silicate	405	170.3 (13.5)	38.5
RbNO ₃	465	194.1 (10.9)	57.7
K-silicate/RbNO ₃	420 / 437*	202.5 (17.4)	64.6
RbNO ₃ /K silicate	437 / 420*	202.3 (21.1)	64.4
K-silicate+RbNO ₃	429	204.4 (12.9)	66.1

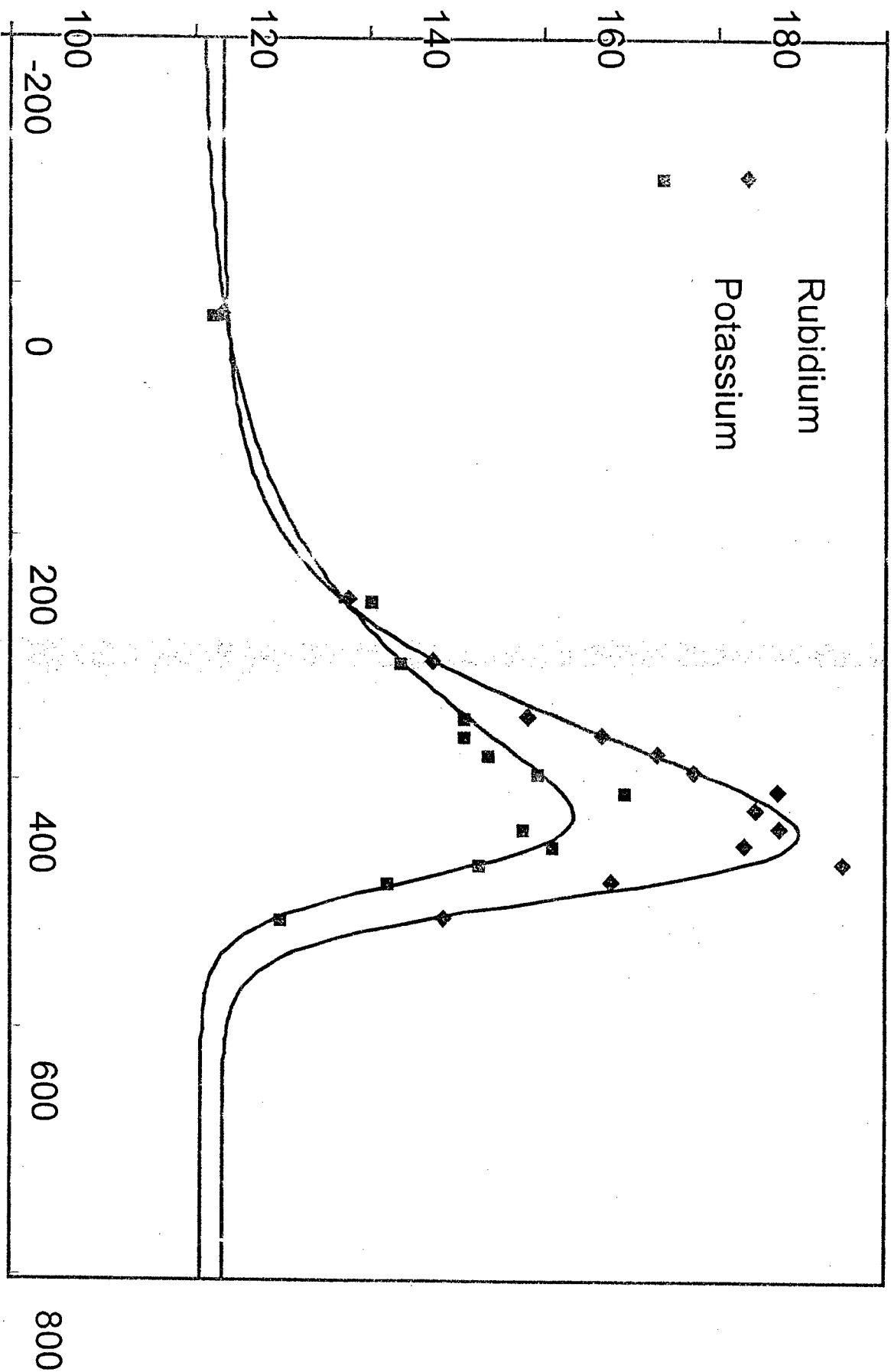
*Temperatures obtained from Figure 1. Vertical lines connect groups that are not significantly different at $p < 0.05$ by Student Newman Keuls.

Figure 1. Flexural Strength as a Function of Temperature for Potassium
Salt (Tuf-Coat) and RbNO_3 Treated Porcelain Specimens



200

Modulus of Rupture, MPa



Rubidium

Potassium

Temperature, °C

Figure 2. Differential Scanning Calorimetry for Optec HSP Porcelain



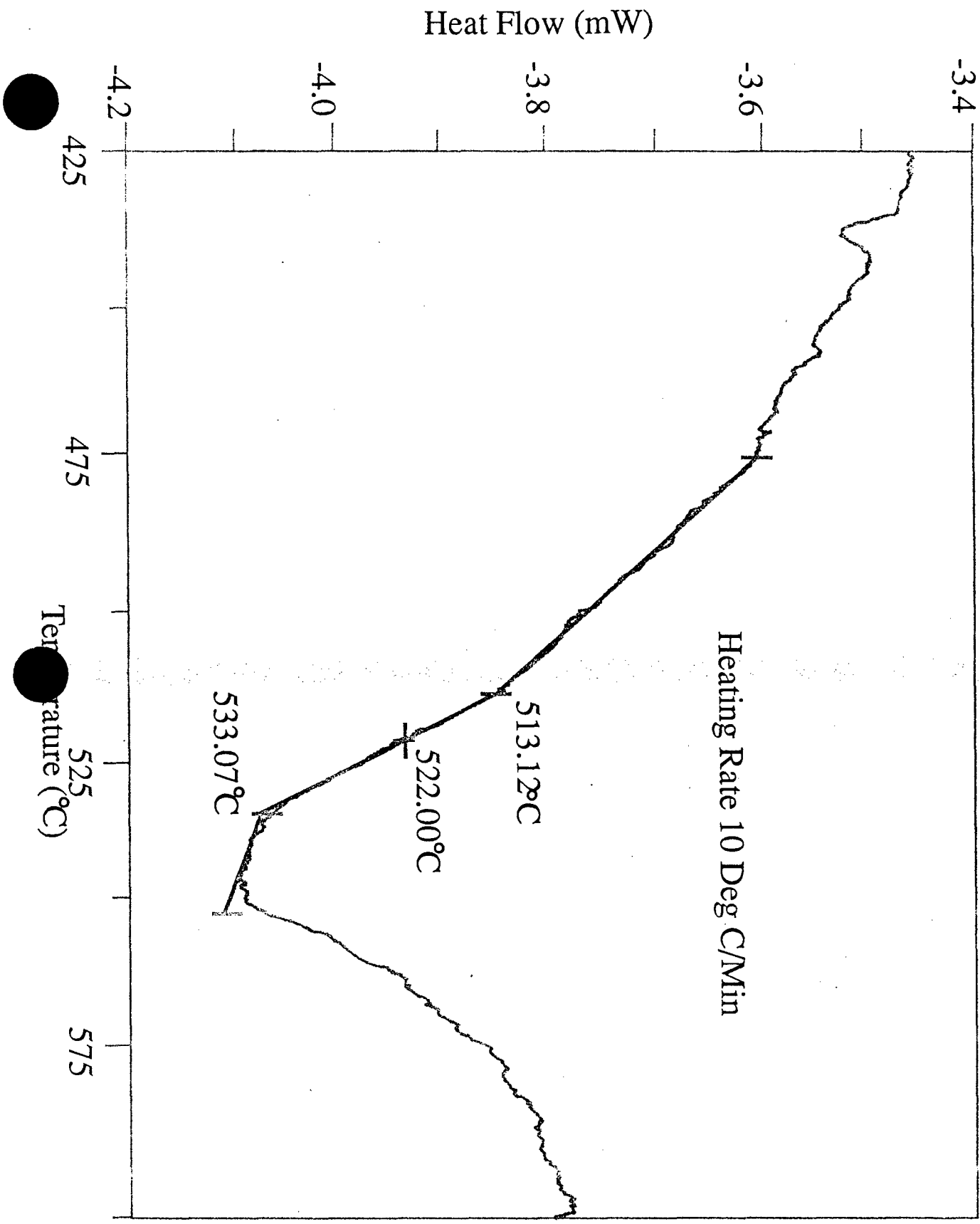


Figure 3. Elemental Analysis of Leucite-Reinforced Porcelain Before and After Ion Exchange With Potassium Salt (Tuf-Coat)



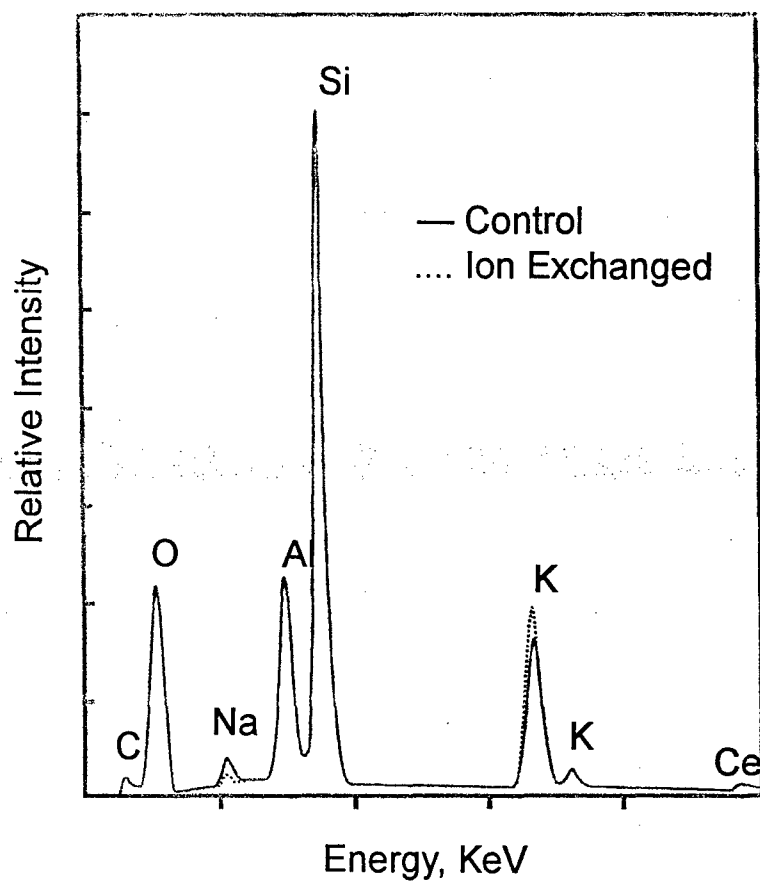


Figure 4. Elemental Analysis of Leucite-Reinforced Porcelain Before
and After Ion Exchange With RbNO_3



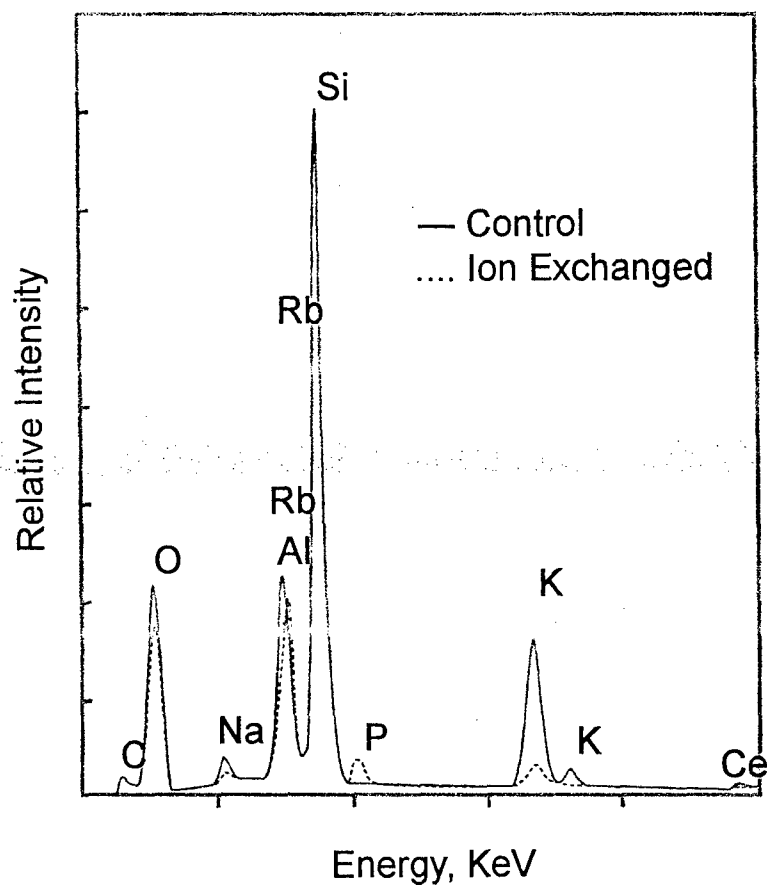
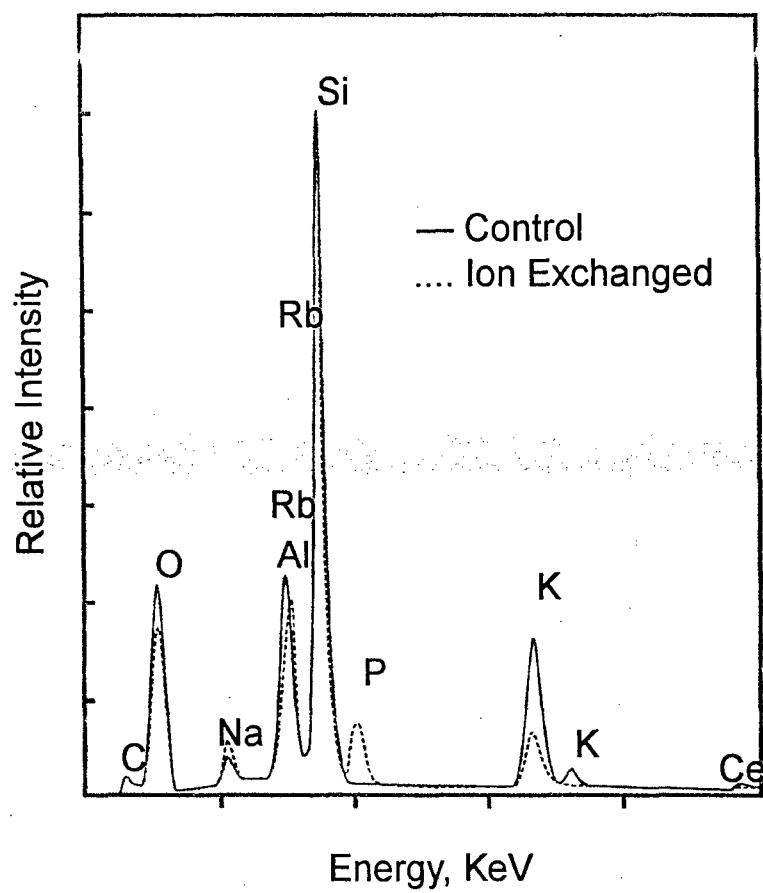


Figure 5. Elemental Analysis of Leucite-Reinforced Porcelain Before and After Ion Exchange With Potassium Salt (Tuf-Coat) and RbNO_3 Mixture



V. DISCUSSION

Ion exchange strengthening of glasses and ceramic materials is a diffusion-controlled process. Concentration of diffusing ions, temperature, and time are the major interacting variables, however composition of the substrate also plays an important role (Kingery, 1976). Because the driving force for diffusion is an ion concentration gradient, ceramic composition should influence the amount of ion exchange that is possible. Previous studies have demonstrated this variation in degree of strengthening among ceramics of differing composition (Seghi *et al.*, 1990).

Elements within the ceramic other than diffusible species influence the reaction. For example, boron in borosilicate glass is thought to depress ion exchange, since no strengthening results when either low or high sodium content samples are subjected to treatment. Alkali-alumino-silicates, on the other hand, are characterized as being highly conducive to ion exchange strengthening. It has been suggested that the effect of alumina within the glass network, rather than an increased exchange reaction, is responsible for this observation (Nordberg *et al.*, 1964). In a study of seven dental porcelains, ion exchange yielded the highest flexural strength increase in a porcelain exhibiting relatively low sodium content (Seghi *et al.*, 1990). Consequently, ion mobility may be of greater importance than actual ion concentration.

Besides determining the concentration of diffusing ions and their relative mobilities, the ceramic composition influences the glass transition temperature (T_g) (Seghi *et al.*, 1990). Knowledge of T_g for the particular ceramic is required when use of the ion exchange process is being considered. As the treatment temperature approaches T_g , residual stress developed during the exchange is quickly lost, due to structural rearrangement and stress relaxation

(annealing). An abrupt drop in biaxial flexural strength for both potassium and rubidium ion exchange treatments, coincides with the T_g (513° C) for Optec HSP porcelain, as seen in Figure 1. The optimal temperature for potassium ion exchange was approximately 100° C below T_g , coinciding with conditions previously reported (Denry *et al.*, 1993). In contrast, the optimal temperature for rubidium exchange occurred at approximately 50° C below T_g . Rubidium ion, because of its' relative larger size, requires higher temperatures for diffusion. Consequently, a narrower temperature range for effective treatment exists.

The biaxial flexural strength increase of 38.5%, obtained with potassium ion exchange of leucite-reinforced porcelain, is in agreement with increases of 37% and 38% previously reported (Holloway *et al.*, 1993; Crimaldi *et al.*, 1994). In comparison, strength increases from 32% to 97% have been reported after potassium ion exchange with conventional feldspathic porcelains (Anusavice *et al.*, 1991). In leucite-reinforced materials low sodium concentration may be a factor however, lower matrix glass volume (due to a high crystalline content), may account for relatively low strengthening seen with potassium ion exchange. Qualitative analysis results with energy dispersive x-ray spectroscopy (EDS) suggest potassium exchange occurred to a minimal extent relative to rubidium exchange (Figure 3 and 4). Low relative strengthening along with minimal exchange evidenced by qualitative analysis, suggests ion exchange using potassium may not have involved the leucite crystalline phase. Because the glass matrix composition in leucite-reinforced porcelain is similar to that of conventional feldspathic porcelains, however, potassium ion exchange is expected to some degree.

The mean biaxial flexural strength increase after rubidium exchange was significantly higher than with potassium exchange, as expected (Table 2). The marked reduction in

concentration profile for potassium seen in Figure 4, suggests rubidium exchange occurred to a greater extent. In addition, the decrease in concentration profile for sodium suggests rubidium exchange can occur with sodium as well as potassium ions. Increased strength values observed after rubidium exchange may also be due to the relative size of the rubidium ion, reported to be 33% larger in volume than potassium (Denry *et al.*, 1993). Employing a larger ion, with more opportunities for exchange with smaller ions (*i.e.*, sodium and/or potassium), would result in greater crowding of the surface microstructure and higher surface compressive stress.

Rubidium exchange of leucite-reinforced ceramic in this investigation yielded a mean biaxial flexural strength increase of 58%. In comparison, rubidium exchange of a conventional feldspathic porcelain yielded a strength increase of 82%, in a previous investigation (Denry *et al.*, 1993). Lower glass content may be a factor accounting for a lower percentage strength increase. However, whether rubidium exchange directly or indirectly, involved the crystalline leucite cannot be determined from this investigation. The marked reduction in potassium concentration profile after rubidium exchange (Figure 4), however, may be suggestive of leucite involvement.

Leucite is characterized by a high potassium content, higher than the surrounding glass matrix (Rouf *et al.*, 1980; Denry *et al.*, 1993). In addition, Optec HSP, leucite-reinforced ceramic, contains at least 45% leucite by weight (Katz, 1989). The possibility of ion exchange within the crystalline phase is intriguing, when the high volume of leucite present in these materials is considered.

Leucite's open crystalline structure may aid in ion exchange. According to a ceramic publication, "Leucite is a potassium aluminosilicate and is in a group of minerals characterized

by large cavities in their anionic lattice that allow good ion-exchanging properties" (Narayszabo, 1969; quoted by Denry *et al.*, 1993). Chemical strengthening techniques not only improve the strength of the matrix glass, but also improve the strength of the crystalline phase (Kingery *et al.*, 1975).

Substitution of intermediate-sized ions for small ions prior to exchange with larger ions would, theoretically, simplify the total reaction, allowing it to proceed to a greater extent. In this investigation, potassium exchange followed by rubidium exchange yielded only slightly greater strength values than treatment with rubidium exchange alone. A small difference in sodium and potassium concentration profiles after potassium exchange seen in Figure 3, may explain the small difference between rubidium exchange of untreated disks, and rubidium exchange of disks treated first with potassium (Table 2).

Specimens treated with potassium followed by rubidium were not statistically different in strength than specimens treated with rubidium followed by potassium. The low treatment temperature used may explain the similar outcomes for both consecutive treatments (Table 2). Substitution of large ions within the glass by smaller ions requires a more fluid glass state. The low temperature (420° C) used may not have been sufficient to permit potassium exchange with rubidium ions previously substituted. Higher temperatures above the T_g of the glass may be required for potassium for rubidium (*i.e.*, small ion for large ion) exchange to proceed.

Ion exchange treatment with multiple ionic species would appear to be a quicker and more convenient way of improving strength. In this investigation, treatment with a mixture of potassium and rubidium ions yielded strength equivalent to that obtained with consecutive treatments (Table 2). The relatively low concentration profile for potassium seen in Figure 5

suggests rubidium for potassium exchange occurred. However, because of the high concentration profile for sodium, it is uncertain whether potassium for sodium exchange occurred to any extent. Differences in ion mobilities are a factor along with other variables previously discussed.

Ion exchange involving multiple ions requires further investigation. Experimentation including ion exchange sequencing, concentration of exchange agents, and treatment temperatures, is needed in order to determine peak treatment conditions for specific porcelain systems. In addition, the porcelains themselves might be specifically formulated to allow for maximum strengthening through subsequent ion exchange.

VI. SUMMARY

Ion exchange is a strengthening technique that is applicable to most dental ceramics. Previous work has shown that conventional feldspathic and alumina reinforced porcelains can be strengthened using ion exchange treatment with rubidium nitrate as well as conventionally using a potassium salt. Leucite-reinforced all-ceramic restorations are increasing in popularity due to their translucency, color control, bondability and improved strength. Ion exchange may be a practical way of strengthening these restorations without affecting their desirable optical properties. The following results and conclusions can be drawn from this investigation:

- 1) Ion exchange with rubidium nitrate yielded significantly higher mean biaxial flexural strength values than with the potassium exchange ($p < 0.05$).
- 2) The optimal treatment temperature for potassium exchange was 405°C , approximately 100°C below the T_g (513°C).
- 3) The optimal treatment temperatures for rubidium exchange was 465°C , approximately 50°C below the T_g .
- 4) Consecutive ion exchange treatment yielded a 64% increase in mean biaxial flexural strength over untreated controls, regardless of order.
- 5) Treatment with a mixture of both rubidium nitrate and potassium paste yielded the greatest increase in strength (66%) over untreated controls, although not significantly greater than with rubidium alone.
- 6) Potassium and rubidium ion exchange treatments were accomplished without visible changes in color and translucency to the ceramic.

VII. SIGNIFICANCE

Ion exchange was introduced into dentistry in 1970, when metal-ceramic restorations were in vogue. This may be the main reason this process has been relatively ignored. Today, strengthening by ion exchange is more applicable than ever due to esthetic emphasis and growing popularity of all-ceramic restorations.

It is well established that the internal surfaces of all-ceramic restorations are subject to high tensile forces which can lead to failure. Ion exchange may be a practical technique for improving the strength and durability of these restorations while retaining the desirable optical properties characteristic of leucite-reinforced, as well as other all-ceramic restorative systems.

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VITA

Jose de Jesus Villalobos [REDACTED]

[REDACTED] b. At one year of age, his family immigrated to the United States and settled in Southern California. He graduated from Palm Springs High School in 1979. That same year he entered College of the Desert where he spent one year. He transferred to The University of San Diego where he majored in Biology. He was awarded a Bachelor of Arts degree from The University of San Diego in December 1983.

In July 1984 he entered the University of California, San Francisco School of Dentistry and received a Doctorate of Dental Surgery degree in June 1988.

In July 1988, he began a General Practice Residency in Hospital Dentistry at Rancho Los Amigos Medical Center, Downey, California. On December 17, 1988, while in residency, he married Cynthia M. Bartel. Upon completion of his residency in July 1989, he obtained his United States Citizenship and was commissioned in the United States Air Force Dental Corps. His first assignment was at Nellis Air Force Base, Las Vegas, Nevada, where he served as a staff general dentist.

[REDACTED] his first daughter, Nicole Marie was born. [REDACTED] his second daughter, Teresa Ann was born. In June of 1994, he entered the University of Texas Health Science Center at San Antonio, Texas where he is presently pursuing a Post-Doctoral degree in Prosthodontics. [REDACTED] third daughter, Lisa Renee was born. In June of 1995, he was admitted as a candidate for the Masters of Science Degree at the Graduate School of Biomedical Sciences.

