

INVESTIGATION OF A TWO STEP ION EXCHANGE IN MIXED ALKALI
GLASSES

BY

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TABLE OF CONTENTS

	Page
Acknowledgments	iii
Table of Contents	iv
List of Tables	vi
List of Figures.....	viii
Abstract	xii
I INTRODUCTION.....	1
II LITERATURE SURVEY	2
A. Glass Strengths	2
B. Ion Exchange	4
C. Diffusion.....	7
D. Relaxation.....	12
E. Mixed Alkali Effect	14
F. Patent Background Information.....	18
III EXPERIMENTAL PROCEDURE	21
A. Ion Exchange	21
1) Glass Rod Preparation.	21
2) Exchange Medium.....	21
3) Immersion.....	23
B. Determination of Exchange depth and Diffusion Coefficients.....	25
1) WDS.....	25
2) Mass Change.	27
C. Flexural Strength	28
IV RESULTS.....	30
A. Depth of Exchange	30
B. Mass Change.....	45
C. Glass Strengths	52
V DISCUSSION	60
A. Composition of Salt Bath and Effect on Exchange Depth.....	60
1) First Step Exchange.....	60
2) Two Step Exchanges.	61
i) 100% NaNO ₃ and 100% KNO ₃	62

ii) Treatment B.....	63
iii) Treatment C.....	65
iv) Treatment D.....	66
B. Temperature Effects.....	67
1) Treatment A.....	67
C. Effect of 1-step and 2-step Exchanges on Fracture Strength.....	67
1) Treatment A.....	68
2) 100% NaNO ₃	69
3) 100% KNO ₃	70
4) Treatment B.....	71
5) Treatment C.....	72
6) Treatment D.....	73
VI SUMMARY AND CONCLUSIONS.....	75
REFERENCES.....	78

LIST OF TABLES

	Page
Table I. Cation Coordination Numbers (CN), Ionic Radii (r_i), Cation – Oxygen Internuclear Distances (r_{i-O}) and Calculated radii of Coordination Polyhedra ($r_{[i-O]}$), Radii (r_{FCS}) and Circumference Lengths of the First Coordination Shells (L_{FCS}) Around Coordination Polyhedra in Silicates.....	16
Table II. Strain Energy, E_S , Strain Intensity Index, N_d , Difference in Cation Coordination Number (CNA), and Difference in Length of the Circumference of the First Coordination Shell (ΔL_{FCS}) for Various Alkali Cation Pairs in Mixed Alkali Silicate Glasses.....	17
Table III. Average Height at Which Samples Broke After Second Treatment with Various Amounts of $LiNO_3$ Added.....	19
Table IV. Composition of Schott AR-Glas®.....	21
Table V. Compositions of Exchange Mediums.....	23
Table VI. Temperatures and Times of the 1-step and 2-step Treatments.....	25
Table VII. Calculated MSD Exchange Depth and Diffusion Coefficient for Glass Rods Treated with Treatment A at 580 °C for Times Between 10 Minutes and 30 Minutes.....	32
Table VIII. Calculated MSD Exchange Depth and Diffusion Coefficient for Glass Rods Treated with Treatment A for 30 Minutes at 580 °C Followed by Treatment D at 450 °C for Times Between 30 Minutes and 24 Hours.....	43
Table IX. Weibull Modulus and Characteristic Strengths for Treatment A at 580 °C.....	54
Table X. Weibull Modulus and Characteristic Strengths for Treatment A for 20 Minutes at 580 °C (Preheated for 20 Minutes at 580 °C) Followed by 100% $NaNO_3$ at 450 °C.....	55
Table XI. Weibull Modulus and Characteristic Strengths for Treatment A for 20 Minutes at 580 °C (Preheated for 20 Minutes at 580 °C) Followed by 100% KNO_3 at 450 °C.....	56
Table XII. Weibull Modulus and Characteristic Strengths for Treatment A for 30 minutes at 580 °C (Preheated for 20 Minutes at 580 °C) Followed by Treatment B at 450 °C.....	57
Table XIII. Weibull Modulus and Characteristic Strengths for Treatment A for 30 Minutes at 580 °C (Preheated for 20 Minutes at 580 °C) Followed by Treatment C at 450 °C.....	58

Table XIV. Weibull Modulus and Characteristic Strengths for Treatment A for 30 minutes at 580 °C (Preheated for 20 minutes at 580 °C) Followed by Treatment D at 450 °C.....	59
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List of Figures

	Page
Figure 1. “Stuffing” process schematic during a low temperature ion exchange of Na ⁺ and K ⁺ ions.....	5
Figure 2. Specific mass change of flat glass samples as a function of square root of time exchanged in 100% LiNO ₃ bath at multiple temperatures.....	11
Figure 3. Effect of strengths on chemically tempered glass as a function of the square root of time.....	14
Figure 4. Schematic of exchange rod holders used. Left holder made out stainless steel base with steel rod. Right holder made out of bronze plates and steel rods.....	24
Figure 5. Left: side view of mounted WDS samples Right: Bottom view of mounted WDS samples.....	26
Figure 6. Normalized Na ⁺ and K ⁺ intensities as a function of depth for untreated Schott AR-Glas® rods.....	31
Figure 7. Normalized Na ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged for 10 min, 20 min, and 30 min with Treatment A at 580 °C.....	31
Figure 8. Normalized K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged for 10 min, 20 min, and 30 min with Treatment A at 580 °C.....	32
Figure 9. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 30 minutes at 450 °C.....	33
Figure 10. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 1 Hour at 450 °C.....	34
Figure 11. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 2 Hours at 450 °C.....	34
Figure 12. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 4 Hours at 450 °C.....	35

Figure 13. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 12 Hours at 450 °C.....	35
Figure 14. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 24 Hours at 450 °C.....	36
Figure 15. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 1 Hour at 450 °C.....	37
Figure 16. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 2 Hours at 450 °C.....	37
Figure 17. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 4 Hours at 450 °C.....	38
Figure 18. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 12 Hours at 450 °C.....	38
Figure 19. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 24 Hours at 450 °C.....	39
Figure 20. Normalized K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 24 Hours at 450 °C for times between 1 hour and 24 hours.....	40
Figure 21. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D for 30 minutes at 450 °C.....	41
Figure 22. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D for 1 Hour at 450 °C.....	41
Figure 23. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D for 4 Hours at 450 °C.....	42

Figure 24. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D for 8 Hours at 450 °C.....	42
Figure 25. Normalized Na ⁺ and K ⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D for 24 Hours at 450 °C.....	43
Figure 26. Calculated diffusion coefficient (D _{Na→Li}) as a function of the square root of time for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D at 450 °C.....	44
Figure 27. Calculated diffusion coefficient (D _{K→Li}) as a function of the square root of time for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D at 450 °C.....	45
Figure 28. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A at 580 °C (preheated at 580 °C for 20 minutes) for times between 5 minutes and 30 minutes.....	46
Figure 29. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A at 625 °C (preheated at 625 °C for 20 minutes) for times between 5 minutes and 40 minutes.....	46
Figure 30. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 20 minutes at 580 °C followed by 100% NaNO ₃ at 450 °C for times between 30 minutes and 24 hours.....	47
Figure 31. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 20 minutes at 580 °C followed by 100% NaNO ₃ at 450 °C for times between 30 minutes and 2 hour.....	48
Figure 32. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 20 minutes at 580 °C followed by 100% KNO ₃ at 450 °C for times between 1 hour and 24 hours.....	48
Figure 33. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 20 minutes at 580 °C followed by 100% KNO ₃ at 450 °C for times between 1 hour and 4 hours.....	49
Figure 34. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 30 minutes at 580 °C followed by Treatment B at 450 °C for times between 30 minutes and 24 hours.....	49

Figure 35. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 30 minutes at 580 °C followed by Treatment B at 450 °C for times between 30 minutes and 12 hours.....	50
Figure 36. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 30 minutes at 580 °C followed by Treatment C at 450 °C for times between 1 hour and 24 hours.....	50
Figure 37. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 30 minutes at 580 °C followed by Treatment D at 450 °C for times between 30 minutes and 24 hours.....	51
Figure 38. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples as shipped.....	52
Figure 39. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples heated to 580 °C for 20 minutes then allowed to air cool.....	53
Figure 40. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A at 580 °C for times between 5 minutes and 30 minutes.....	54
Figure 41. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A for 20 minutes at 580 °C followed by 100% NaNO ₃ at 450 °C for times between 30 minutes and 24 hours.....	55
Figure 42. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A for 20 minutes at 580 °C followed by 100% KNO ₃ at 450 °C for times between 1 hour and 24 hours.....	56
Figure 43. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A for 30 minutes at 580 °C (preheated for 20 minutes at 580 °C) followed by Treatment B at 450 °C for times between 30 minutes and 24 hours.....	57
Figure 44. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A for 30 minutes at 580 °C followed by Treatment C at 450 °C for times between 1 hour and 24 hours.....	58
Figure 45. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A for 30 minutes at 580 °C followed by Treatment D at 450 °C for times between 30 minutes and 24 hours.....	59

ABSTRACT

Investigations into both 1-step and 2-step ion exchange strengthening techniques in mixed alkali glasses were examined. A “high” temperature 1-step exchange ($\text{Li}^+ \rightarrow \text{Na}^+$), which was conducted above the glass transition temperature to strengthen the rods by way of mismatch thermal expansion coefficients. Further a 2-step exchange was conducted by taking previously exchanged ($\text{Li}^+ \rightarrow \text{Na}^+$) rods and “stuffing” them below the glass transition temperature ($\text{Na}^+ \rightarrow \text{Li}^+$ and $\text{K}^+ \rightarrow \text{Li}^+$), resulting in a compressive layer in the surface of the glass structure. The effects of ion exchanges were examined by WDS, mass change analysis, and strength data. The effect of a mixed alkali glass being exchanged with multiple exchange mediums and treatments were examined and explained through this data. Strength increases of 85% were reported for 1-step exchanges with Li^+ , 100% for 2-step exchange with Na^+ , and 160% for 2-step exchanges with K^+ . Diffusion coefficients between multiple ion pairs were also calculated where possible. Also, some strange phenomena explained by the mixed alkali effect were observed for both the high temperature exchange and the low temperature exchanges.

INTRODUCTION

Applications for strengthened glass articles are increasing as society progresses. The use of glass for modern applications is vast, but the limiting strength of glass makes the use of glass unrealistic in applications demanding high and consistent strengths. Techniques such as chemical etching, flame polishing, thermal tempering, and ion exchange strengthening have been used in order to increase glass articles strengths. Chemical etching, and flame polishing strengthen by decreasing the depth and sharpness of the surface flaws. while thermal tempering and ion exchange create surface compressive stresses that help to inhibit the propagation of surface flaws. Although thermal tempering is an effective method of strengthening glass, it is limited by the dimensions of the glass. Glass articles generally must be flat and at least 3 mm thick to effectively temper the glass article.

Ion exchange strengthening has advantages over the other strengthening techniques since it can strengthen thinner and various complex shapes. Its main disadvantage for soda-lime silicate glass is the time needed to properly strengthen the glass. Shorter exchange times, which still lead to high and consistent strengths, are essential for any realistic use in industry. The use of a 2-step ion exchange strengthening process allows for the surface of the glass to be filled with Li^+ ions quickly at a temperature above the glass transition temperature in the first step and then allows larger alkali ions to exchange with these Li^+ ions in the surface of the glass at a temperature below the glass transition temperature for the second step. The second step causes a compressive layer on the surface and thus strengthens the glass articles. Although the second step may take longer than the first step, the combined time to strengthen the glass articles may be less than that of current ion exchange treatments used. Thus, there is a need to investigate the possibility of a 2-step ion exchange at times that would permit the use of ion exchange strengthening in processing equipment and various other applications. This is the subject of the current thesis.

LITERATURE SURVEY

A. Glass Strengths

Theoretically glasses have the potential to be far stronger than other materials such as metals and ceramics. Unfortunately, the theoretical strength of glass is far higher than that observed in commercially produced glass. The theoretical strength of a “perfect” glass is related to the stress required to pull two atoms apart from one another. Doremus derived the theoretical cohesive strength or ultimate strength as

$$\sigma^2 = \frac{\gamma E}{4 a} \quad (1)$$

Where σ is the stress at failure in a flaw free glass, γ is the interfacial (fracture) surface energy, E is the Young’s modulus, and “ a ” is the inter atomic separation distance.^{1 p. 162} Using eq. 1

Doremus calculated an approximate ultimate strength of a soda-lime silicate glass of 16 GPa.¹

^{p.162} A typical soda-lime glass broken at room temperature has strength of around 166 MPa^{1 p. 154} less than 1% of its potential ultimate strength. This deviation from the theoretical strength can be attributed to surface flaws produced during the forming and processing of glass articles.

The development of glass strengthening techniques was and continues to be needed to help diminish the effects of surface flaws on glass strength. These techniques include chemical etching, mechanical and flame polishing, ion exchange, and thermal tempering. Chemical etching, mechanical polishing, and flame polishing, help to strengthen glass articles by eliminating the amount of defects and limiting the length and shape of surface cracks. Ion exchange and thermal tempering techniques induce a compressive layer at the surface of the glass article which helps to negate the effects of the surface flaws.

Since, these surface flaws or surface cracks greatly affect the strength of glass, the effect of the size, shape and depth of surface cracks has been greatly investigated. Inglis solved the elastic problem with an assumed crack shape of an elliptical nature, which is given by:

$$\frac{\sigma}{S} = \frac{1 + \frac{2c}{a} - \frac{(c+a)^2 x^2}{a^4}}{1 + \frac{(c^2 - a^2)x^2}{a^4}} \quad (2)$$

Where σ is the stress along the inside of the crack surface, S is the tensile stress that the crack is subject to, c is the crack depth (semimajor axis of the ellipse), a is the half-width of the crack (semiminor axis of the ellipse), and x is the distance from the crack tip parallel to the sample surface.^{1 p. 160} If we look at the stress right at the crack tip (i.e. $x=0$) and look at the equation in terms of the radius of curvature $\rho = a^2/c$ of the crack tip, the stress is given by^{1 p.161}:

$$\frac{\sigma}{S} = 1 + \frac{2\sqrt{c}}{\rho} \approx 2\frac{\sqrt{c}}{\rho} \quad (3)$$

Eq. (2) and Eq. (3) show that an applied stress is enhanced at the crack tip. Since the shape, size, and depth of these surface cracks are still uncertain, a method for solving for the fracture stress in which the changes in the radius of the crack tip are ignored. The Griffith equation which approaches the problem from fracture energy, rather than stress magnification at the crack tip, and is given by:

$$S_f^2 = \frac{2E\gamma}{\pi c} \quad (4)$$

Where S_f is the fracture stress, c is the crack depth, γ is the fracture surface energy, and E is Young's modulus.^{1 p. 165} According to Doremus, the Griffith equation provides a necessary but not sufficient condition for fracture, where the Inglis equations provide the correct fracture criterion. This is because the 2nd law of thermodynamics shows that the fracture stress is limited by the Griffith equation but could be greater.^{1 p. 165}

Inducing a compressive stress in the surface of the glass helps to prevent the propagation of these surface cracks. The compressive layer stops flaws from propagating since the applied stress needed to overcome this compressive layer is larger. Thus, it is essential for the compressive layer to be deeper than the largest flaw in the glass surface, to ensure that every flaws detriment to the glass strength is diminished by the compressive layer. The use of chemical strengthening is one such way to induce a compressive surface layer in glass.

B. Ion Exchange

Two unique ion exchange techniques have been developed to induce a compressive layer sufficient in strengthening glass. The first being a low temperature process (i.e. below the glass transition temperature, T_g), in which larger alkali ions in an exchange medium exchange with smaller alkali ions in the glass surface. This exchange process is referred to as a “stuffing” exchange and larger ions occupying the smaller ionic site create compressive stresses. Commonly, this ion exchange method is used to exchange larger K^+ ions in a molten salt bath with Na^+ ions in the glass surface. The second process is a high temperature exchange (i.e. above T_g), in which smaller alkali ions in an exchange medium are exchanged with larger alkali ions in the glass surface. The exchange of these smaller ions results in a difference in thermal expansion between the surface layer and the bulk glass, resulting in a compressive surface layer when the glass is cooled, similar to that in a low expansion glaze on a ceramic substrate. A common example of this high temperature exchange is a process that allows Li^+ ions in a sufficiently high temperature medium to exchange with Na^+ ions in the glass surface. Both of these exchanges can be described by:

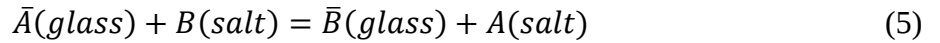


Figure 1 shows a model for a low temperature ion exchange between an exchange medium containing K^+ ions and a glass containing Na^+ ions.² Since the “stuffing” technique is below the glass transition temperature, and usually well below the strain point, the glass structure is rigid. Thus, when the larger ions are “stuffed” into smaller ionic sites in the glass surface residual compressive stresses are induced. The effectiveness of this exchange is

dependent on the time and temperature of exchange, the composition of the exchange medium, and stresses present in the glass at the time of exchange.³

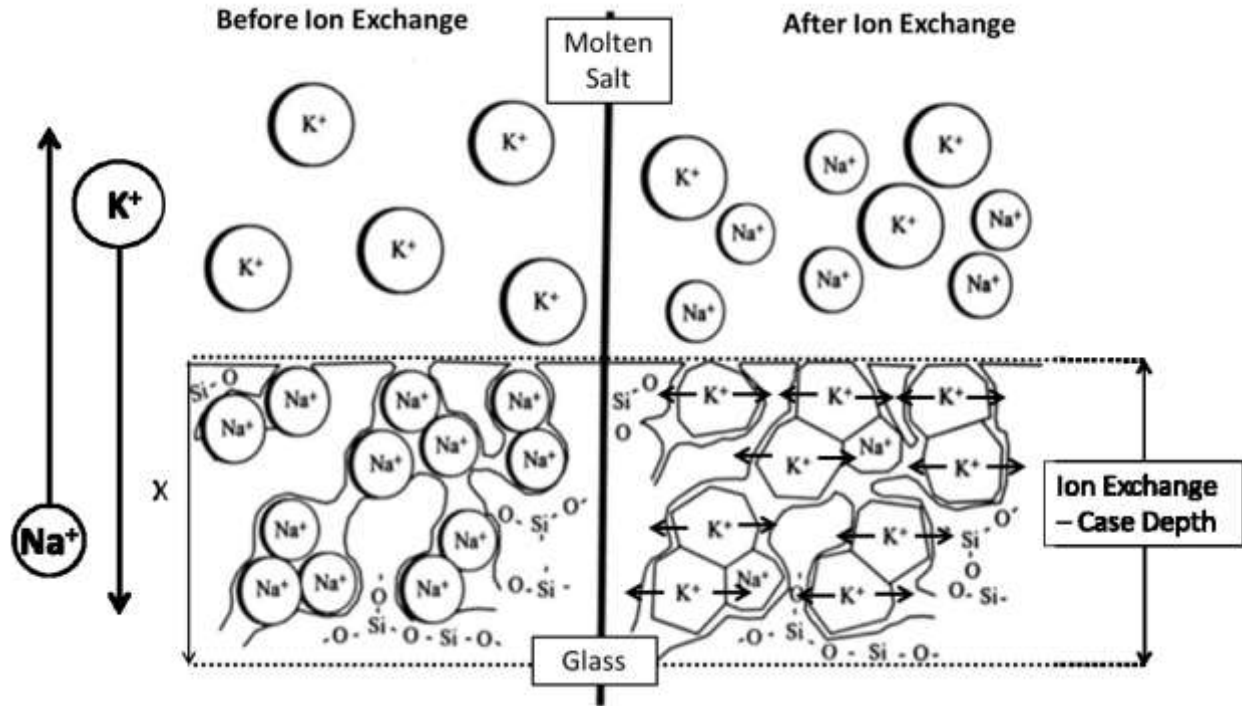


Figure 1. “Stuffing” process schematic during a low temperature ion exchange of Na⁺ and K⁺ ions.

During the “stuffing” exchange the exchange of larger ions for smaller ions causes the volume of the glass to expand and thus creating compressive stresses. An equation was developed that relates the change in volume to the stress created in the surface layer and is given by:

$$\sigma = \frac{1}{3} \frac{\Delta V}{V} \frac{E}{(1 - \mu)} \quad (6)$$

Where σ is the surface compressive stress, ΔV is the change in volume of ions in an initial volume V associated with the exchange of ions, E is Young’s modulus, and μ is Poisson’s ratio.³ This equation neglects the effects of stress relaxation. In the case of smaller A ions in the glass being exchanged with B ions in an exchange medium $\Delta V/V$ can be expressed as:

$$\frac{\Delta V}{V} = \frac{4\pi}{3} (R_B^3 - R_A^3) X C_A \quad (7)$$

Where R_B is the radius of type B ions, R_A is the radius of type A ion, X is the fractional exchange of these ions, and C_A is the original concentration of ions A in the glass.³ The fractional exchange of these ions is proportional to the square root of time of the exchange as well as the inter-diffusion coefficient. The stress calculated during the “stuffing” exchange by eq. 5 does not account for the temperature induced stress relaxation, stresses induced during the exchange, surface defects, and impurities in the exchange medium.³

Alternatively, the high temperature exchange technique takes advantage of the change of thermal expansion coefficients created when smaller alkali ions exchange with larger alkali ions in the glass. When this exchange occurs above the glass transition temperature the structure is allowed to significantly relax and stresses are not induced during the exchange. The exchanged surface layers structure is changed to adapt to the new smaller ions and the surface layer has a different (usually smaller) thermal expansion coefficient than the rest of the bulk glass. When cooled the lower thermal expansion coefficient causes a residual compressive surface layer.

If we treat new structure in the surface layer as a glaze of the same Young’s modulus as the interior, we can express the compressive stress induced, σ , by:

$$\sigma = (\alpha_1 - \alpha_2) \Delta T \left(\frac{E}{1 - \mu} \right) \frac{A_1}{A} \quad (8)$$

Where α_1 is the thermal expansion coefficient of the bulk material, α_2 is the thermal expansion coefficient of the glaze, ΔT is the change in temperature, E is Young’s modulus, μ is Poisson’s ratio, A_1 is the cross section of the glazed material, and A is the cross section of the bulk material.⁴ This equation would only be an estimate for the compressive stress at the surface due to the differences in thermal expansion. Eq. 8 does not take into account the fact that the surface layer may have a different Young’s modulus and Poisson’s ratio than the rest of the bulk glass in our case. Also, during the diffusion process there would be a concentration gradient of the smaller exchanged ions in the surface layer of the glass. Thus, α_2 would be a function of the

distance into the surface layer. Lastly ΔT would have to be the change in temperature once the glass structure had “frozen” in, or the temperature below T_g .

C. Diffusion

Both of these ion exchange techniques are governed by the inter-diffusion of alkali ions exchanging with one another. Assuming a constant diffusion coefficient where the chemical potential is controlled by the concentration gradient, in one dimension the exchange can be described by Fick’s first law of diffusion, given by:

$$J_{i,x} = -D_i \left(\frac{\partial C_i}{\partial x} \right)_T \quad (9)$$

Where $J_{i,x}$ is the flux of material i in the x -direction, D_i is the diffusion coefficient of ion i , and is the $\left(\frac{\partial C_i}{\partial x} \right)_T$ concentration gradient of ion i at constant temperature T .^{5 p. 128} The concentration gradient of the similarly charged exchanging alkali ions induces a thermodynamic chemical potential between the alkali species resulting in the flow of ions in the direction of lesser concentration. For electric neutrality and stoichiometry to be conserved, the slowest exchanging species governs the rate of diffusion for the system. The rate of diffusion of the faster moving species decreases, and the rate of diffusion of the slower moving species decreases, due to the gradient in the electric potential caused by inter-diffusion.⁶ Thus, the effective rate of diffusion is controlled by the relationship of diffusing species associated in the exchange, which can be expressed as:

$$\tilde{D} = \frac{D_A D_B}{N_A D_A + N_B D_B} \quad (10)$$

Where $\tilde{D}$ is the effective diffusion coefficient, D_A is the diffusion coefficient of species A, D_B is the diffusion coefficient of species B, N_A is the mole fraction of species A, and N_B is the mole fraction of species B.⁶

Fick’s first law is useful when relating the rate of mass flow in a set direction to its concentration gradient in any location. On a macroscopic scale, the first law is especially useful when analyzing mass flow in steady state situations, where the concentration gradient of

diffusing components changes as a function of location, but not as a function of time.^{5 p. 133}

When relating the diffusing components as a function of location and time, Fick's second law is needed, and in one dimension is given by:

$$\frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} \quad (11)$$

Where C_i is the concentration of substance i , t is time, x is the direction of diffusion, and D is a constant diffusion coefficient.^{5 p. 134} When examining the exchange of alkali ions during the ion exchange process, a non-steady state approach is needed, and thus solving Fick's second law is necessary. When glass rods are being exchanged, solving Fick's second law in cylindrical coordinates is needed. When considering a long circular cylinder where diffusion is everywhere radial, the concentration of diffusing species is only a function of r and t , and the diffusion equation becomes:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D \frac{\partial C}{\partial r} \right) \quad (12)$$

Where C is the concentration, t is time, r is the radial distance, and D is a constant diffusion coefficient.^{7 p. 69} Using the method of separation of variables it can be shown that

$$C = u e^{-D\alpha^2 t} \quad (13)$$

is a solution of eq. 12 for constant D provided that u is a function of r only, that satisfies:

$$\frac{d^2 u}{dr^2} + \frac{1}{r} \frac{du}{dr} + \alpha^2 u = 0 \quad (14)$$

Which is Bessel's equation of order zero.^{7 p. 72} Solutions to eq. 14 can be expressed in terms of Bessel functions, chosen so the initial and boundary conditions are satisfied.^{7 p. 72}

According to Crank^{7 p. 72-73}, for a cylinder of radius a , and boundary conditions:

$$C = C_o, \quad r = a, \quad t \geq 0 \quad (15)$$

$$C = f(r), \quad 0 < r < a, \quad t = 0 \quad (16)$$

The solution to eq. 14 is given by:

$$C = C_o \left(1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{1}{\alpha_n} \frac{J_0(r\alpha_n)}{J_1(a\alpha_n)} e^{-D\alpha_n^2 t} \right) + \frac{2}{a^2} \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t} \frac{J_0(r\alpha_n)}{J_1^2(a\alpha_n)} \int r f(r) J_0(r\alpha_n) dr \quad (17)$$

Where the α_n 's are the positive roots of

$$J_0(a\alpha_n) = 0 \quad (18)$$

If the concentration is initially uniform throughout the cylinder, i.e. $f(r) = C_1$ eq. 17 becomes:

$$\frac{C - C_1}{C_o - C_1} = 1 - \frac{2}{a} \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t} \frac{J_0(r\alpha_n)}{\alpha_n J_1(a\alpha_n)} \quad (19)$$

And the corresponding quantity of diffusion substance that has entered or left the cylinder is given by:

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} e^{-D\alpha_n^2 t} \quad (20)$$

Where M_t is the quantity of diffusion substance that has entered or left the cylinder, and M_{∞} is the amount of diffusing substance that has entered or left the cylinder at $t = \infty$.^{7 p. 73} Eq. 19 and eq. 20 both describe the diffusion of ions during the ion exchange process in a cylindrical glass rod. According to Crank^{7 p. 73}, the corresponding solution that is useful for small times is given by:

$$\begin{aligned} \frac{C - C_1}{C_o - C_1} = & \sqrt{\frac{a}{r}} \cdot \text{erfc}\left(\frac{a-r}{2\sqrt{Dt}}\right) + \frac{(a-r)\sqrt{Dta}}{4ar^{\frac{3}{2}}} \cdot \text{ierfc}\left(\frac{a-r}{2\sqrt{Dt}}\right) \\ & + \frac{(9a^2 - 7r^2 - 2ar)Dt}{32a^{\frac{3}{2}}r^{\frac{5}{2}}} \cdot i^2 \text{erfc}\left(\frac{a-r}{2\sqrt{Dt}}\right) + \dots \end{aligned} \quad (21)$$

Which holds true provided r/a is not small. Crank^{7 p. 74}, also shows that for small times, the amount of diffusing species entering or leaving the cylinder can be given by:

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \left(\frac{Dt}{a^2} \right)^{\frac{1}{2}} - \frac{Dt}{a^2} + \frac{1}{3\sqrt{\pi}} \left(\frac{Dt}{a^2} \right)^{\frac{3}{2}} + \dots \quad (22)$$

Diffusion of ions during the ion exchange process is also dependent on temperature and thus the diffusion coefficient follows the Arrhenius equation given by:

$$D = D_o e^{\frac{-\Delta E_a}{RT}} \quad (23)$$

Where D is the diffusion coefficient dependent on the temperature, D_o is the diffusion coefficient, ΔE_a is the activation energy, R is the universal gas constant, and T is the temperature.⁶ The diffusion process causes a change in concentration in the surface and as diffusion continues the rate of exchange is altered. The exchange depth is found to be proportional to the square root of time of exchange, i.e. as the time of exchange increases at a specific temperature, the rate of inter-diffusion between ions decreases due to the greater depth required during the exchange.³

The exchange of ions also results in a change in mass of the samples being submerged in the exchange medium. This change in mass can be calculated by integrating the concentration function over the closed space of the sample. These calculated changes in mass were shown in eq. 20 and eq. 22, for cylindrical shaped samples that undergo a diffusion process similar to ion exchange.^{7 p. 73-74} Chizhik and Sidelnikov used a similar technique when investigating the kinetics of reaction in an ion-exchange with soda-lime silicate glass. Their process examined the exchange of lithium ions in a salt bath exchanging with sodium ions in flat glass samples at low temperatures. This low temperature exchange results in the fracture of the glass samples after exchange due to the tensile stresses induced during the exchange. However, they were able to calculate the diffusion coefficients of the process by examining the change in mass per unit surface area of the samples. Figure 2 shows the specific mass change as a function of the square root of time of exchange in a pure LiNO_3 salt bath at different temperatures.⁸

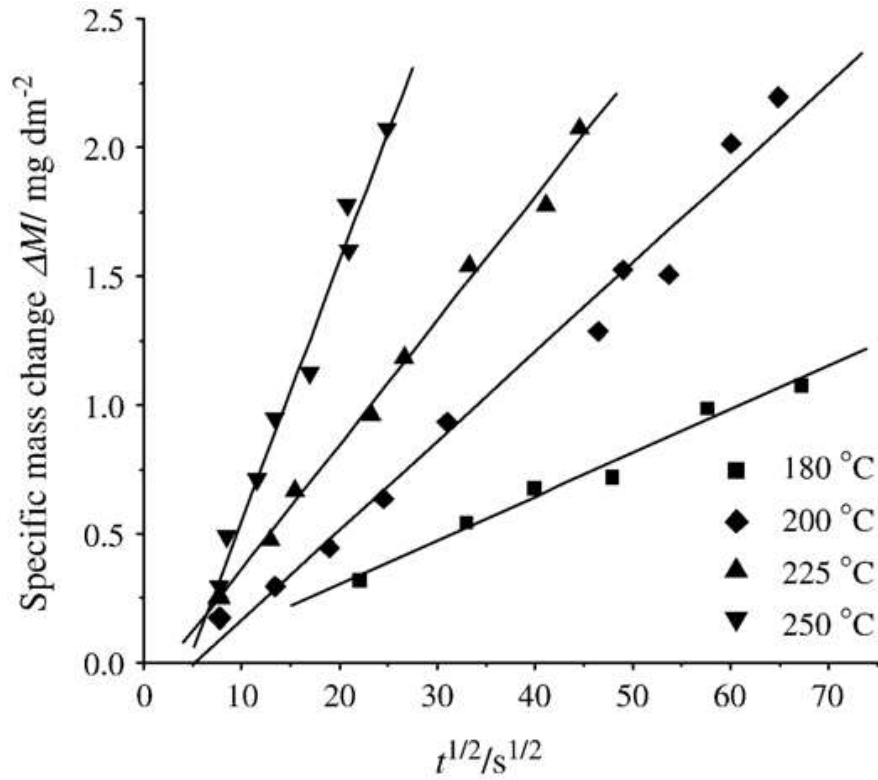


Figure 2. Specific mass change of flat glass samples as a function of square root of time exchanged in 100% LiNO₃ bath at multiple temperatures.

Chizhik and Sidelnikov used the well-known solution to the diffusion problem in half space given by:

$$C(x, t) = \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (24)$$

Where $C(x,t)$ is the concentration of lithium ions normalized to the amount of sodium ions in the glass samples, x is the distance into the glass sample, D is the diffusion coefficient, t is time of exchange, and $\operatorname{erfc}(z)$ is given by:

$$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^{\infty} e^{-\xi^2} d\xi \quad (25)$$

Upon integrating eq. 24 over the x-dependence of the sample, the change in mass of the sample (2 sides of the samples accounted for) was obtained, and given by:

$$\Delta M(t) = 4 M_o \sqrt{\frac{Dt}{\pi d^2}} \quad (26)$$

Where M_o is the change in mass upon completion of reaction, and d is the thickness of the sample.⁸ Using eq. 26 as well as Figure 2 Chizhik and Sidelnikov were able to calculate the diffusion coefficient for the exchange process for multiple temperatures.

D. Relaxation

During the ion exchange process the concentration of exchanging ions continually increases for greater depths into glass samples. However, as can be seen in Figure 3, the strength of glass articles has a maximum in strength as a function of exchange time. This loss in strength at longer exchange times can be attributed to thermal relaxation of the glass articles and can be quite significant when the exchange temperature is high relative to the glass transition temperature. Bartholomew and Garfinkel developed an equation that shows effects of thermal relaxation in glass samples. The strength of exchanged sample at a specific temperature and time is proportional to the rate of ion-exchange minus the loss in stress due to thermal relaxation and a simplified approach is given by:

$$\frac{d\sigma}{dt} = \frac{k}{\sqrt{t}} - \frac{\sigma}{\tau} \quad (27)$$

Where σ is the stress, t is the time of treatment, k is Boltzmann's constant, and τ is the relaxation time.⁶ Eq. 27 can be manipulated and integrated yielding:

$$\sigma = 2 k \sqrt{\tau} e^{-x^2} \int_0^x e^{-y^2} dy \quad (28)$$

Where $x=(t/\tau)^{1/2}$. Which can also be written as:

$$\sigma = 2 k \sqrt{\tau} F(x) \quad (29)$$

The function $F(x)$ was tabulated by Miller and Gordon and easily shown that

$$\lim_{\tau \rightarrow \infty} \sigma = 2 k \sqrt{t} \quad (30)$$

$$\lim_{t \rightarrow \infty} \sigma = 0 \quad (31)$$

Thus, for very long relaxation times (i.e. relatively low temperature exchanges) the stress build up in the surface of the glass should increase linearly. This appears to be true until the treatment time becomes large relative to the relaxation time at a specific temperature. At this point, the stress in the glass surface begins to decrease and wants to return back to zero stress in the surface. This explains the maximum seen in Figure 3, the stress accumulated due to the ion exchange is beginning to be out-weighted by the stresses induced by thermal relaxation at longer times, and thus begins decreasing.

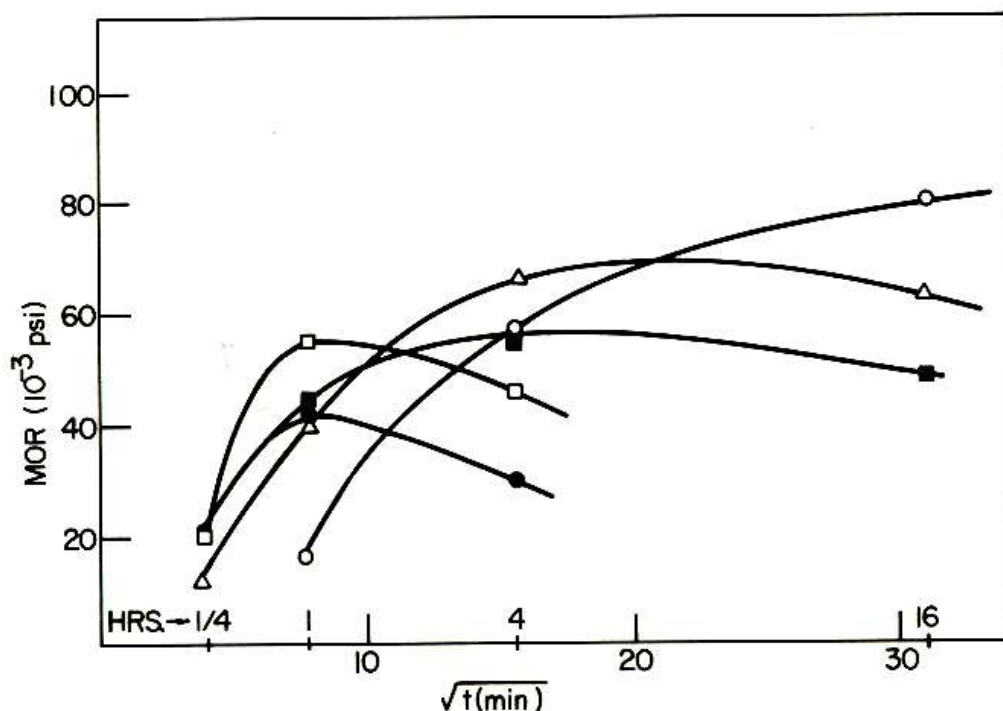


Figure 3. Effect of strengths on chemically tempered glass as a function of the square root of time.

E. Mixed Alkali Effect

The effect of multiple species of alkali ions in a glass structure has been investigated and modeled in detail. In oxide glasses where multiple alkali ions coexist, physical properties of the glass such as viscosity, glass transition temperature, and ionic conductivity deviate from normal linearity when one alkali cation exchanges with another in a fixed concentration of alkali's in a glass. Although there are many models to explain this effect, they all postulate that the ionic movement of alkali ions only occurs between "regular" ionic sites, and local mechanical stresses induced from the exchange of smaller alkali ions exchanging with larger alkali ions, and vice-versa, are somehow absorbed by the surrounding matrix structure, and leaves the structure largely unaffected when an alkali ion occupies a foreign site.⁹ The dominating theories found in literature about the mixed alkali effect propose that the ionic transport of alkali ions in a mixed alkali system are "site preferred", i.e. the mobile alkali ions are unwilling to occupy the foreign

cation sites because of the differences in the surrounding structure such as the coordination number and cavity size.⁹

The theory that defects in the glass can be related to the mixed alkali effect is not new. LaCourse proposed a defect model for the mixed alkali effect where “mixed alkali defects” are defined as alkali cations occupying foreign sites. According to LaCourse’s model, mechanical and electrical strains are localized in these defect sites and cause strains in the surrounding non-bridging oxygen bonds, thus resulting in the reduction of viscosity in the system. When approaching the transition region of the system, stress and structural relaxation converts these defect sites into normal sites with time. The diffusion and conductivity in this model is predicted by assuming that the alkali cations are “site preferred”, and that alkali cations can diffuse along foreign sites but at a reduced rate.¹⁰

The contemporary model for ionic transport in glasses suggests that at temperatures below the glass transition temperature that ionic species are strongly associated with their local environment, which is defined as a regular ionic site.⁹ It is also widely excepted that the ionic species that occupies a regular ionic site determines the local environment that surrounds the cation. For example Li^+ ions have a strong tendency for fourfold coordination of oxygen atoms, where Na^+ ions tend to have 5 or 6 fold coordination with oxygen, and K^+ ions most commonly exhibit a coordination number of 6 to 8 with oxygen ions.⁹ Table I summarizes the alkali ionic radii and coordination numbers for various alkali cations in silicate glasses.⁹

When considering an initially defect free silicate glass structure with glass modifiers A^+ and R^+ in their regular ionic sites, the cations can randomly jump and occupy either host or foreign ionic sites. If A^+ moves into a R^+ site and the A^+ ion is larger, a compressive stress in the radial direction. The total strain induced is given by Frenkel’s eq.:

$$E_s = 8 \pi G r_R (r_A - r_R)^2 \quad (32)$$

Where E_s is the total strain energy, r_R is the radius of the spherical polyhedron associated with the R^+ cation, r_A is the radius of the spherical polyhedron associated with the A^+ cation and G is the shear modulus.⁹

Table I. Cation Coordination Numbers (CN), Ionic Radii (r_i), Cation – Oxygen Internuclear Distances (r_{i-O}) and Calculated Radii of Coordination Polyhedra ($r_{[i-O]}$), Radii (r_{FCS}) and Circumference Lengths of the First Coordination Shells (L_{FCS}) Around Coordination Polyhedra in Silicates.

Ion	CN	r_i, pm	r_{i-O}, pm	$r_{[i-O]}, pm$	r_{FCS}, pm	L_{FCS}, pm
Li	4	59	196	333	470	2951
	6	76	213	350	487	3058
Na	5	100	237	374	511	3209
	6	102	239	376	513	3222
	7	112	249	386	523	3284
	8	118	255	392	529	3322
	9	124	261	398	535	3360
K	6	138	275	412	549	3448
	7	146	283	420	557	3498
	8	151	288	425	562	3529
	9	155	292	429	566	3554
	10	159	296	433	570	3580
	12	164	301	438	575	3611
Cs	8	174	311	448	585	3674
	9	178	315	452	589	3699
	10	181	318	455	592	3718
	11	185	322	459	596	3743
	12	188	325	462	599	3762
Rb	8	161	298	435	572	3592
	9	163	300	437	574	3605
	10	166	303	440	577	3624
	11	169	306	443	580	3642
	12	172	309	446	583	3661
	14	183	320	457	594	3730
O		137				

Calculated values of E_s for guest-host pairs of alkali cation in silicate glasses is summarized in Table II, and the shear modulus was taken to be $G = 3.05 \times 10^{10} \text{ N/m}^2$.⁹

The elastic energy created during the exchange of cations in the silicate matrix can then result in the breaking of bond, and also micro and/or nano-cracks are created. When smaller ions occupy a larger ions site, the rearrangement of the surrounding environment causes these cracks, which then begin to cascade, breaking multiple bonds until the tensile stress induced from the exchange is relieved.⁹ Although the picture for this defect model is not complete, it is presumed that defects are created in both small for large and large for small cation exchanges.⁹

Table II. Strain Energy, E_s , Strain Intensity Index, N_d , Difference in Cation Coordination Number (ΔCN), and Difference in Length of the Circumference of the First Coordination Shell (ΔL_{FCS}) for Various Alkali Cation Pairs in Mixed Alkali Silicate Glasses

Ionic pairs	E_s, eV	N_d	ΔCN	$\Delta L_{FCS}, pm$
Li-Na	2.7 - 4.5	1 - 3	1 - 2	271
Li-K	13.5 - 15.9	3 - 8	4 - 6	578
Li-Cs	23.7 - 26.5	6 - 14	6 - 8	767
Li-Rb	18.2 - 24.5	5 - 12	6 - 8	673
Na-K	4.3 - 5.9	1 - 3	2 - 4	307
Na-Cs	11.2 - 13.3	3 - 7	4 - 6	496
Na-Rb	7.4 - 11.8	2 - 6	4 - 6	402
K-Cs	1.8 - 2.8	1 - 2	2 - 4	189
K-Rb	0.5 - 2.1	0 - 1	2 - 4	95
Cs-Rb	0.5	0 - 1	0 - 2	-

It is well established that defects allow atomic transport to occur, and that these defects accelerate the rate of atomic transport. According to Bendler and Shlesinger's defect diffusion model, the rate of diffusion increases with the increase in number density of single defects and decreases when defects are brought closer together and form clusters.⁹ Belostotsky claimed that, in mixed alkali glasses, the structural defects generated nearest to the vicinity of guest occupied sites, configures the ions in such a way that these mobile ions interact directly with more than one ion of the opposite sign, in mixed alkali glasses these are the non-bridging oxyanions that surround the alkali ions. The "non-equilibrium" ionic sites surrounded by a cluster of anions are assumed to be high energy anion traps.⁹ Belostotsky also concludes that on long time scales in a mixed alkali glass that if the concentration of one alkali cation is much greater than the other alkali cation, that the minority species convert into high energy anion traps.⁹ For example, if a mixed alkali glass has a majority species Na^+ , and a minority species K^+ , that the K^+ ions will eventually all turn into high energy anion traps.

Physical properties of the glass including T_g , and viscosity deviate from linearity when considering the mixed alkali effect. The glass transition temperature is of particular importance when considering the effects of the ion exchange process. In general, the transition of a solid to a viscous fluid can be described as the depolymerization of the dynamic network-forming matrix. As the temperature increases the mean size of statistically polymerized regions grows smaller.

Thus, the rearrangement of ions into foreign ionic sites aids in the breaking up of bonds, and the formation of defects, which increases the fragmentation of the glass network, therefore, lowering the viscosity and decreasing T_g .⁹ The addition of even small amounts of another alkali ion in a glass can loosen the structure and affect the glass transition temperature. Since, this phenomena can be attributed to the defects caused from the rearrangement of ionic sites, the greater the size difference of alkali ions rearranging, the greater deviation from linearity in the T_g .⁹

F. Patent Background Information

Stookey and Hood investigated the effects of a lithium molten salt bath on various glass compositions.¹¹ They found in particular that glasses that have a composition of 55-66% SiO_2 , 10-20% Al_2O_3 , 10-13% Na_2O and/or K_2O , 8-12% TiO_2 , 2-5% Li_2O , and about 2% B_2O_3 have an affinity to create strong articles of glass when exchanged with a lithium enhanced molten salt bath at temperatures above the strain point but below the softening point of the glass. The exchange causes the lithium to exchange with the sodium and/or potassium ions in the surface which in turn creates a lower thermal expansion surface layer that results in glass articles with higher tensile strength. Although a compressive surface layer can be achieved from a lithium enhanced glass surface layer, Stookey and Hood also found that with a sufficient ration of Al_2O_3 and another nucleation agent such as Ti_2O , that the exchange resulted in a crystallized surface layer of beta-spodumene. Beta-spodumene itself has a negative thermal expansion coefficient, and therefore the precipitation of beta-spodumene at the surface results in a drastic difference between the thermal expansion coefficients in the bulk of the glass and the surface, thus causing high tensile strengths.¹¹

The problem with this technique is that the glasses used to strengthen are not common in commercial glasses and also there are very few salt bath mixtures that do not decompose at the temperatures required for this exchange. Also, when the formation of beta-spodumene occurs the surface of the glass-ceramic becomes opaque. Stookey and Hood reported abraded strength increases of up to 330% for samples that did not precipitate beta-spodumene and remained transparent and abraded strength increases of up to 1000% for samples that did precipitate beta-spodumene and became opaque.¹¹

Marusak¹², investigated a double ion-exchange procedure in which he exchanged a lithium silicate glass with a sodium rich bath at temperatures below the strain point, followed by an

exchange with a potassium rich bath at temperatures below the strain point. During these exchanges the lithium from within the glass surface is being replaced with the larger alkali ions in the bath. Marusak found that during this process the lithium leaving the glass and entering the salt bath is acting as a contaminate and that it is important to maintain levels of less than 0.2% lithium content in the bath, especially in the final exchange.¹² One such treatment that Marusak investigated was first submerging the glass samples in a bath of 85% NaNO_3 and 15% Na_2SO_4 for 2 hours at 450 °C, followed by a second treatment in a bath of equal amount NaNO_3 and KNO_3 for 2 hours. He then added small amounts of LiNO_3 into the second bath to investigate the effects of lithium in the second bath. The samples were then subject to a ball drop test, where the heights at which the ball was dropped and the samples broke was recorded. Table III shows the effects that the small amount of lithium added to the bath had on the strengths of the glass samples, which clearly shows that even small amounts of lithium ions in the salt bath has drastic effects on the strengthening of glass articles.¹²

Table III. Average Height at Which Samples Broke After Second Treatment with Various Amounts of LiNO_3 Added.

LiNO_3 (percent)	Avg. Height (inches)
0.0	142
0.5	123
1.0	110
2.0	84

The composition of the salt bath is of particular concern. Many problems can arise when choosing a suitable molten bath in which ion exchange can occur. According to Werner and Erich¹³, chlorides, sulfates, pyrosulfates, nitrates, carbonates, phosphates, nitrites, and oxides are suitable salts to consider for the ion exchange process. They also state that sulfates and chlorides are of particular interest because of their low cost and availability. Werner and Erich¹³, go on to state that it is important to choose a salt that will not decompose at the temperature that the exchange occurs, because often time the decomposition products attack the surface of the glass, and also the gaseous products can be corrosive and result in air pollution. Also, the

decomposition of the salt baths can cause irregularities in the ion exchange process, and removal of these contaminants can prove difficult.¹³

When considering a lithium rich salt bath suitable for a high temperature exchange, many issues arise. Very few salts provide the conditions necessary for a successful exchange of lithium ions in the bath, for sodium ions in the glass surface. Stookey and Hood¹¹, found that as little as 1% lithium ion concentration in a salt bath can successfully exchange glass articles. However there are very few salts that melt at low enough temperatures for an exchange above the strain point to occur. One of the few salts that melt at a sufficiently low temperature is lithium nitrate. But, lithium nitrate begins to decompose at temperatures far below the temperature needed for the glass to relax properly. The use of eutectics is needed to find a suitable salt for a high temperature exchange. Mixing different alkali chlorides also can result in a suitable molten salt bath, but the chlorides are highly corrosive when using stainless steel as the container for holding the molten salt mixture and thus special containers are needed to hold these molten salts. Sillick used a eutectic mixture of 80 mole % Li_2SO_4 20 mole % K_2SO_4 , which provides the necessary conditions for a high temperature exchange to occur.¹⁴

Salts that melt at temperatures low enough for the low temperature exchange i.e. the “stuffing” exchange are limited. Nitrates or nitrates mixtures are the predominate choice when conducting these exchanges. However, even at these lower temperatures the salt bath mixtures still have a tendency to attack the surface of the glass. Lewek¹⁵, looked into salt bath additives that help diminish the effects of surface attacking. He found that the addition of diatomaceous earth helped eliminate surface etching or attacking. Lewek showed that when 2% diatomaceous earth was added to a nitrate bath at 550 °C, and samples were submerged periodically for 8 days that the samples once clean exhibited little to no visible chemical etching or attacking.

EXPERIMENTAL PROCEDURE

A. Ion Exchange

Glass Rod Preparation

The glass tested in these experiments was Schott AR-Glas®, the composition of this glass is shown in Table IV.

Table IV. Composition of Schott AR-Glas®

	Weight % ¹⁶	Mole %
SiO₂	69	70.88
B₂O₃	1	0.89
Al₂O₃	4	2.42
Na₂O	13	12.95
K₂O	3	1.97
BaO	2	0.81
CaO	5	5.5
MgO	3	4.59

The Schott AR-Glas® glass rods, 4 mm in diameter, were cut to lengths varying from 4.8 cm to 5.5 cm. 18-20 glass rods were cut to appropriate length for each ion exchange treatment. Of these samples, 5 glass rods were chosen to be carefully measured and weighed in order to determine the mass change and surface area. The glass rod lengths and diameters were measured and recorded using digital calipers, which measure to a hundredth of a millimeter. Sample mass, was measured before and after exchange on an AT-260 scale, which measure accurately up to a tenth of a milligram.

Exchange Mediums

Multiple molten salt baths of various compositions were chosen to conduct these experiments. The compositions include various combinations of lithium sulfate, sodium sulfate, potassium sulfate, sodium nitrate, potassium nitrate, diatomaceous earth (D.E.), and soda-lime-silicate glass microspheres (SLS microspheres). Investigations into a 1-step exchange, and a 2-step exchange were made. The 1-step exchange was a “high” temperature exchange in which Li⁺ ions exchanged with larger alkali ions at a temperature of 580 °C. Various compositions and

temperatures were used originally, including a lithium nitrate and sodium nitrate mixed salt bath. After various trials it was determined that the mixed nitrate salt bath used was decomposing at the high temperatures used in these experiments. This decomposition ruined the integrity of the bath used for this exchange, stained the glass surface, and chemically attacked the surface of the glass. After these observations the use of another 1-step exchange medium was needed that would eliminate these problems. After, much consideration and testing the exchange medium chosen for the 1-step in these experiments had a composition of 80 mole % Li_2SO_4 , 15 mole % K_2SO_4 , and 5 mole % Na_2SO_4 (Treatment A).

Several 2-step ion exchange treatments were investigated. The 2-step process used the “high” temperature Li^+ ion exchange as the first step. This allowed for a Li^+ rich surface layer in the glass rod samples. The second step was a “low” temperature exchange that allowed the larger Na^+ and/or K^+ ions to “stuff” the Li^+ rich surface layer. In order for the “stuffing” of larger ions for smaller ones to occur a temperature below the glass transition temperature must be used. Thus, considering the properties of the Schott AR-Glas®, a temperature of 450 °C was chosen for the second step. The 2-step exchange process used the 80 mole % Li_2SO_4 , 15 mole % K_2SO_4 , 5 mole % Na_2SO_4 salt bath composition as the first step, followed by exchange with one of three different second step salt bath compositions. These compositions include (Treatment B) 95% NaNO_3 , 3% D.E., 2% SLS microspheres (weight %), (Treatment C) 93% KNO_3 , 2% NaNO_3 , 3% D.E., 2% SLS microspheres (weight %), and (Treatment D) 47.5% KNO_3 , 47.5% NaNO_3 , 3% D.E., 2% SLS microspheres (weight %). The use of D.E. was used in order to negate the effects of chemical attacking of the glass rods¹¹. Also, SLS microspheres acted as “getters” for the the Li^+ ions that are diffusing out of the surface layer of the glass rods into the salt bath. Table V summarizes the salt compositions and the temperatures at which they are used.

Table V. Compositions of Exchange Mediums

1 st -Step Exchange Medium		
Treatment Name	Composition (mole %)	Temperature (°C)
Treatment A	80% Li ₂ SO ₄ 15% K ₂ SO ₄ 5% Na ₂ SO ₄	580
2 nd -Step Exchange Mediums		
Treatment Name	Composition (weight %)	Temperature (°C)
Treatment B	95% NaNO ₃ 3% D.E. 2% SLS microspheres	450
Treatment C	93% KNO ₃ 2% NaNO ₃ 3% D.E. 2% SLS microspheres	450
Treatment D	47.5% KNO ₃ 47.5% NaNO ₃ 3% D.E. 2% SLS microspheres	450

Immersion

Schott AR-Glas® glass rods were exchanged with the baths discussed above to investigate the strength as well as the diffusion of alkali ions. Each rod was scored with a diamond wheel blade and broke to the appropriate length (approximately 5 cm). 2 custom exchange holders were made in order to suspend the rods in the baths as shown in Figure 4. One being made of stainless steel and allowing 18 samples to be exchanged at once and the other being made of primarily bronze and allowing 20 samples to be exchanged at once. Each exchange holder allowed glass rods to be suspended vertically in the exchange medium and only putting points of contact at the bottom of the rods and at one point on the sides of the rod. The containers that held the salt bath were made of stainless steel.

Before each exchange each holder was washed with hot water to remove any impurities and allowed to dry. The baths were prepared and put in furnace at appropriate temperature and a thermocouple was put into the bath to ensure the bath equilibrated to the proper temperature. Each bath was stirred prior to exchange, but not during an exchange. Samples were then put into the exchange holders and then placed into the furnace to preheat prior to insertion into the exchange bath in order to avoid thermal shock. High temperature exchange was preheated for 20 min at 580 °C, this allowed adequate time for the glass to get to temperature and relax before the Li⁺ exchange began. Low temperature exchanges were preheated for 5 min at 450 °C, which allowed samples to heat up enough that thermal shock was avoided, but kept the samples at low enough of a temperature that relaxation

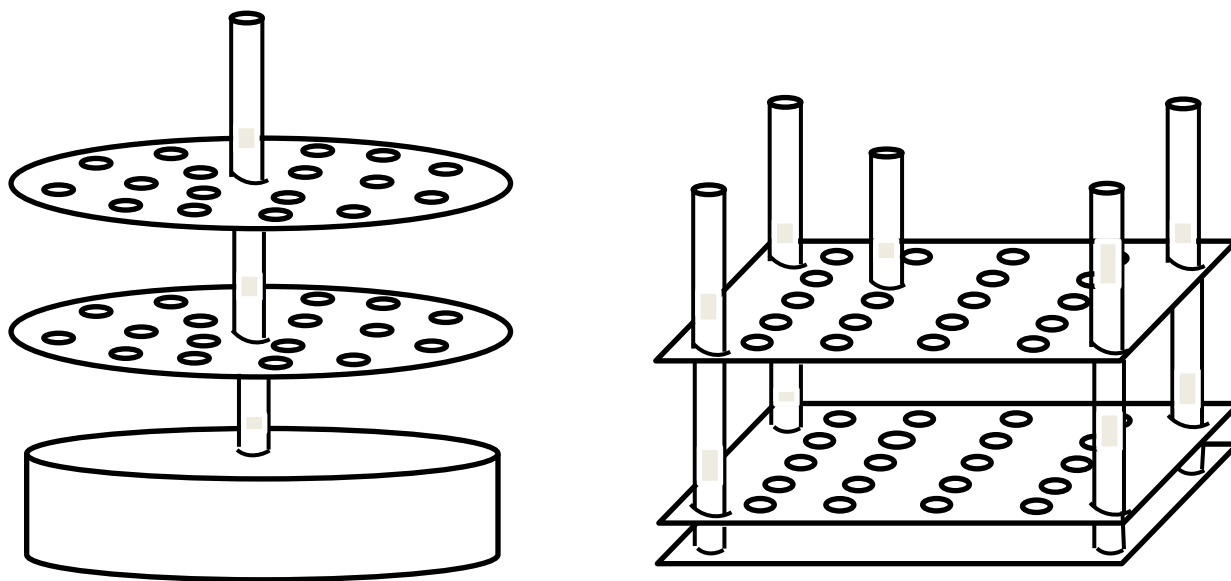


Figure 4. Schematic of exchange rod holders used. Left holder made out stainless steel base with steel rod. Right holder made out of bronze plates and steel rods.

of the glass could not occur. The samples were then placed into the salt bath for appropriate times. After each exchange, samples were removed from the salt bath and allowed to cool in air to room temperature. Samples were then carefully washed in water and allowed to dry on paper towels. Once, dry samples were labeled and placed in a plastic bag until further testing was necessary. Table VI shows the different treatments investigated in these experiments

Table VI. Temperatures and Times of the 1-step and 2-step Treatments

1 st Treatment	Temp. (°C)	Time	2 nd Treatment	Temp. (°C)	Time
Treatment A	580	5 min.	-	-	-
		10 min.	-	-	-
		15 min.	-	-	-
		20 min.	-	-	-
		30 min.	-	-	-
Treatment A	625	5 min.	-	-	-
		10 min.	-	-	-
		15 min.	-	-	-
		20 min.	-	-	-
		40 min.	-	-	-
Treatment A	650	5 min.	-	-	-
		10 min.	-	-	-
Treatment A	580	30 min.	100% NaNO ₃	450	30 min.
					1 Hr.
					2Hrs.
					24 Hrs.
Treatment A	580	30 min.	100% KNO ₃	450	1 Hr.
					2 Hrs.
					4 Hrs.
					24 Hrs.
Treatment A	580	30 min.	Treatment B	450	30 min.
					1 Hr.
					2 Hrs.
					4 Hrs.
					12 Hrs.
Treatment A	580	30 min.	Treatment C	450	24 Hrs.
					1 Hr.
					2 Hrs.
					4 Hrs.
					12 Hrs.
Treatment A	580	30 min.	Treatment D	450	24 Hrs.
					30 min.
					1 Hr.
					4 Hrs.
					8 Hrs.
					24 Hrs.

B. Determination of Exchange Depth and Diffusion Coefficients

WDS

The exchange depth of lithium, sodium, and potassium was determined using wavelength-dispersive spectroscopy (WDS). Various ion exchanged glass rod were first ground down to ensure that the exchanged layer at the end of the rod was removed. Then the samples were labeled, taped together and placed atop each other to allow multiple samples to be tested at once. Samples were then placed in an epoxy resin mixed with SLS microspheres and hardener

and allowed to harden as shown in Figure 5. After the epoxy mixture hardened the group of samples were then sanded and polished down to 1 micron.

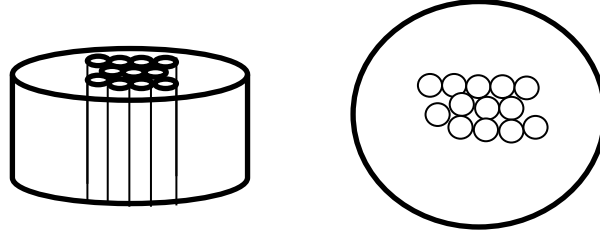


Figure 5. Left: side view of mounted WDS samples Right: Bottom view of mounted WDS samples

The cross-sections of the samples were coated with Au/Pd conductive coating before being placed into the vacuum chamber of the WDS. The vacuum chamber was then pumped down overnight before the samples were ready to be tested. The WDS was then set to test for Si, Na, K, O, and Ca. Although lithium was a desired element to be tested for the WDS is incapable of testing for elements lighter than boron. The WDS was then set to do 10 line scans of 250-350 microns in increments of .5 μm . The data was then placed into an excel spreadsheet and the average of the 10 line scans was taken and graphed.

The depth of exchange was determined by examination of the WDS line scans. The mean square displacement (MSD) was determined by comparing the Einstein relation to the Calculated Concentration equation.

$$\langle x^2 \rangle = 2Dt \quad (33)$$

Where $\langle x^2 \rangle$ is the mean square displacement, D is the diffusion coefficient, t is the time. Using eq. 21 and assuming the dimensionless constant Dt/a is sufficiently small eq. 21 becomes,

$$\frac{C - C_1}{C_o - C_1} = \sqrt{\frac{a}{r}} \cdot \text{erfc}\left(\frac{a - r}{2\sqrt{Dt}}\right) \quad (34)$$

Where C is the concentration of diffusing species, C_1 is the initial concentration of diffusing species in the cylinder, C_o is the initial concentration of the species being diffused within the cylinder, a is the radius of the glass rod, r is the radius, D is the diffusion coefficient, t is the time of diffusion, and $\text{erfc}(z)$ is given by eq. 25. If let $x=a-r$ where x is the distance into the glass rod, then eq. 34 becomes,

$$\frac{C - C_1}{C_o - C_1} = \sqrt{\frac{a}{a-x}} \cdot \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (35)$$

Since the diffusion distance is small in comparison to the radius of the glass rods $a/(a-x) \approx 1$. So if we substitute eq. 33 in for x in eq. 35 we find,

$$\frac{C - C_1}{C_o - C_1} = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) = \text{erfc}\left(\frac{\langle x^2 \rangle^{\frac{1}{2}}}{2\sqrt{Dt}}\right) = \text{erfc}\left(\frac{\sqrt{2Dt}}{2\sqrt{Dt}}\right) = \text{erfc}\left(\frac{1}{\sqrt{2}}\right) = .317 \quad (36)$$

Thus,

$$d = \sqrt{2Dt} \quad (37)$$

where, d is the distance of diffusion at the point where the concentration of the “in diffusing” species is about 32% of the surface concentration. Using eq. 36, eq. 37 and the concentration profiles found by the WDS data one can determine the different Diffusion coefficients $D_{a \rightarrow b}$ where a and b are the different ions being exchanged during each treatment.

Mass Change

5 glass rods from each batch of samples described in Table III were chosen in order to calculate the change in mass per unit surface area for each exchange. Each of the 5 samples was weighed to the nearest tenth of a milligram before each exchange. The diameter and length of each rod was also measured with digital calipers to the nearest hundredth of a millimeter before each exchange. After samples were exchanged, all impurities removed from the surface, and dried, each of the 5 samples were then weighed again to the nearest tenth of a milligram. These

values were recorded in an Excel spreadsheet, and used to calculate the change in mass per unit surface area (mg/cm²). The change in mass per unit surface area was then plotted against their corresponding times (t^{1/2}) for each group of treatments. According to Crank, when considering eq. 21 the corresponding equation for small times is,

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \left(\frac{Dt}{a^2} \right)^{\frac{1}{2}} - \frac{Dt}{a^2} + \frac{1}{3\sqrt{\pi}} \left(\frac{Dt}{a^2} \right)^{\frac{3}{2}} + \dots \quad (38)$$

Where M_t is the Mass change at time t , M_∞ is the Mass change at time $t=\infty$, (complete exchange) D is the diffusion Coefficient, t the time, and a the radius of the glass rod. When the dimensionless constant Dt/a^2 is sufficiently small, eq. 38 can be reduced to,

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \left(\frac{Dt}{a^2} \right)^{\frac{1}{2}} \quad (39)$$

Using eq. 39 and the slope of mass change per unit surface area (mg/cm²) as a function of sqrt(t), the diffusion coefficients for various exchanges could be calculated.

Substituting T_1 and T_2 and their respective diffusion coefficients into eq. 23 and dividing the two equations we can solve for ΔE_a , which yields:

$$\Delta E_a = R \cdot \ln \left(\frac{D_{T_1}}{D_{T_2}} \right) \cdot \left(\frac{T_1 \cdot T_2}{T_1 - T_2} \right) \quad (40)$$

where, D_{T_1} is the diffusion coefficient at temperature T_1 and D_{T_2} is the diffusion coefficient at temperature T_2 .

C. Flexural Strength

The flexural strength of all glass rod samples was determined using a 4-point bending apparatus. The 4-point bend apparatus allowed 50 mm glass rods to be tested with an automated Instron. The apparatus was taken apart and cleaned before each new sample was loaded in order to avoid any residual glass particles from affecting the testing of the next glass sample. The Instron arm moved at a rate of 1.0 mm/min and data was collected at 10 points/sec. The distance

between the two inner support rods and the two outer support rods was 20 mm and 40 mm respectively. The applied force at the time of fracture was recorded for each sample and the fracture strength was calculated using:

$$\sigma = \frac{8F(O_s - I_s)}{\pi D^3} \quad (41)$$

Where σ is the fracture strength, F is the load at the time of fracture, O_s is the span of the outer support rods, I_s is the span of the inner support rods, and D is the diameter of the glass rod. The diameter of the samples were measured at each end of the glass rod and averaged together to get the diameter of the center of the rod before each sample was broken.

RESULTS

A. Depth of Exchange

Many alkali rich salt mixtures were investigated to determine the depth of exchange of multiple alkali ions. The initial high temperature Li^+ ion exchange used Treatment A, salt bath mixture to exchange the Na^+ ion in the glass with Li^+ ions from the bath. Figure 6 shows the WDS intensities of sodium and potassium ions for an untreated Schott AR-Glas® rod. Figure 6 shows that there is some discrepancy when assigning a point to the surface, i.e. $d=0$, where d is the depth into the rod. Since an exact value for the surface is not clear, an error exists within our WDS data. It is assumed that the surface is at the midpoint of our intensity curve (i.e. the value between $I=0$ and $I=C$ where C is the average intensity of alkali ions in the glass surface). We know that the actual surface must be somewhere between these two points. When examining Figure 6 in this fashion it suggests that the actual surface is $\pm 2\mu\text{m}$ from the chosen point. This error is considered when calculating the diffusion coefficients from the WDS data.

Figure 7 shows the exchange profile and the intensity of sodium concentration as a function of depth for multiple exchange times for Treatment A at 580 °C. Figure 8 shows the exchange profile and intensity of potassium concentration as a function of depth for multiple exchange times for Treatment A at 580 °C. Here the glass samples were preheated to 580 °C for 20 min prior to being submerged in the bath for short periods of time.

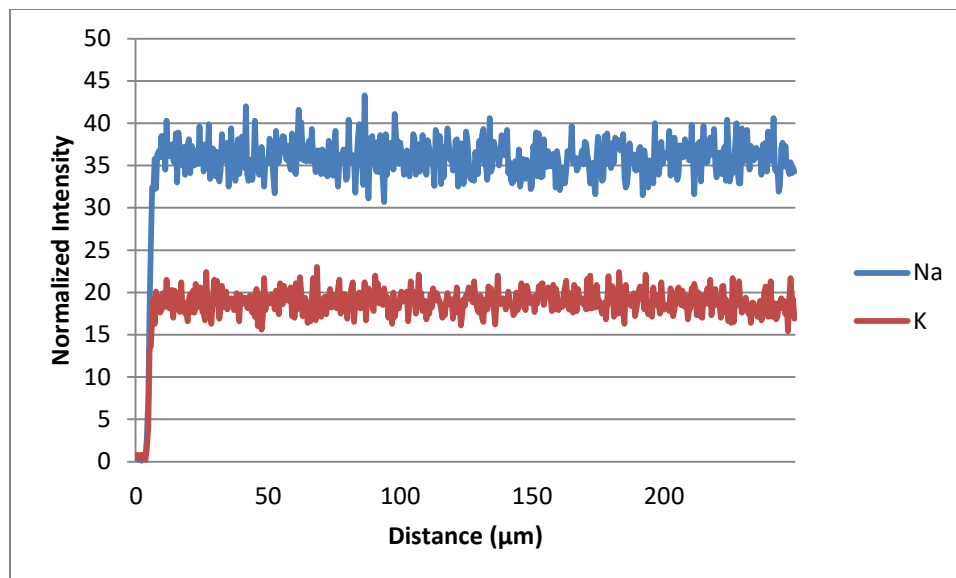


Figure 6. Normalized Na^+ and K^+ intensities as a function of depth for untreated Schott AR-Glas® rods.

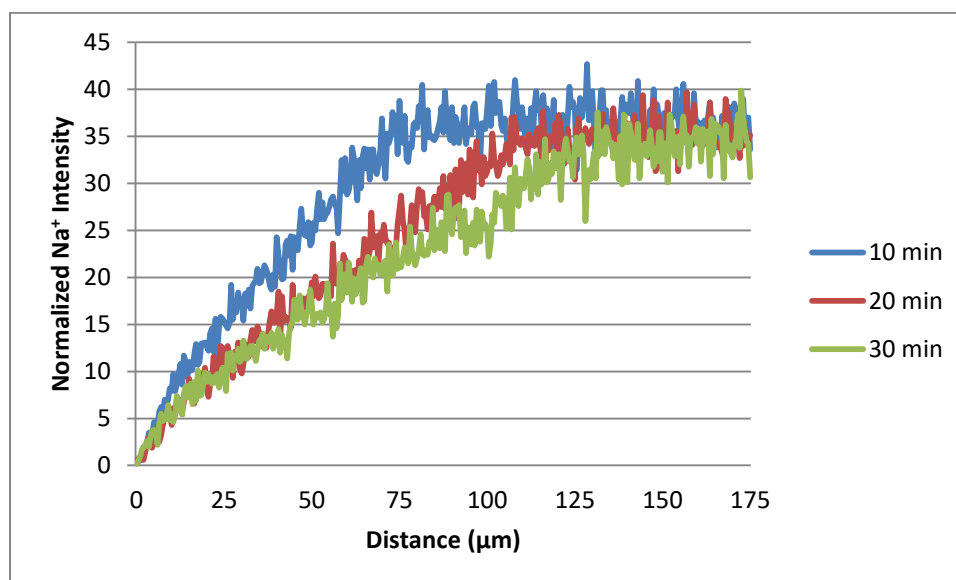


Figure 7. Normalized Na^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged for 10 min, 20 min, and 30 min with Treatment A at 580 °C.

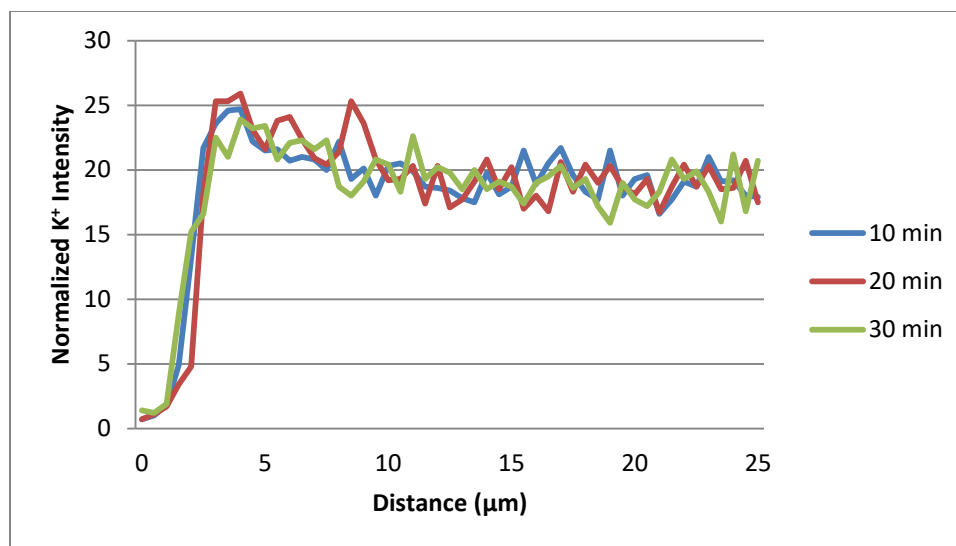


Figure 8. Normalized K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged for 10 min, 20 min, and 30 min with Treatment A at 580 °C.

Although, the WDS data does not show the lithium ion concentration profile, we can use the concentration profiles of sodium and potassium ions to infer what a lithium concentration would look like. Where the profile of the sodium ions resembles an error function, the lithium profile would resemble a compliment error function. Using eq. 36 and eq. 37 we can use these profiles to extrapolate the mean square displacement (MSD) of the Li^+ ions, and also the diffusion coefficient for lithium ions exchanging for sodium ions in the surface of the glass rods. Table VII shows the MSD exchange depth of Li^+ ions exchanging with Na^+ ions as well as the calculated diffusion coefficient.

Table VII. Calculated MSD Exchange Depth and Diffusion Coefficient for Glass Rods Treated with Treatment A at 580 °C for Times Between 10 minutes and 30 minutes.

Depth and Diffusion for Treatment A at 580 °C		
Time (min.)	$d_{Li^+ \rightarrow Na^+}$ (μm)	$D_{Li^+ \rightarrow Na^+}$ (cm ² /s)
10	43.5-47.5	1.57×10^{-8} - 1.88×10^{-8}
20	63-67	1.65×10^{-8} - 1.87×10^{-8}
30	78-82	1.69×10^{-8} - 1.87×10^{-8}

The second low temperature exchange was investigated for various salt bath compositions for times between 30 minutes and 24 hours. These salt baths include Treatment B, Treatment C, and Treatment D. Each of the second exchanges was conducted after a 30 min exchange in Treatment A at 580 °C. Figures 9-14 show the WDS intensities of Na⁺ and K⁺ for Treatment B at 450 °C as a function of depth.

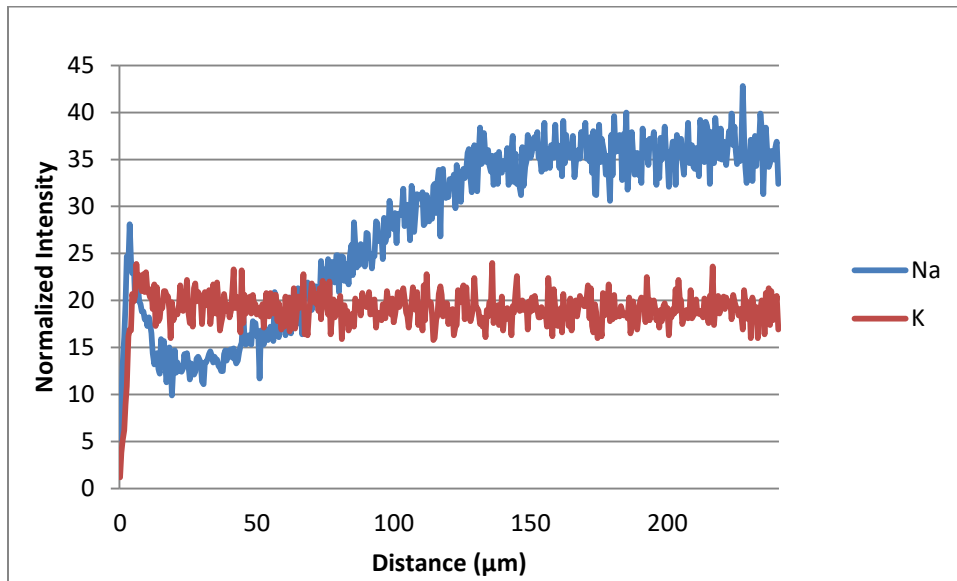


Figure 9. Normalized Na⁺ and K⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 30 minutes at 450 °C.

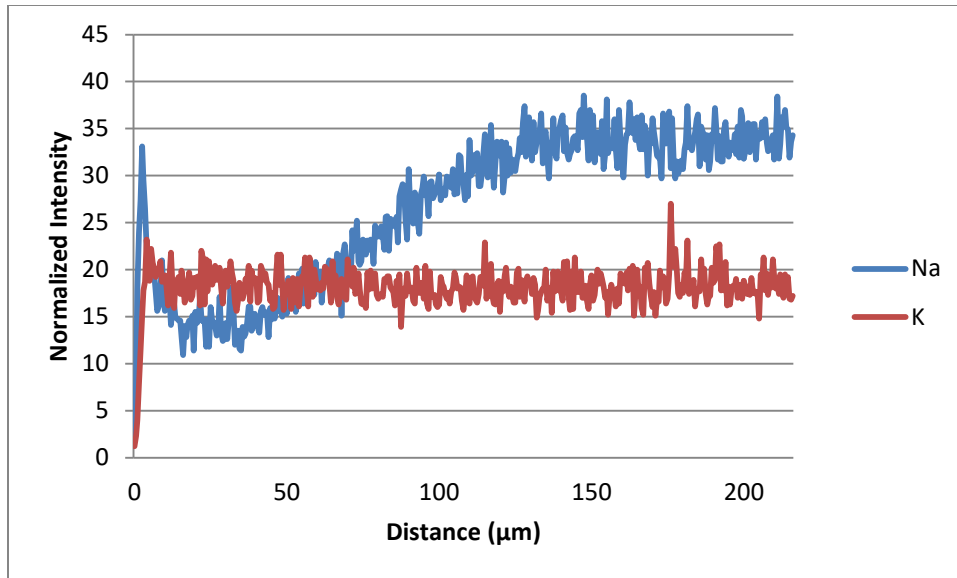


Figure 10. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 1 Hour at 450 °C.

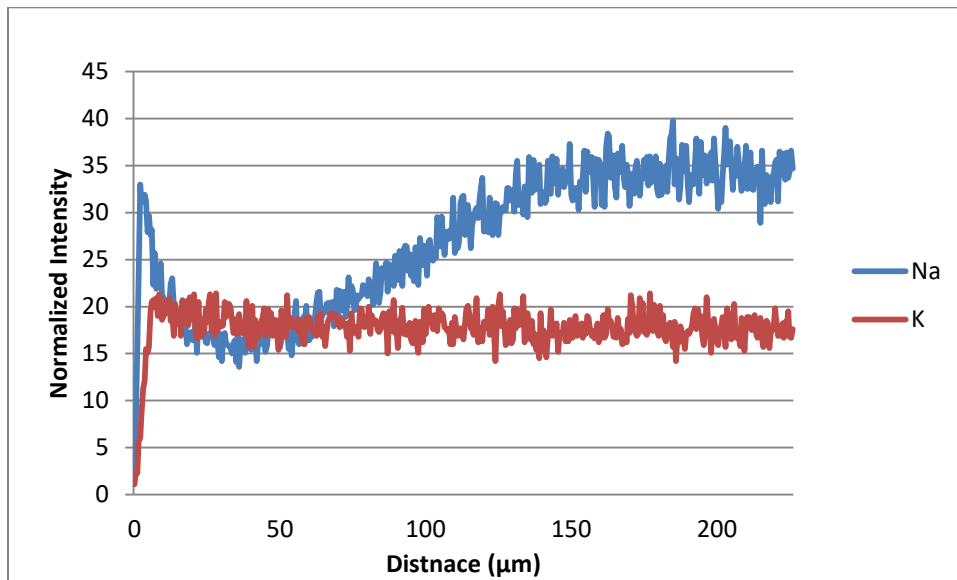


Figure 11. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 2 Hours at 450 °C.

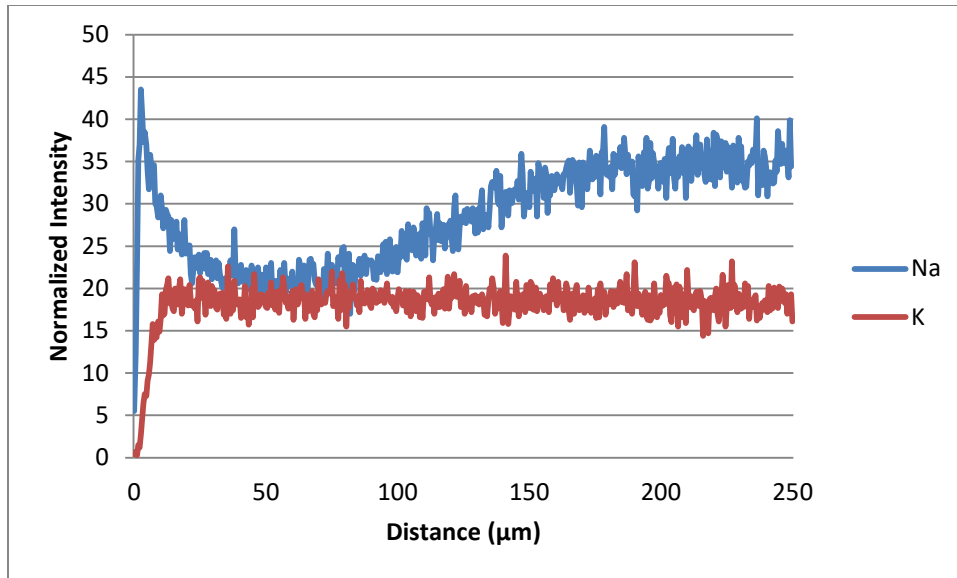


Figure 12. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 4 Hours at 450 °C.

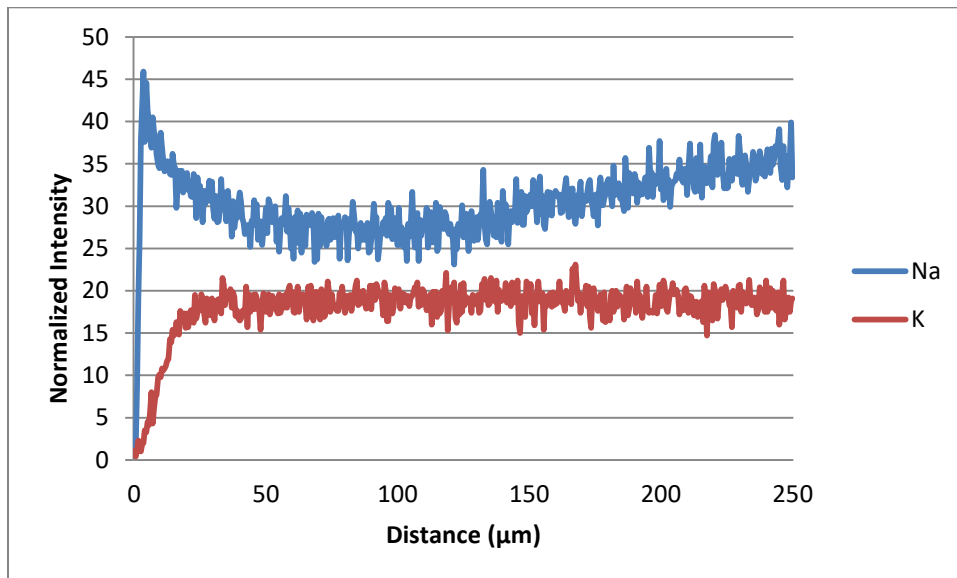


Figure 13. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 12 Hours at 450 °C.

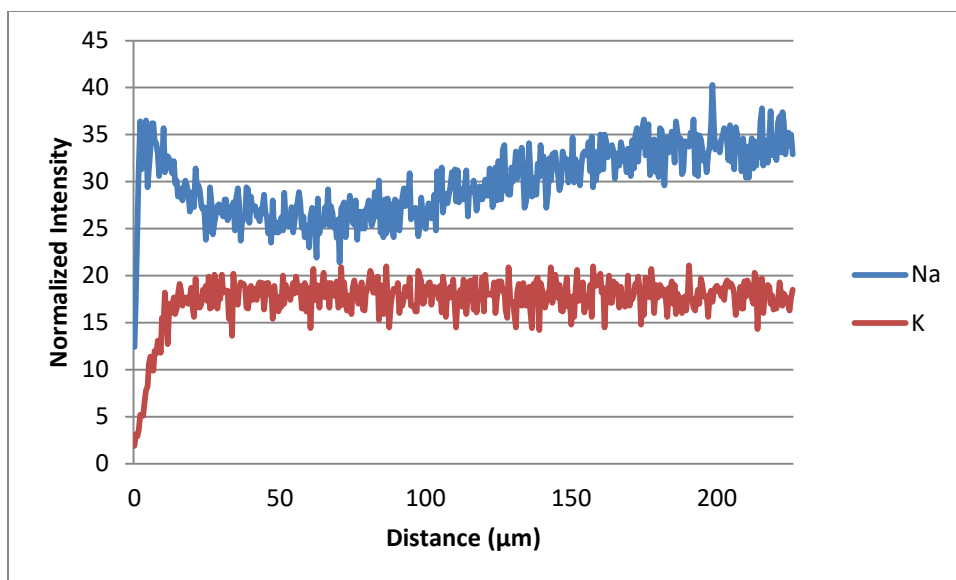


Figure 14. Normalized Na⁺ and K⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment B for 24 Hours at 450 °C.

Figures 15-19 show the intensity of sodium and potassium ions as a function of depth into the glass rods after Treatment A for 30 min at 580 °C followed by Treatment C at 450 °C for times between 1 hour and 24 hours.

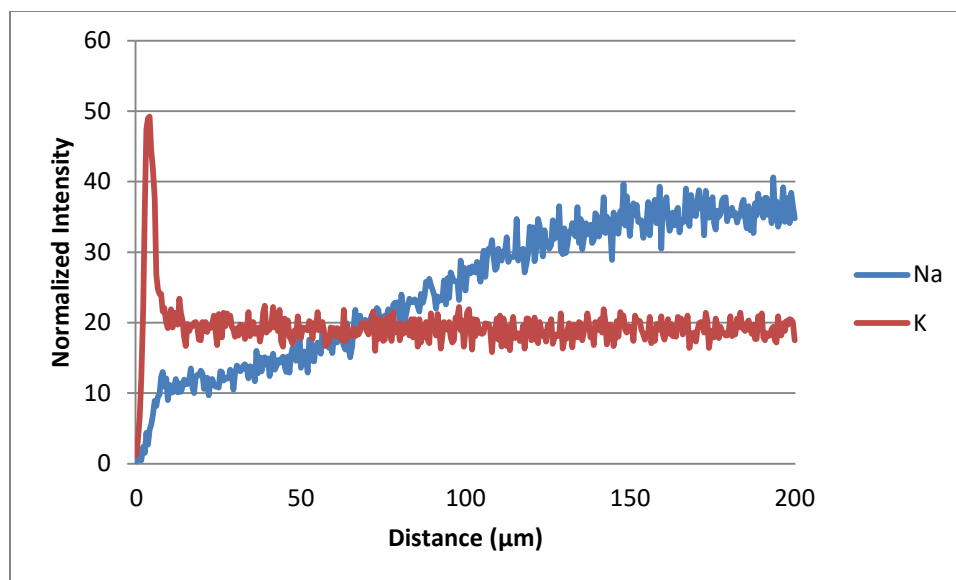


Figure 15. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 1 Hour at 450 °C.

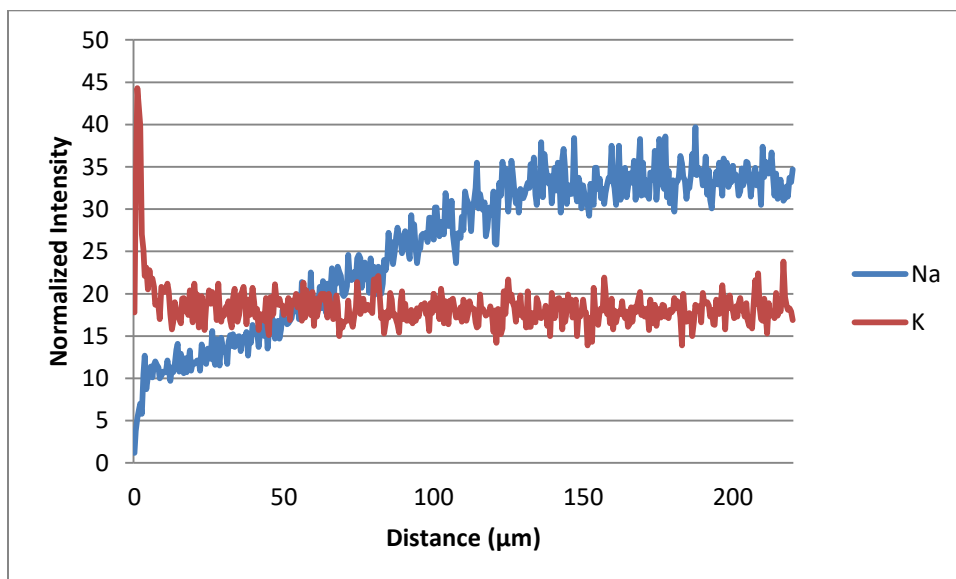


Figure 16. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 2 Hours at 450 °C.

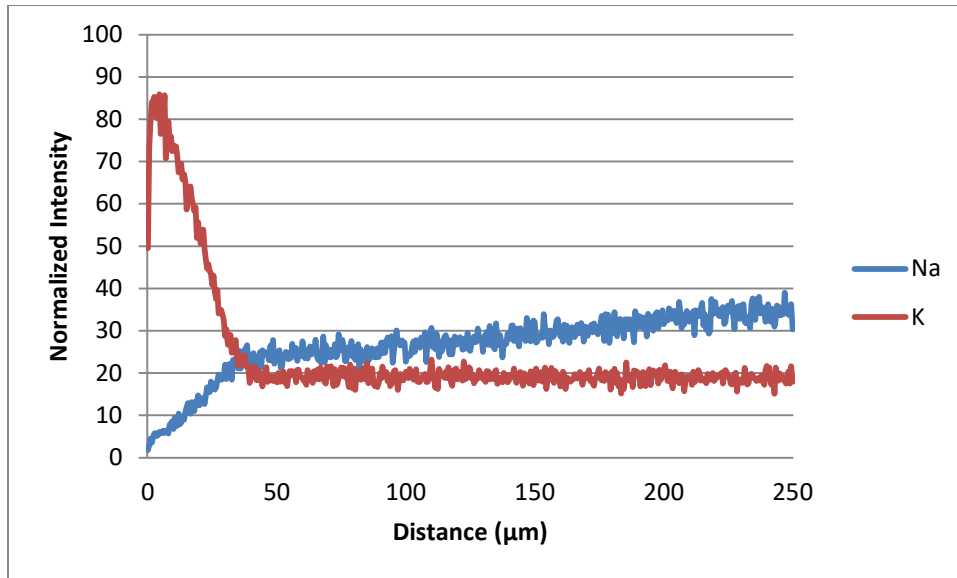


Figure 17. Normalized Na⁺ and K⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 4 Hours at 450 °C.

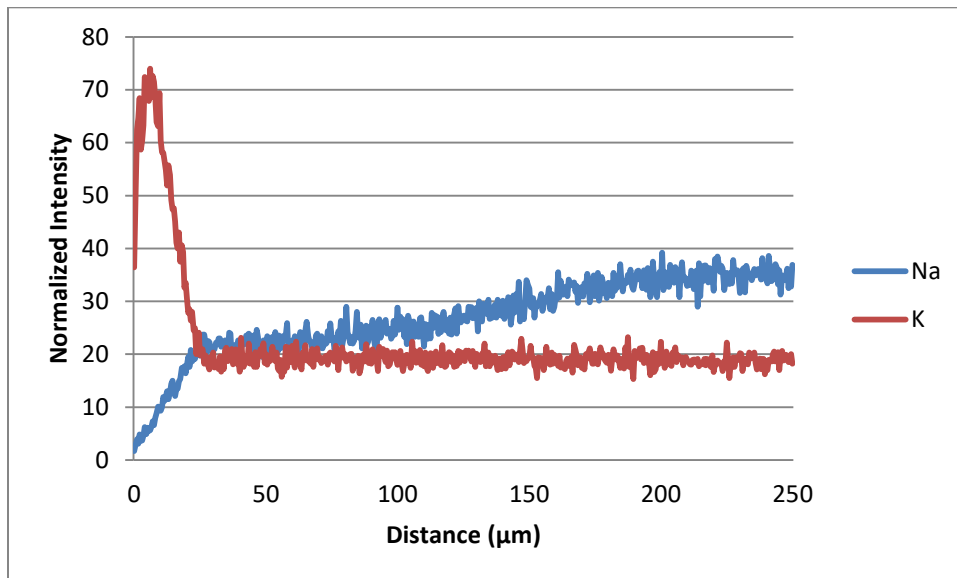


Figure 18. Normalized Na⁺ and K⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 12 Hours at 450 °C.

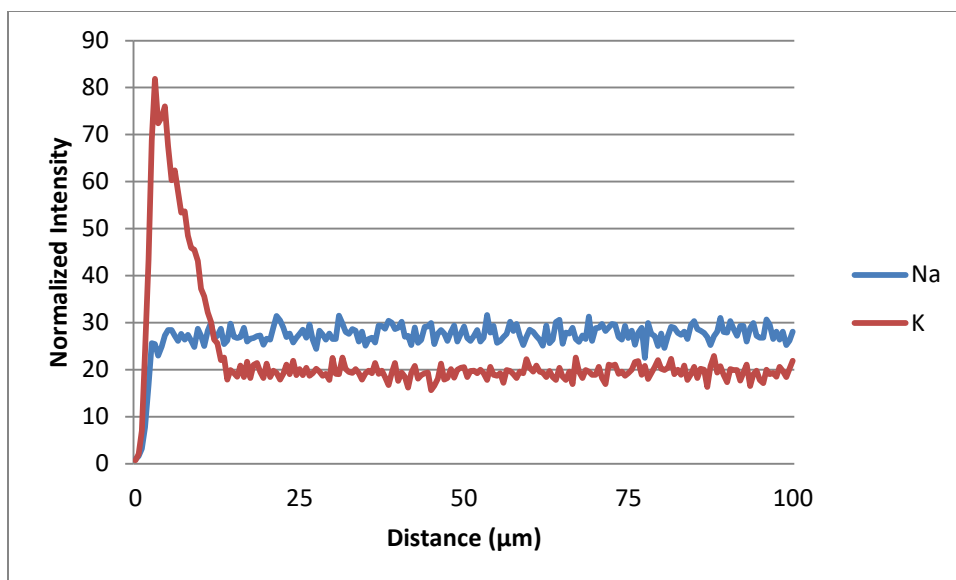


Figure 19. Normalized Na⁺ and K⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 24 Hours at 450 °C.

Looking at the concentration profile of potassium ions as a function of depth for different times also may prove useful in investigating the effect of Treatment C on the previously lithium exchanged glass rods. Figure 20, shows the intensity of potassium ions as a function of depth into the glass rods, and compares them for different treatment times.

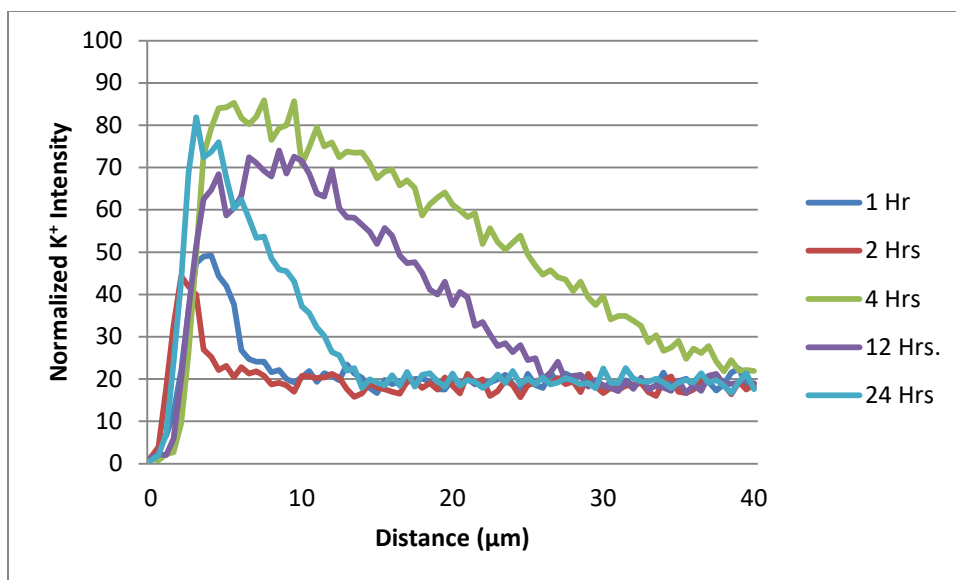


Figure 20. Normalized K⁺ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment C for 24 Hours at 450 °C for times between 1 hour and 24 hours.

Figures 21-25, show the intensity of sodium and potassium ions as a function of depth into the glass rods after Treatment A for 30 min at 580 °C followed by Treatment D at 450 °C for times between 30 minutes and 24 hours

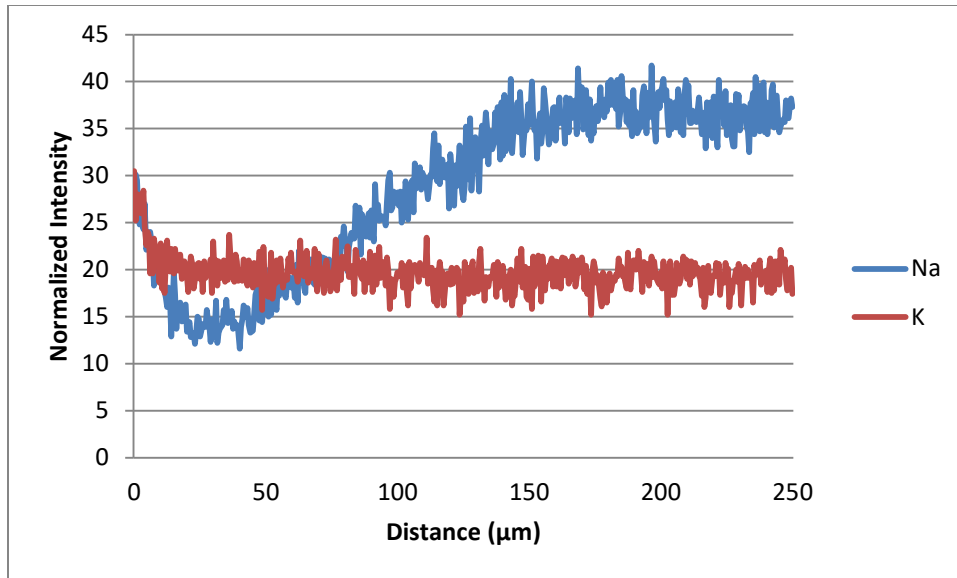


Figure 21. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D for 30 minutes at 450 °C.

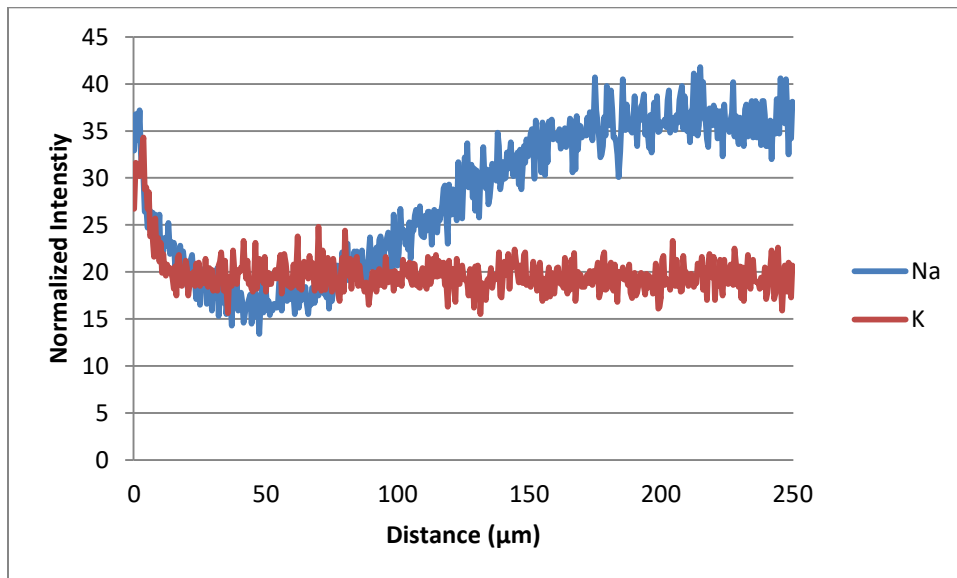


Figure 22. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D for 1 Hour at 450 °C.

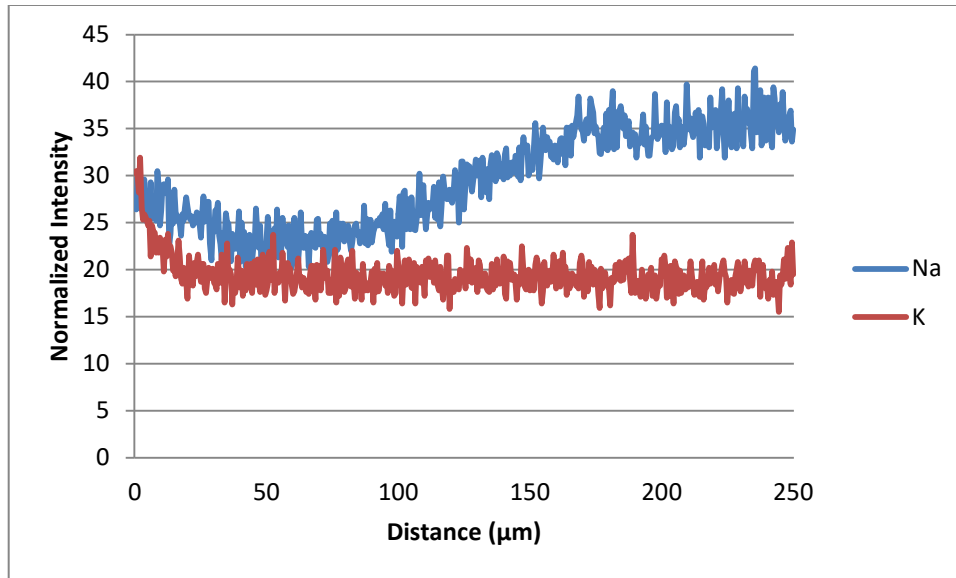


Figure 23. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D for 4 Hours at 450 °C.

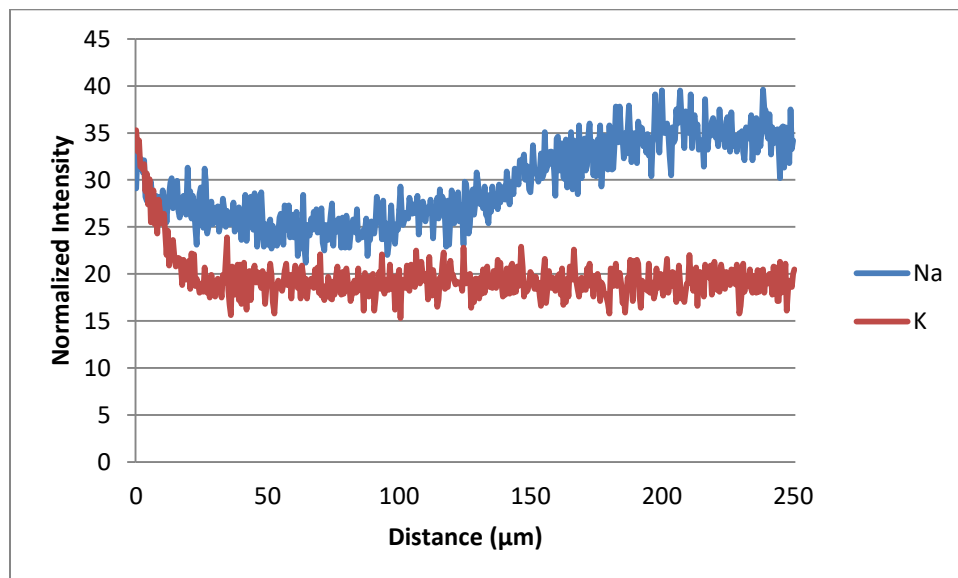


Figure 24. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D for 8 Hours at 450 °C.

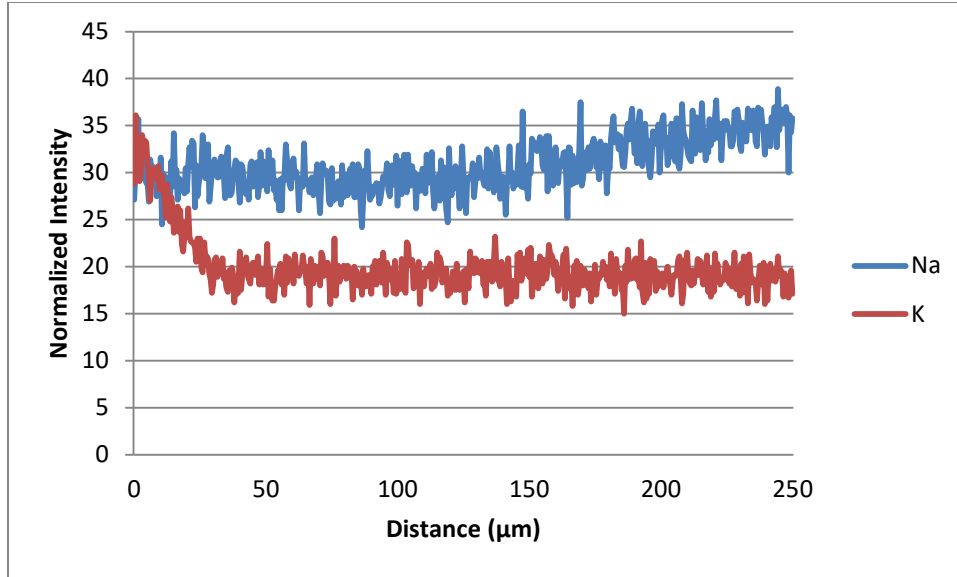


Figure 25. Normalized Na^+ and K^+ Intensity as a function of depth for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D for 24 Hours at 450 °C.

Assuming that the surface layer was completely exchanged with lithium ions in the first exchange (Treatment A for 30 minutes at 450 °C), and that during the second exchange that the potassium and sodium ions in the bath (Treatment D) are exchanging with the lithium ions in the glass surface, we can calculate the diffusion coefficients for the exchange of these ion pairs. Using Figures 21-25, eq. 36, and eq. 37 diffusion coefficients were calculated and recorded in Table VIII.

Table VIII. Calculated MSD Exchange Depth and Diffusion Coefficient for Glass Rods Treated with Treatment A for 30 min at 580 °C Followed by Treatment D at 450 °C for Times Between 30 minutes and 24 hours.

Depth and Diffusion of Treatment D at 450 °C after Treatment A for 30 min at 580 °C				
Time (Hrs.)	$d_{\text{Na} \rightarrow \text{Li}}$ (μm)	$D_{\text{Na} \rightarrow \text{Li}}$ (cm^2/s)	$D_{\text{K} \rightarrow \text{Li}}$ (μm)	$D_{\text{K} \rightarrow \text{Li}}$ (cm^2/s)
0.5	7.5-11.5	1.56×10^{-10} - 3.67×10^{-10}	2.5-6.5	1.74×10^{-11} - 1.17×10^{-10}
1	11-15	1.68×10^{-10} - 3.13×10^{-10}	3.5-7.5	1.70×10^{-11} - 7.81×10^{-11}
4	22.5-26.5	1.76×10^{-10} - 2.44×10^{-10}	7.5-11.5	1.95×10^{-11} - 4.59×10^{-11}

8	31.5-35.5	1.72×10^{-10} - 2.19×10^{-10}	10-14	1.74×10^{-11} - 3.40×10^{-11}
24	-	-	15.5-19.5	1.39×10^{-11} - 2.20×10^{-11}

Figure 26 and Figure 27 show the trend of the diffusion coefficients $D_{\text{Na} \rightarrow \text{Li}}$, and $D_{\text{K} \rightarrow \text{Li}}$ as a function of the square root of time respectively.

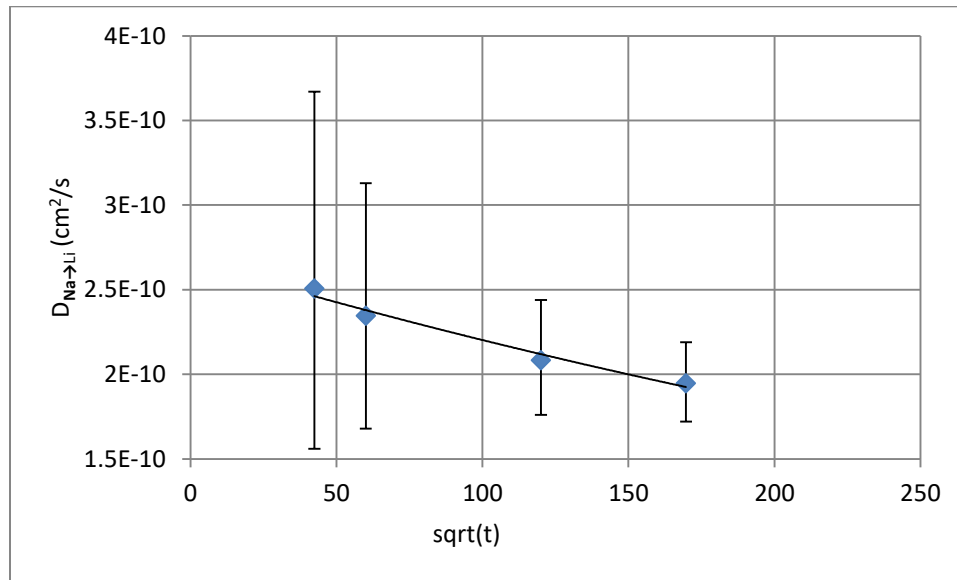


Figure 26. Calculated diffusion coefficient ($D_{\text{Na} \rightarrow \text{Li}}$) as a function of the square root of time for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D at 450 °C.

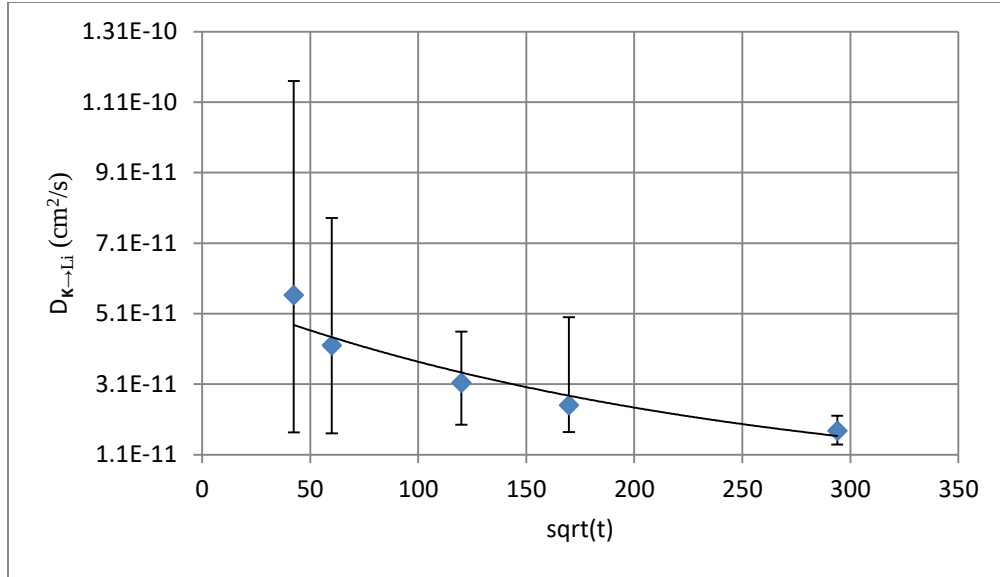


Figure 27. Calculated diffusion coefficient ($D_{K \rightarrow Li}$) as a function of the square root of time for Schott AR-Glas® rods exchanged with Treatment A for 30 minutes at 580 °C followed by exchange with Treatment D at 450 °C.

B. Mass Change

It is assumed that no exchange of ions between the salt bath and the glass rods has occurred prior to each exchange. Thus, it was assumed that at $\text{sqrt}(t)=0$, $\Delta M(t)=0$, when calculating the slope of each treatment. Figure 28 and Figure 29, shows the change in mass per unit surface area $\Delta M(t)$ as a function of the square root of time for Treatment A at 580 °C and 625 °C respectively. The exchange of lithium ions in the bath for sodium ions in the glass should yield a negative mass change per unit surface area as was observed.

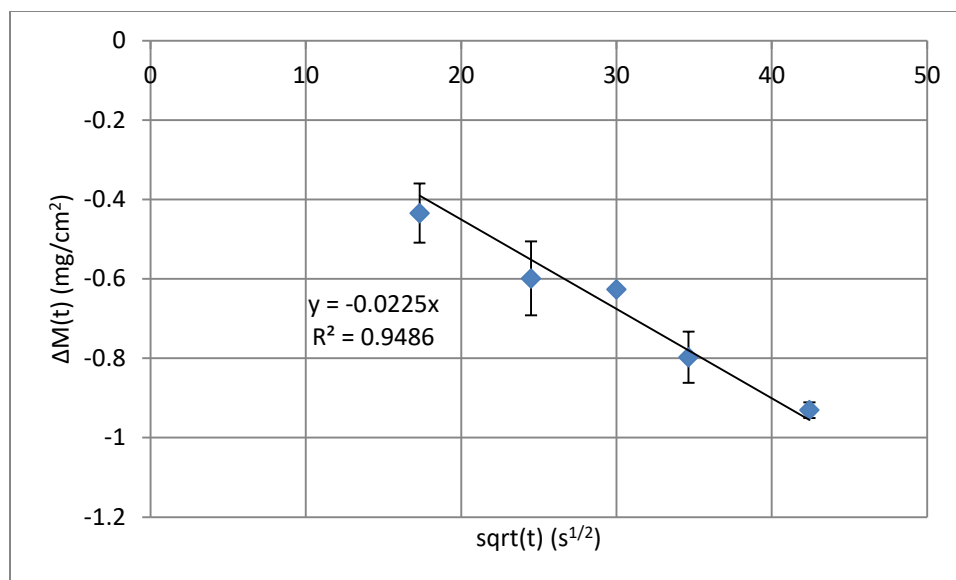


Figure 28. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A at 580 °C (preheated at 580 °C for 20 minutes) for times between 5 minutes and 30 minutes.

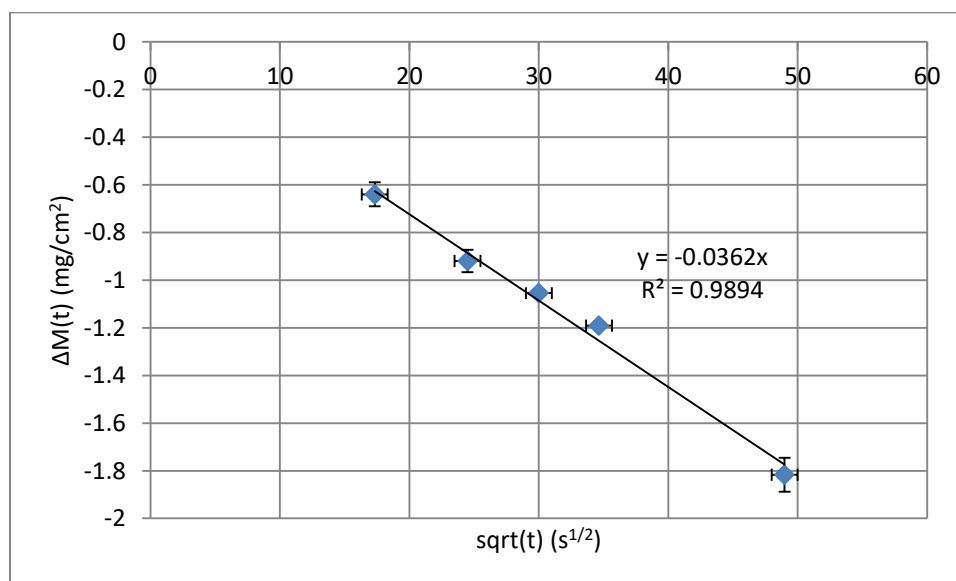


Figure 29. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A at 625 °C (preheated at 625 °C for 20 minutes) for times between 5 minutes and 40 minutes.

If we assume that during this exchange that the lithium ions in the bath are only exchanging with sodium ions in the glass, we are able to calculate the diffusion coefficient for this exchange. Using Figure 28 and eq. 39 a diffusion coefficient of $D_{\text{Li} \rightarrow \text{Na}} = 1.58 \times 10^{-8} \text{ cm}^2/\text{s}$ for Treatment A at 580 °C. Similarly using Figure 26 and eq. 39 a diffusion coefficient of $D_{\text{Li} \rightarrow \text{Na}} = 4.18 \times 10^{-8} \text{ cm}^2/\text{s}$ for Treatment A at 625 °C. Using these diffusion coefficients for different temperatures we can calculate the activation energy for the lithium ions in Treatment A exchanging with the sodium ions in the Schott AR-Glas® rods with eq. 40, which yields $\Delta E_{\text{Li} \rightarrow \text{Na}} = 137.7 \text{ kJ/mol}$. Also using the Arrhenius diffusion equation and the activation energy we can calculate D_0 for this exchange, being $D_0^{\text{Li} \rightarrow \text{Na}} = 4.27 \text{ cm}^2/\text{s}$.

The 2-step exchanges change in mass were also recorded, and although multiple alkali ion exchanges are occurring at once the overall trend of the change in mass per unit surface area in the glass rods helps to show what is happening during these second step processes. Figures 30-37, show $\Delta M(t)$ as a function of the $\text{sqrt}(t)$ for Treatment A for 30 minutes at 580 °C followed by 100% NaNO_3 , 100% KNO_3 , Treatment B, Treatment C, and Treatment D all at 450 °C respectively.

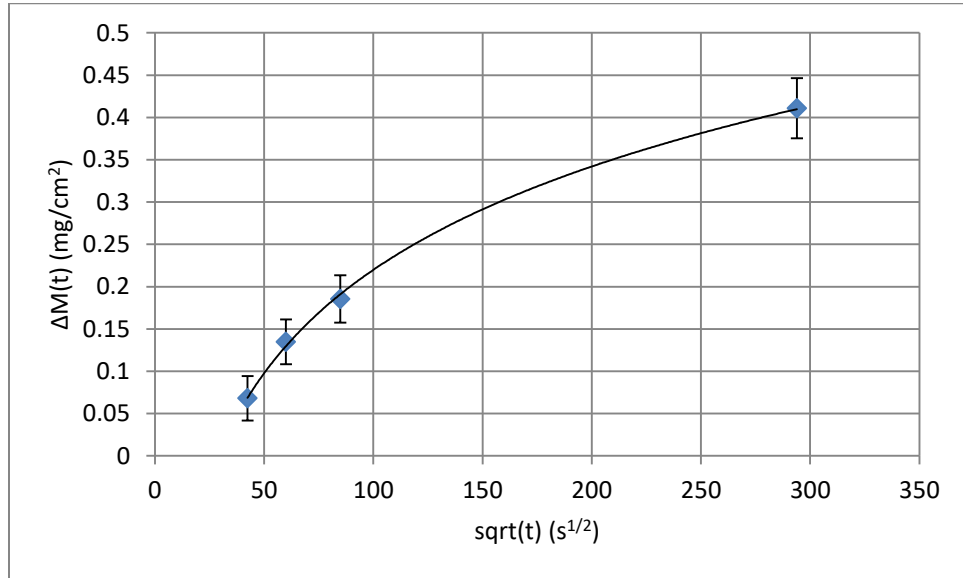


Figure 30. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 20 minutes at 580 °C followed by 100% NaNO_3 at 450 °C for times between 30 minutes and 24 hours.

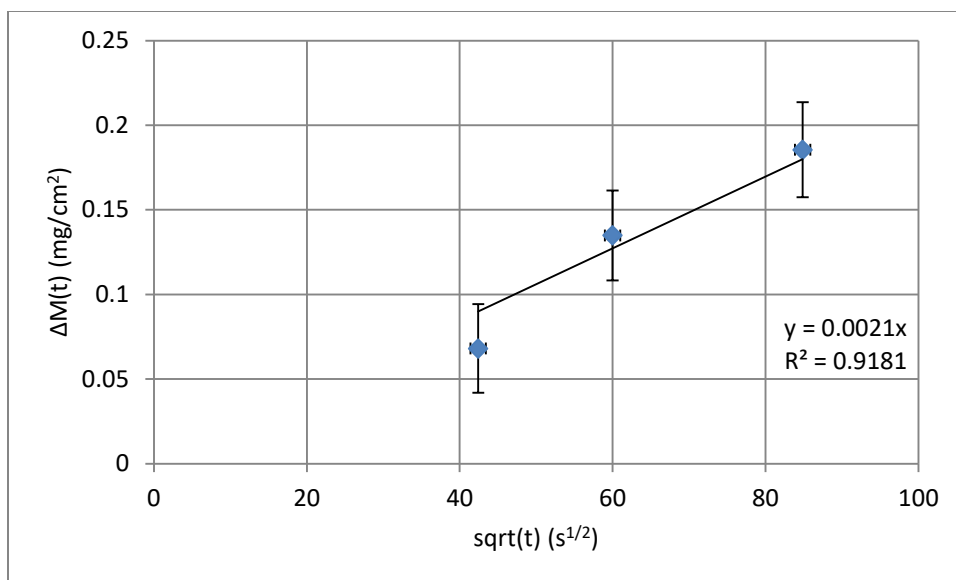


Figure 31. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 20 minutes at 580 °C followed by 100% NaNO_3 at 450 °C for times between 30 minutes and 2 hours.

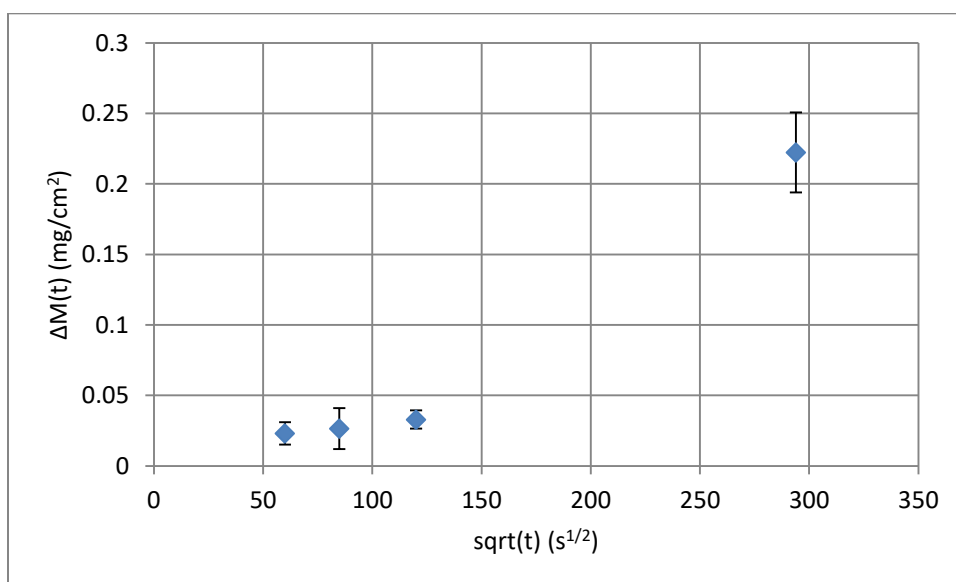


Figure 32. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 20 minutes at 580 °C followed by 100% KNO_3 at 450 °C for times between 1 hour and 24 hours.

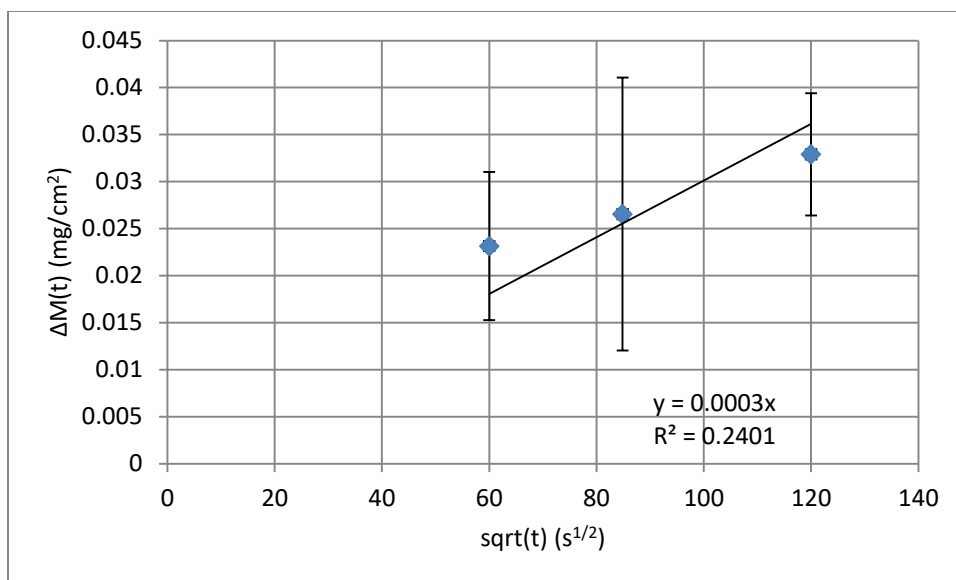


Figure 33. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 20 minutes at 580 °C followed by 100% KNO₃ at 450 °C for times between 1 hour and 4 hours.

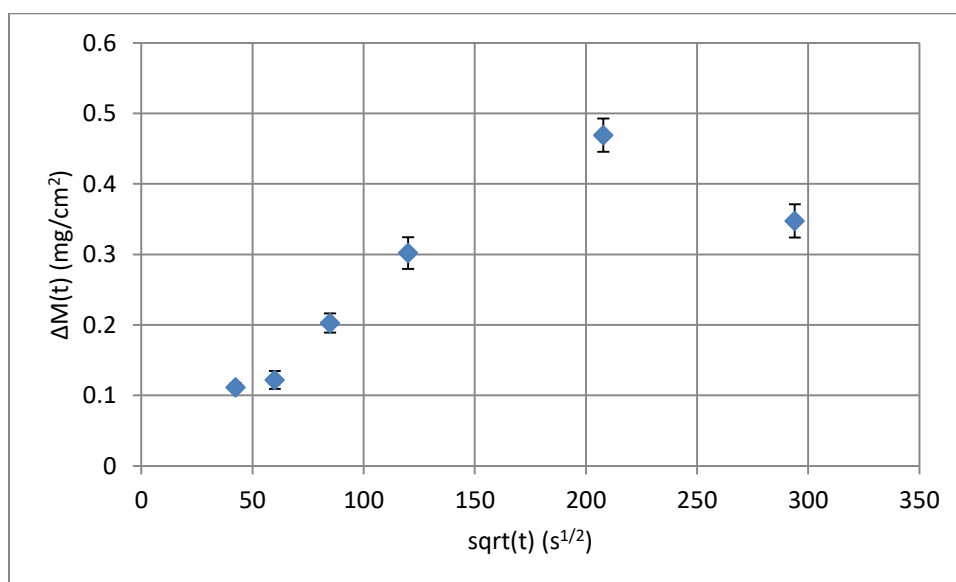


Figure 34. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 30 minutes at 580 °C followed by Treatment B at 450 °C for times between 30 minutes and 24 hours.

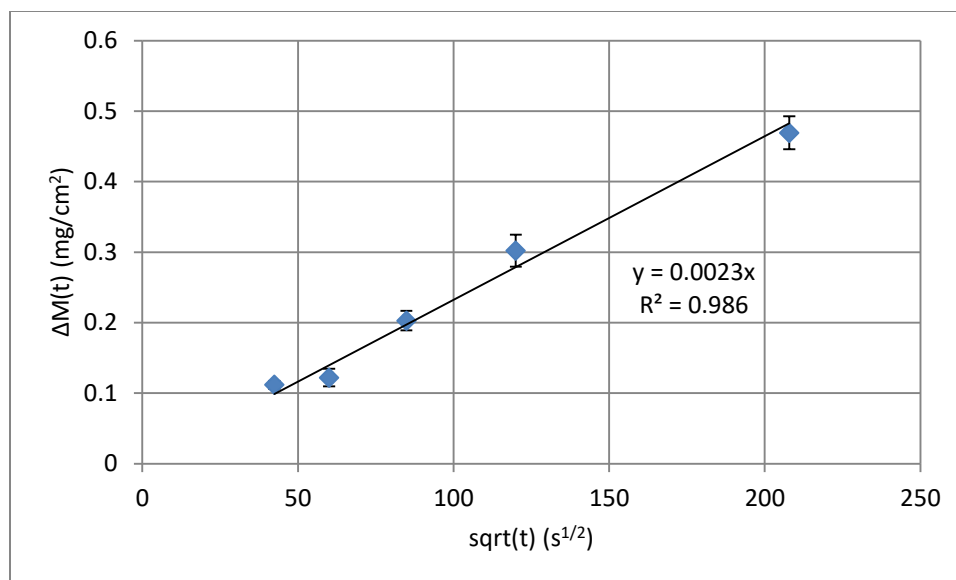


Figure 35. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 30 minutes at 580 °C followed by Treatment B at 450 °C for times between 30 minutes and 12 hours.

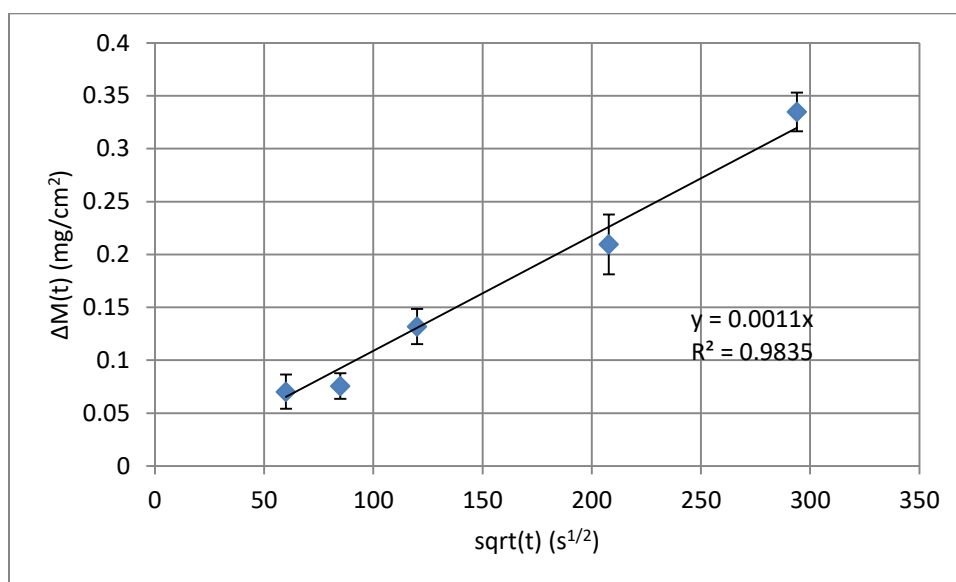


Figure 36. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 30 minutes at 580 °C followed by Treatment C at 450 °C for times between 1 hour and 24 hours.

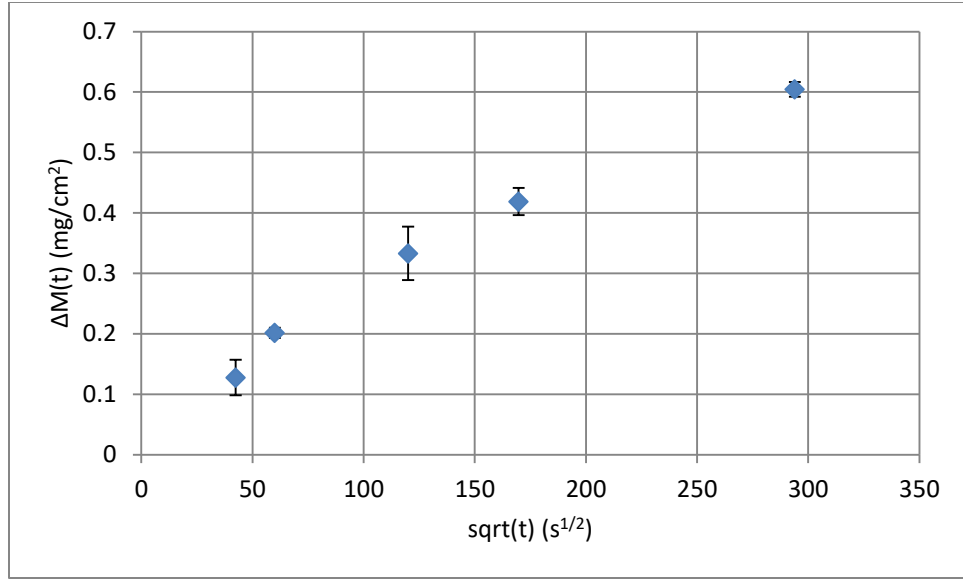


Figure 37. Change in mass per unit surface area ($\Delta M(t)$) as a function of the square root of time for Treatment A for 30 minutes at 580 °C followed by Treatment D at 450 °C for times between 30 minutes and 24 hours.

If we assume that the lithium ions exchanged completely with the sodium ions during the first high temperature exchange with Treatment A for 30 minutes at 580 °C, then we can calculate the diffusion coefficient for either sodium or potassium ions exchanging with lithium ions in the second lower temperature exchanges. Using Figure 31 and eq. 39 the calculated diffusion coefficient for sodium ions from the salt bath exchanging with lithium ions in the glass surface is $D_{Na \rightarrow Li} = 1.18 \times 10^{-10} \text{ cm}^2/\text{s}$ during the 100% NaNO_3 exchange at 450 °C in the 2-step process. Using Figure 35 and eq. 39 the calculated diffusion coefficient for $\text{Na}^+ \rightarrow \text{Li}^+$ in the glass surface is $D_{Na \rightarrow Li} = 1.42 \times 10^{-10} \text{ cm}^2/\text{s}$ during the Treatment B at 450 °C second step process. Similarly assuming the a complete high temperature lithium exchange in the surface of the glass rods during the Treatment A for 30 minutes at 580 °C as before. We can calculate the diffusion coefficient for potassium ions exchanging with lithium ions in the second lower temperature $\text{K}^+ \rightarrow \text{Li}^+$ exchange. Using eq. 39 as well as Figure 33 the calculated value for potassium ions exchanging with lithium ions during the 100% KNO_3 at 450 °C second step exchange is $D_{K \rightarrow Li} = 2.69 \times 10^{-13} \text{ cm}^2/\text{s}$. The calculated diffusion coefficient, $D_{K \rightarrow Li} = 8.14 \times 10^{-12} \text{ cm}^2/\text{s}$ was calculated using Figure 36 and eq. 39 for Treatment C at 450 °C during the second step process .

Looking at Figure 37 we can see that the initial exchange rate of sodium and potassium ions decreases with time of exchange. Calculating a diffusion coefficients $D_{\text{Na} \rightarrow \text{Li}}$ and $D_{\text{K} \rightarrow \text{Li}}$ for Treatment D at 450 °C proves difficult to calculate using eq. 39 for a variety of reasons discussed later.

C. Glass Strengths

To determine properly if the glass rods were actually strengthened during these processes, it is necessary to compare the strengths of the treated rods to the strengths of the untreated rods. The following figures and tables show the strengthening results for the treatments considered in these experiments including the characteristic strengths and Weibull modulus for both the 1-step and 2-step exchanges.

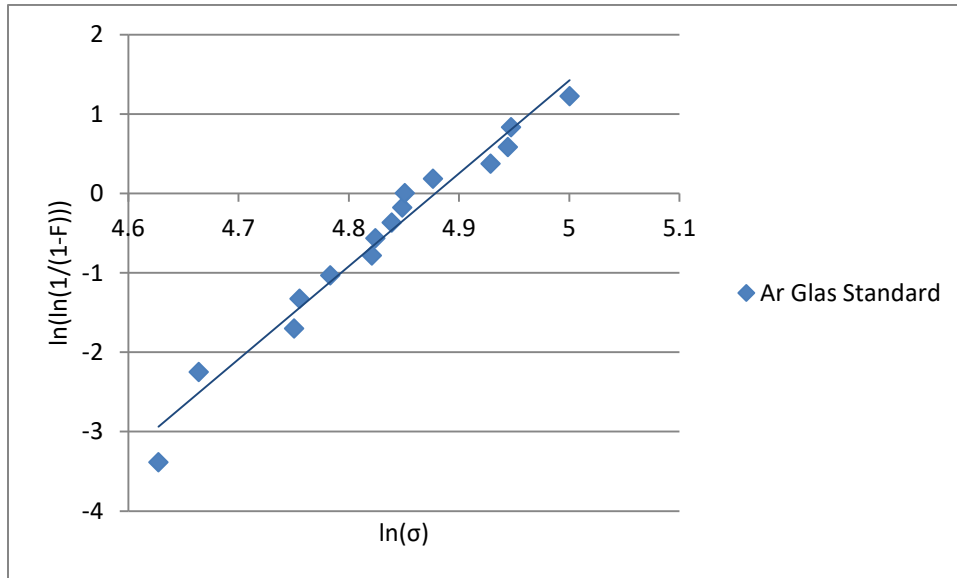


Figure 38. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples as shipped.

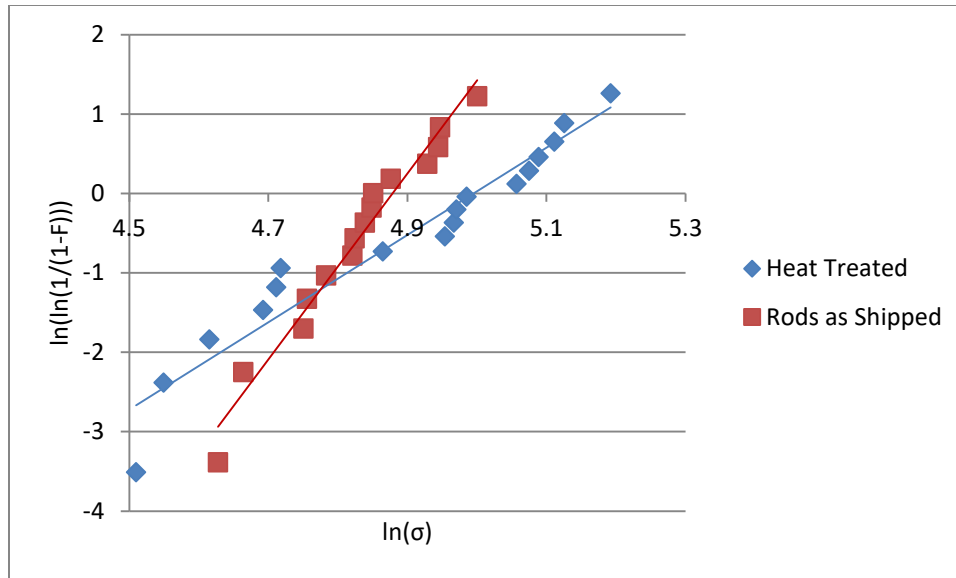


Figure 39. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples heated to 580 °C for 20 minutes then allowed to air cool.

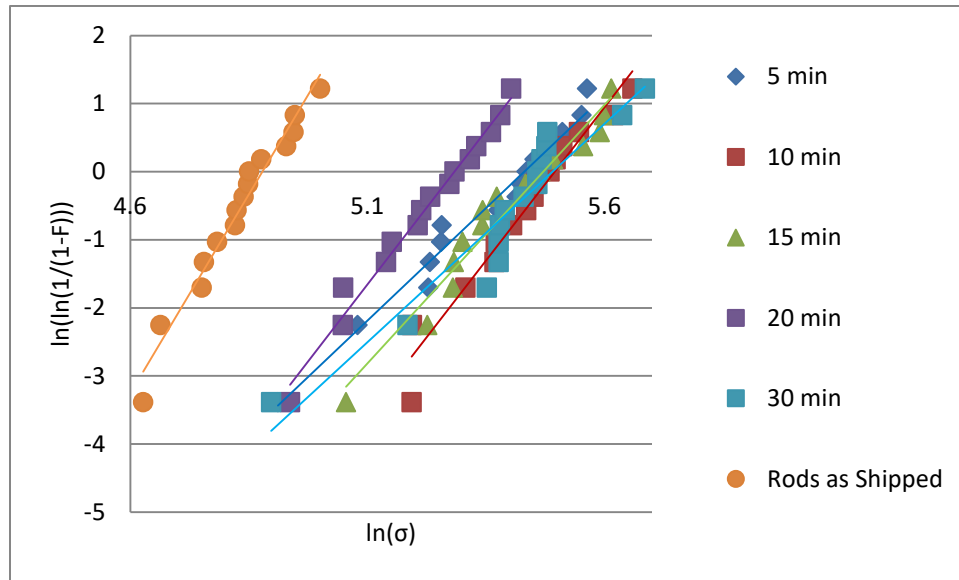


Figure 40. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A at 580 °C for times between 5 minutes and 30 minutes.

Table IX. Weibull Modulus and Characteristic Strengths for Treatment A at 580 °C

Glass Preheat Temperature (°C)	Glass Preheat Time (min.)	Glass Exchange Temperature (°C)	Glass Exchange Time (min.)	Weibull Modulus	Characteristic Strength (MPa)
Control Rods				11.7	131
580	20	-	-	5.5	148
580	20	580	5	6.6	228
580	20	580	10	9.0	244
580	20	580	15	7.6	238
580	20	580	20	9.0	197
580	20	580	30	6.4	242

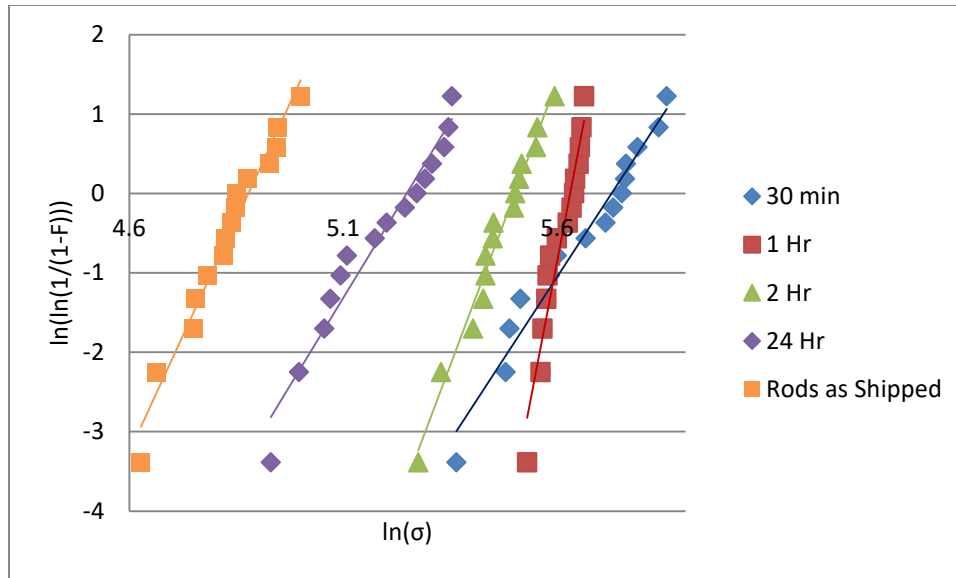


Figure 41. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A for 20 minutes at 580 °C followed by 100% NaNO₃ at 450 °C for times between 30 minutes and 24 hours.

Table X. Weibull Modulus and Characteristic Strengths for Treatment A for 20 Minutes at 580 °C (Preheated for 20 Minutes at 580 °C) Followed by 100% NaNO₃ at 450 °C.

Glass Preheat Temperature (°C)	Glass Preheat Time (min.)	Glass Exchange Temperature (°C)	Glass Exchange Time (Hours)	Weibull Modulus	Characteristic Strength (MPa)
Control Rods				11.7	131
Treat. A for 20 min. at 580 °C (preheated 20 min. at 580 °C)				9.0	197
450	20	450	0.5	8.3	306
450	20	450	1	28.2	279
450	20	450	2	14.2	245
450	20	450	24	8.9	190

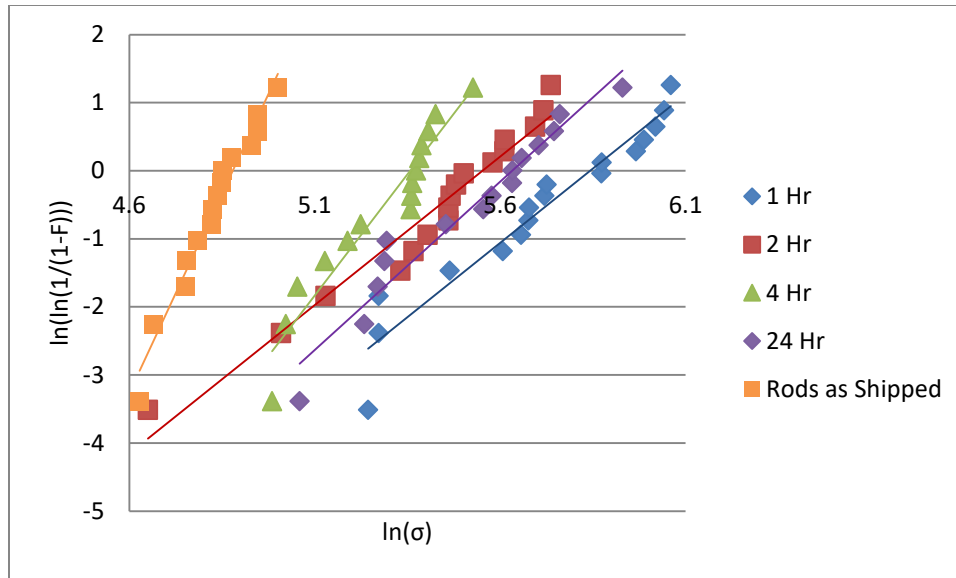


Figure 42. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A for 20 minutes at 580 °C followed by 100% KNO₃ at 450 °C for times between 1 hour and 24 hours.

Table XI. Weibull Modulus and Characteristic Strengths for Treatment A for 20 Minutes at 580 °C (Preheated for 20 Minutes at 580 °C) Followed by 100% KNO₃ at 450 °C.

Glass Preheat Temperature (°C)	Glass Preheat Time (min.)	Glass Exchange Temperature (°C)	Glass Exchange Time (Hours)	Weibull Modulus	Characteristic Strength (MPa)
Control Rods				11.7	131
Treat. A for 20 min. at 580 °C (preheated 20 min. at 580 °C)				9.0	197
450	20	450	0.5	4.4	345
450	20	450	1	4.4	258
450	20	450	2	7.1	212
450	20	450	24	4.9	279

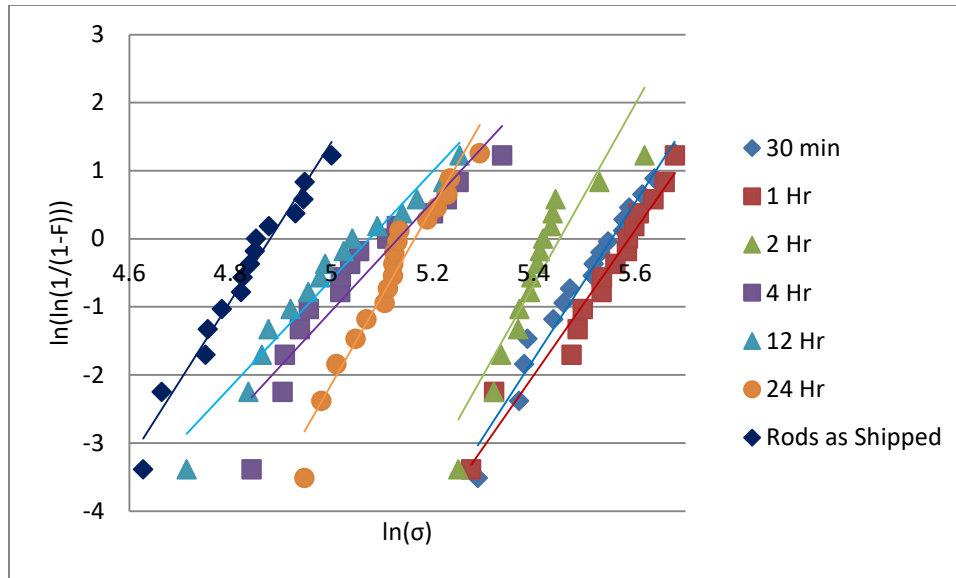


Figure 43. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A for 30 minutes at 580 °C (preheated for 20 minutes at 580 °C) followed by Treatment B at 450 °C for times between 30 minutes and 24 hours.

Table XII. Weibull Modulus and Characteristic Strengths for Treatment A for 30 minutes at 580 °C (Preheated for 20 Minutes at 580 °C) Followed by Treatment B at 450 °C.

Glass Preheat Temperature (°C)	Glass Preheat Time (min.)	Glass Exchange Temperature (°C)	Glass Exchange Time (Hours)	Weibull Modulus	Characteristic Strength (MPa)
Control Rods				11.7	131
Treat. A for 30 min. at 580 °C (preheated 20 min. at 580 °C)				6.4	242
450	5	450	0.5	11.5	258
450	5	450	1	10.6	267
450	5	450	2	13.2	233
450	5	450	4	8.0	169
450	5	450	12	8.0	157
450	5	450	24	13.0	175

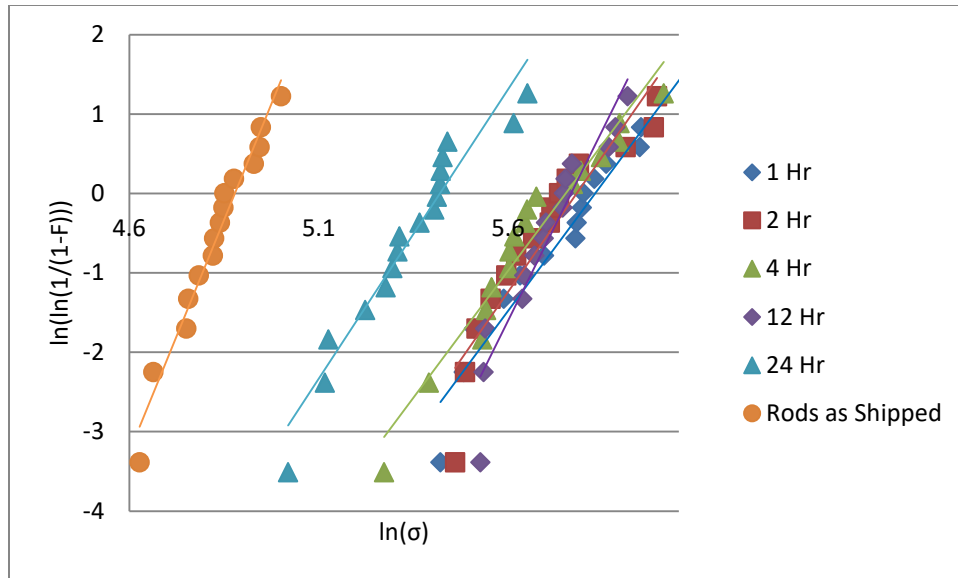


Figure 44. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A for 30 minutes at 580 °C followed by Treatment C at 450 °C for times between 1 hour and 24 hours.

Table XIII. Weibull Modulus and Characteristic Strengths for Treatment A for 30 Minutes at 580 °C (Preheated for 20 Minutes at 580 °C) Followed by Treatment C at 450 °C.

Glass Preheat Temperature (°C)	Glass Preheat Time (min.)	Glass Exchange Temperature (°C)	Glass Exchange Time (Hours)	Weibull Modulus	Characteristic Strength (MPa)
Control Rods				11.7	131
Treat. A for 30 min. at 580 °C (preheated 20 min. at 580 °C)				6.4	242
450	5	450	1	6.4	340
450	5	450	2	6.9	324
450	5	450	4	6.4	315
450	5	450	12	9.6	319
450	5	450	24	7.3	226

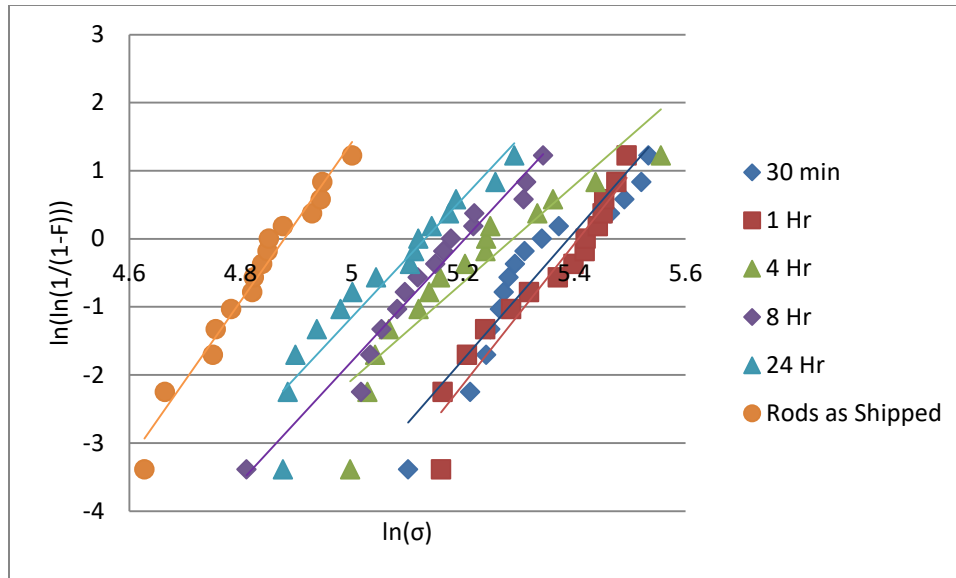


Figure 45. Weibull plot for 4-point bend strength of Schott AR-Glas® rod samples ion exchanged with Treatment A for 30 minutes at 580 °C followed by Treatment D at 450 °C for times between 30 minutes and 24 hours.

Table XIV. Weibull Modulus and Characteristic Strengths for Treatment A for 30 Minutes at 580 °C (Preheated for 20 Minutes at 580 °C) Followed by Treatment D at 450 °C.

Glass Preheat Temperature (°C)	Glass Preheat Time (min.)	Glass Exchange Temperature (°C)	Glass Exchange Time (Hours)	Weibull Modulus	Characteristic Strength (MPa)
Control Rods				11.7	131
Treat. A for 30 min. at 580 °C (preheated 20 min. at 580 °C)				6.4	242
450	5	450	0.5	9.3	220
450	5	450	1	10.3	223
450	5	450	4	7.1	198
450	5	450	8	8.8	182
450	5	450	24	8.8	169

DISCUSSION

A. Composition of Salt Bath and Effect on Exchange Depth

First Step Exchange:

The time dependence of exchange depth of 80% Li_2SO_4 , 15% K_2SO_4 , 5% Na_2SO_4 (mole %) (Treatment A) was determined by exchanging Schott AR-Glas® rods of the same composition and starting with the same thermal history. This exchange allowed for lithium ions in the bath to exchange with the larger alkali ions in the glass surface. Since smaller ions were exchanging for larger ions in this treatment, the exchange temperature must be above the glass transition temperature (T_g) but below the glass softening temperature (T_s) of the glass rods. Using temperatures below T_g does not allow the glass structure to relax properly, and a build up of tension in the glass surface causes the glass rods to crack where the smaller lithium ions exchange with larger sodium ions when cooled. Using temperatures above T_s allows the glass rods to deform. But, using a temperature in between T_g and T_s allows the glass structure to significantly relax, thus allowing the ions to exchange without stresses accumulating in the surface of the glass rods, while also not allowing the rods to deform.

The composition of Treatment A was carefully chosen to avoid chemical attack of the glass surface. The addition of potassium sulfate lowered the salt bath melt temperature due to a eutectic between the two salts. Sodium sulfate was added so that the salt bath would not be contaminated with sodium ions from the glass when exchanging with the lithium ions. In this exchange, the volume of the salt material containing available Li^+ ions can be thought of as virtually infinite.

The concentration profiles for times between 10 minutes and 30 minutes at 580 °C are shown in Figure 7 and Figure 8. Also the change in mass per unit surface area as a function of the square root of time is presented for times between 5 minutes and 30 minutes at 580 °C in Figure 28. The glass rods exchanged in Treatment A followed a typical linear relationship for the mass change per unit surface area as a function of the square root of time as shown in Figure 28. Using eq. 39 and the results from Figure 28 a diffusion coefficient of $D_{\text{Li} \rightarrow \text{Na}} = 1.58 \times 10^{-8} \text{ cm}^2/\text{s}$ was calculated for Treatment A at 580 °C. We can compare this value to the values calculated and shown in Table VII. The Table VII diffusion coefficients for lithium ions in the

salt bath exchanging with the sodium ions in the glass rods are $D_{\text{Li} \rightarrow \text{Na}} = 1.57 \times 10^{-8} - 1.88 \times 10^{-8} \text{ cm}^2/\text{s}$. This is a 0.6-17.3% difference between calculated diffusion coefficients using the mass change data and the WDS data. This difference may be attributed to the slight increase in concentration of potassium ions in the surface of the glass rods. Also, when analyzing the WDS data the inherent error in choosing the surface properly makes it difficult to compare the two data sets with accuracy. Although one can say that the diffusion coefficients calculated are a good estimation, the errors associated with the two data sets makes it difficult to draw any conclusions about the movement of potassium ions.

The Intensity of K^+ ions as a function of the depth into the glass rods can be seen in Figure 8. This figure shows that the potassium ions in the glass surface are not exchanging with the lithium ions in the bath. This suggests that the potassium ions are in high energy anion traps. Since the concentration of potassium ions in the untreated glass rods is much less than the sodium concentration, these anion traps allow the glass to exchange similarly to a single alkali glass. Thus, these anion traps allow the lithium ions to ignore the exchange for potassium ions and only exchange with the higher concentration sodium ions in the glass. These results also seem to suggest that there is a small increase in the concentration of potassium ions in the surface of the glass rods.

When calculating the diffusion coefficient from eq. 39 and Figure 28, the mass increase from the heavier potassium ions exchanging for the sodium ions in the glass surface was not considered. This increase in mass is a contributing factor to the slope of Figure 28. Thus, if we could subtract this contribution from Figure 28, it would result in a more negative slope, and hence a larger diffusion coefficient ($D_{\text{Li} \rightarrow \text{Na}}$). This may account for the different diffusion coefficients calculated from mass change and WDS data.

Two step Exchanges:

Concentration profiles and mass change of samples were determined by treating samples with Treatment A for 30 minutes at 580 °C (preheated for 20 minutes at 580 °C) followed by treatments in an array of other salt baths with different compositions. These compositions include 100% NaNO_3 , 100% KNO_3 , Treatment B (95% NaNO_3 , 3% D.E., 2% S.L.S. glass spheres), Treatment C (93% KNO_3 , 2% NaNO_3 , 3% D.E., 2% S.L.S. glass spheres), and

Treatment D (47.5% NaNO₃, 47.5% KNO₃, 3% D.E., 2% S.L.S. glass spheres) (weight %) all treated at 450 °C. The 100% NaNO₃, and 100% KNO₃ treatments were preheated for 20 minutes at 450 °C prior to being submerged. While Treatment B, Treatment C, and Treatment D, were preheated for 5 minutes at 450 °C prior to being submerged in the second treatment. The temperature for the second step exchanges must be below T_g. This allows for the larger sodium and potassium ions in these baths to exchange with the lithium rich surface of the previously exchanged glass rods. The larger ions exchanging with smaller ions while the glass structure is not relaxed causes a compressive layer on the surface of the glass.

100% NaNO₃, and 100% KNO₃

Results for the change in mass per unit surface area as a function of the square root of time for the 100% NaNO₃, 2-step exchange process are shown in Figure 30 and Figure 31. The results in Figure 30 show that the rate of exchange between the sodium ions in the bath and lithium ions in the surface of the glass decreases at larger times. This decrease in the rate of exchange can be attributed to the decreasing trend in concentration as a function of the depth in the glass rods. Thus, at larger times the concentration of lithium ions decreases, and the concentration of sodium ions increases at even small depths. The thermodynamic drive for the exchange of sodium ions for lithium ions is decreased as the concentration of lithium is decreased, and causes the diffusion coefficient $D_{Na \rightarrow Li}$ to decrease for larger times. If we look at short times, we can assume that the lithium concentration in the surface is essentially constant and calculate a diffusion coefficient for this process. Using eq. 39 and Figure 31 a diffusion coefficient of $D_{Na \rightarrow Li} = 1.18 \times 10^{-10} \text{ cm}^2/\text{s}$ was calculated.

Results for the change in mass per unit surface area as a function of the square root of time for the 100% KNO₃, 2 step exchange process are shown in Figure 32 and Figure 33. The results in Figure 26 show that for small times, the exchange of potassium ions for lithium ions in the surface follows a linear trend. Using eq. 39 and Figure 33 a diffusion coefficient of $D_{K \rightarrow Li} = 2.69 \times 10^{-13} \text{ cm}^2/\text{s}$ was calculated. Although more data points are needed, it is apparent that there is an increase in the rate of diffusion between some pair of ions. This could be attributed to potassium ions exchanging with sodium ions deeper in the glass rods at larger times. Also it is possible that a mixed alkali affect in the glass surface is occurring, which decreases the glass

transition temperature of the surface layer in the glass leading to lower strengths (as observed) and a glass structure that allows a more rapid interdiffusion.

Neither of the 100% NaNO₃ and 100% KNO₃ second step exchange samples were tested with the WDS to determine the depth of exchange. This is because the glass rods treated for longer times appeared to have a translucent white layer on the surface of the rods. This was attributed to the nitrate baths chemically attacking the glass surface, and thus weakening these samples. As noted, we abandoned this bath composition in favor of less aggressive compositions.

Treatment B

Results showing the exchange depth, and intensity of sodium and potassium ions can be seen in Figures 9-14 for the second step exchange using Treatment B at 450 °C for times between 30 minutes and 24 hours. These results show that the sodium ions in the bath appear to be exchanging with both the lithium and potassium ions in the surface of the glass rods. At small times (Figures 6-8) the intensity of sodium ions, which is directly proportional to the concentration of sodium ions, is near that of the untreated samples shown in Figure 6. This suggests that sodium ions in the bath are exchanging with the lithium rich surface of the glass rods. At longer times the intensity of sodium ions at the surface is greater than that of the untreated samples. Also the intensity at the surface of the potassium ions follows an error function trend with an intensity of zero at the surface, implying the concentration of potassium at the surface is also zero. This evidence suggests that, as expected, the sodium ions are also exchanging with the potassium ions in the glass surface at longer times of exchange. Perhaps the diffusion rate of the Na⁺→K⁺ exchange is so small at shorter times that it is not possible to observe in the data. The strength tests, discussed later on, also helps to confirm that the Na⁺→K⁺ exchange is occurring more frequently for longer exchanges. As time of exchange lengthens the rate of diffusion for this exchange increases as the rate of diffusion of the Na⁺→Li⁺ exchange decreases. The decrease in the rate of diffusion of the Na⁺→Li⁺ can be attributed to the limited amount of lithium ions in the glass for the sodium ions to exchange with. Another possible explanation could be that in the immediate surface of the glass the amount of lithium ions far exceeds that of the potassium ions. Thus, the potassium ions are caught in high energy anion traps and the sodium ions in the bath are unable to exchange with the potassium ions in the surface for short time periods. However, as the sodium ions exchange with the lithium ions in

the surface of the glass, and the amount of lithium in the surface layer diminish to less of that of the potassium ions, thus allowing the potassium ions to break free of their anion traps. This could be attributed to the mixed amount of alkali ions in the surface to decrease the T_g of the surface layer of the glass rods and thus lowering the energy needed for the potassium ions in these anion traps to be exchanged with the sodium ions in the bath.

When looking at very short diffusion depths it becomes much more difficult to pin point the depth of diffusion between diffusing ion pairs. When taking line scans of the samples the curvature of the glass rods makes the exact origin of the surface hard to determine. Also when averaging these lines scans to extrapolate more accurate data to examine, we may be averaging different depths of the sample mistakenly. Although this effect is most likely miniscule when examining deeper layers of the glass rods, this could distort the data for small distances in the glass rods, and may be the reason why we cannot accurately determine the diffusion coefficients of the $\text{Na}^+ \rightarrow \text{K}^+$ for small times.

The change in mass per unit surface area as a function of the square root of time can be seen in Figure 34 and Figure 35. The calculated diffusion coefficient for sodium ions exchanging with the lithium for short times using the results from Figure 35 and eq. 39 is $D_{\text{Na} \rightarrow \text{Li}} = 1.42 \times 10^{-10}$. When calculating this diffusion coefficient only sodium for lithium ions was considered.

Figure 35 shows that for short times the change in mass per unit surface area appears to be linear with respect to the square root of time. However, the data point for the 24 hour exchange in the Treatment B in Figure 34 suggests that the mass change per unit surface area decreases. This could be because the sodium ions in the bath have saturated the lithium ions in the surface of the glass rods. Thus, the $\text{Na}^+ \rightarrow \text{Li}^+$ exchange has depleted the lithium ions in the glass at long time periods and suggests that sodium ions are primarily exchanging with the potassium ions in the glass later in the exchange process. As explained above the rate of diffusion of sodium ions for potassium ions in the glass appears to be increasing for longer times as well. These two factors would account for a decrease in the mass change per unit surface area for long times and also account for the observed decrease in strength. Additional lithium ion concentration data for these different treatment times would help elucidate what is happening in this process.

Treatment C

Results showing the intensity of potassium and sodium ions as a function of the depth into the glass rods are shown in Figures 15-19 for this second step exchange for times between 1 hour and 24 hours. The exchange of potassium ions in the bath for lithium ions in the glass surface was expected and confirmed as can be observed in these figures. Looking at Figure 20, we can see the intensity of potassium ions as a function of depth into the glass rods for multiple times. It can be observed that the depth of exchange increases for times between 1 hour and 4 hours as would be expected. However, the depth of exchange then recedes at larger times, as can be seen in Figure 20 for times of 12 hours and 24 hours. This phenomenon may be more easily explained if we had some data showing the concentration profile of lithium ions as a function of depth in the glass rods.

From Figure 19 we can see that the sodium ions intensity approaches a constant concentration for long periods of time in a second step exchange with Treatment C. This concentration appears to be lower than that of the untreated sample. The sodium ions concentration gradient prior to the second exchange appears to be equilibrating with the lithium ions concentration gradient at long times in this second treatment. This still does not explain the decreasing depth of potassium for long time treatments, but suggests that there is some sort of thermodynamic drive that forces the potassium ions to recede to lesser depths at large times of exchange. This thermodynamic drive could be attributed to the mixed alkali effect occurring throughout the surface of the glass rods. Further examination of the mixed alkali effect on the glass transition temperature is needed to help explain this phenomenon.

Results for the change in mass per unit surface area as a function of the square root of time for Treatment C at 450 °C are shown in Figure 36. The mass change per unit surface area appears to have a regular linear behavior as a function of the square root of time. The calculated diffusion coefficient using these results as well as eq. 39 is $D_{K \rightarrow Li} = 8.14 \times 10^{-12} \text{ cm}^2/\text{s}$. The reason for this linear relationship is unclear when compared with the WDS results for different times. Once again, the use of more information, such as concentration of lithium ions in these exchange processes, could prove useful in explaining these phenomena.

Treatment D

The results for the intensity of sodium and potassium ions as a function of the depth are shown in Figures 21-25. Both sodium and potassium ions in the salt bath are exchanging with the lithium ions in the surface of the glass. Using these figures as well as eq. 37 and eq. 38 diffusion coefficients $D_{\text{Na} \rightarrow \text{Li}}$ and $D_{\text{K} \rightarrow \text{Li}}$ were calculated and the results, seen in Table VI, and in Figure 26 and 27, show that the inter-diffusion rate for both sodium and potassium ions exchanging with lithium ions decreases as a function of the square root of time. This suggests that the diffusion coefficients are not only dependent on the square root of time but on the concentration of lithium ions throughout the glass rods. The exchange rate of the larger alkali ions for lithium ions in the glass rods decreases as the amount of lithium ions available for exchange decreases. However, when calculating the diffusion coefficients from the WDS data the error associated is quite large. This error is significant when dealing with the short treatment times because the distances associated with the exchange are so short. This makes it difficult to confirm that the inter-diffusion rate is actually decreasing with treatment time.

The WDS intensity, and therefore the concentration of sodium ions vs. depth approach a constant for longer times, which can be explained by the depletion of lithium ions in the glass rods, as well as the sodium ions striving to achieve an equilibrium value. Looking at the intensities of sodium ions for long time periods it is apparent that the concentration is less than that of the untreated sample shown in Figure 6 toward the surface layer of the glass rod. The concentration then returns to that of the untreated glass rod at deeper layers as expected. The concentration value of sodium is unable to return to that of the untreated sample at the surface because some of the lithium ions available for exchange are exchanged with potassium ions and thus unavailable to the sodium ions in the bath.

The change in mass per unit surface area as a function of the square root of time is shown in Figure 37 for this exchange. This figure shows that the rate of mass change per unit surface area per unit $\sqrt{t}$ decreases for this exchange process. This is explained by the depletion of lithium ions at longer periods of time. Thus, since the rate of diffusion decreases as explained in this section, the change in mass also decreases as time increases. Calculating the diffusion coefficients using Figure 37 is not possible using eq. 39 because the equation assumes that the

diffusion coefficient is a constant. Also, without knowing the lithium concentrations, calculating a value of M_∞ is not possible.

B. Temperature Effects

Treatment A

Studying the effects of temperature on the exchange of lithium ions exchanging for sodium ions in the first step exchange allows us to calculate some physical constants that help us to understand the diffusion process. The results from Figures 28 and 29 and the use of eq. 39 allows us to calculate the diffusion coefficients for the $\text{Li}^+ \rightarrow \text{Na}^+$ exchange in Treatment A of $D_{\text{Li} \rightarrow \text{Na}} = 1.58 \times 10^{-8} \text{ cm}^2/\text{s}$ and $D_{\text{Li} \rightarrow \text{Na}} = 4.18 \times 10^{-8} \text{ cm}^2/\text{s}$ for at temperatures of 580 °C and 625 °C respectively. Using these diffusion coefficients, eq. 40 we calculate an activation energy $\Delta E^a_{\text{Li} \rightarrow \text{Na}} = 137.7 \text{ kJ/mol}$, and diffusion coefficient $D_o^{\text{Li} \rightarrow \text{Na}} = 4.27 \text{ cm}^2/\text{s}$ were calculated for Treatment A exchanging with Schott AR-Glas® rods. With this information it is possible to calculate the diffusion coefficient $D(T)$ for different temperatures, and also the exchange depth of this process at different temperatures and times. The calculated diffusion depth of lithium ions in Treatment A for 30 minutes at 580 °C using eq. 36 is 75 microns. This compares quite well to the observed depth of 80 microns as seen in Figure 7 for the same treatment conditions.

The temperature effect on the Treatment A exchange with Schott AR-Glas® rods follows the typical Arrhenius diffusion equation as expected. Unfortunately, the temperature in which the exchange can be performed is still governed by the glass composition itself. A temperature above the T_g and below T_s must be chosen for an exchange of this type to avoid cracking or deformation of samples.

C. Effect of 1-step and 2-step ion exchange on Fracture Strength

Although determining case depth and diffusion data is necessary to understanding the systems studied, it is also necessary to conduct flexural fracture strength experiments to properly evaluate the effectiveness of ion exchange treatments. The use of high temperature exchanges allows for the glass rods to relax which also influences the fracture strength of the rods. The compressive layer produced in the surface of the rods during exchange treatments is a function of the stresses built up from either, the change in thermal expansion coefficients in the first

exchange, or the stuffing effect in the second exchange, as well as the stress relaxations in the exchanged surface region. These relaxation effects are critical to the effectiveness of ion exchange for temperatures above and near T_g . Using the results from section C of the result section Weibull Moduli and Characteristic Strengths for each set of data was calculated. Weibull Modulus was calculated by taking the slope of the Weibull plots for each set of data, and characteristic strengths were calculated by using the fracture strength value where the trend line crosses the x-axis e.g. where $\ln(\ln(1/(1-F))) = 0$ ($F = 0.63$) The Weibull plots and summary of Weibull Modulus and Characteristic strengths are presented in Figures 38-45 and Tables IX-XIV.

Treatment A

Figure 40 shows the Weibull plots for glass rods exchanged with Treatment A at 580 °C for times between 5 minutes and 30 minutes. When compared to the results of the untreated samples shown in Figure 38 the 10 minute and 30 minute exchange at 580 °C showed the greatest improvement of strength. Table IX shows the results for times between 5 minutes and 30 minutes as well as the untreated rods, rods heated to 580 °C for 20 minutes and allowed to cool in air. Table IX also shows the thermal history of each rod and the temperature and time of each exchange. The Characteristic strength increased from 131 MPa to 244 MPa in the 10 minute exchange, and from 131 MPa to 242 MPa in the 30 minute exchange. However, the Weibull modulus decreased from 11.7 to 9.0 in the 10 minute exchange and 11.7 to 6.4 in the 30 minute exchange.

The increase in strength for all Treatment A times between 5 minutes and 30 minutes at 580 °C appears to be relatively the same with characteristic strengths of 197-244 MPa and Weibull modulus' of 6.4-9.0. The strength should increase with longer treatment times from an increased depth of penetrating lithium ions. The lithium rich layer having a smaller CTE creates a compressive layer at the surface. Thus, a thicker lithium rich layer results in more compression at the surface of the glass. Therefore, longer treatment times should produce stronger rods. Since this does not appear to be the case for longer treatment times there must be some structural relaxation effects, and mixed alkali effects that tamper with the strengthening. Since the glass rods are above the glass transition temperature during this exchange the glass structure itself is also changing to accommodate the new lithium ion. Lithium ions have a strong tendency to

fourfold coordination with oxygen ions where sodium ions prefer either a five or six fold coordination. Also, defect generation could also be a factor in the strengthening of the glass rods. Although the glass rods are above the glass transition temperature during the exchange and the rods should be properly relaxed to negate these affects, the change in strain displacement could cause more bonds to break and further change the structure of the glass at the surface. For longer treatment times, the structure of the glass is changed deeper throughout the glass rods, and could diminish the strengthening of the rods.

Figure 39 shows the Weibull plot for glass rods heated to 580 °C for 20 minutes and then allowed to cool in air. These rods showed an increase in characteristic strength from 131 MPa to 148 MPa when compared to untreated rods, with a decrease in Weibull modulus from 11.7 to 5.5. This shows that when the glass rods are heated to temperatures above T_g and allowed to cool in air that the rods experience some thermal tempering effects as well. Although these effects are small, it is worth mentioning when comparing with the ion exchange strengthened glass samples.

100% NaNO₃

Figure 41 shows the Weibull plots for samples treated in Treatment A for 20 minutes at 580 °C (preheated for 20 minutes at 580 °C) followed by 100% NaNO₃ at 450 °C (preheated for 20 minutes at 450 °C) for times between 30 minutes and 24 hours. The Weibull modulus and characteristic strengths of these samples are recorded in Table X. Data for untreated samples, as well as the Treatment A for 20 minutes at 580 °C Weibull modulus were added for comparison. The strongest samples made during this process resulted from the 30 minute second step exchange. When compared to the control rods the characteristic strength increased by 134% from 131 MPa to 306 MPa in the 30 minute second step exchange. However, the Weibull modulus decreased from 11.7 to 8.3 in the same exchange. Comparing these rods to the Treatment A for 20 minutes at 450 °C first step exchange we see an increase in characteristic strength of 55% from 197 MPa to 306 MPa in the 30 minute second step exchange. These two exchanges have comparable Weibull modulus' of 9.0 in the first step exchange and 8.3 in the second step exchange.

Although the 30 minute second step exchanged rods were the strongest, other trends are noticeable. The rods get weaker as the length of treatment time increased. This, is because the 100% NaNO_3 bath chemically attacked the surface of the glass rods. Thus, the longer the rods were submerged in this bath the surface of the glass rods deteriorated, and became a translucent white color. This change in surface color was most apparent in the 24 hour second treatment. Also, the Weibull modulus of the 1 hour and 2 hour second treatment exchange increased to 28.2 and 14.2 and characteristic strengths of 279 and 245 respectively. Although these samples have weakened when compared to the 30 minute second step exchange the 1 hour exchange had an increase in strength of 112% when compared to the untreated rods and 41% when compared to the Treatment A for 20 minutes at 580 °C first step process. The 2 hour second step treatment rods had an increase in strength of 87% when compared to the untreated rods, and 24% increase in strength when compared to the related first step process.

100% KNO_3

Figure 42 shows the Weibull plots of samples treated via Treatment A at 580 °C for 20 minutes (preheated for 20 minutes at 580 °C) followed by a 100% KNO_3 treatment at 450 °C for times between 1 hour and 24 hours (preheated for 20 minutes at 450 °C). The Weibull moduli and characteristic strengths for samples treated in this manner, as well as untreated rods and relevant 1-step process, are shown in Table XI. The 30 minute second step exchange with the 100% KNO_3 bath showed the most increase in strength. When compared to the untreated samples the 30 minute samples showed an increase of characteristic strength from 131 MPa to 345 MPa, a strength increase of 163%. However the Weibull modulus drastically decreased from 11.7 to 4.4. Comparing these 30 minute samples to the 1-step Treatment A for 20 minutes at 580 °C samples we see an increase of characteristic strength from 197 MPa to 345 MPa, a strength increase of 75%. But, the Weibull modulus of the 2-step samples once again decreases significantly from 9.0 to 4.4.

Strengths of samples treated in this 2-step exchange decreased when treated for longer times. The samples show characteristic strengths of 345 MPa, 258 MPa, and 212 MPa for 2-step treatment times of 1 hour, 2 hours, and 4 hours respectively. This decrease, once again is caused by the molten salt bath attack on the glass surface. This could be visually seen in these samples with a white translucent film on the surface of the rods. However, the 24 hour treatment second

step treatment samples had a characteristic strength of 279 MPa. This is an increase in strength when compared to the 2 hour and 4 hour 2-step treatment in 100% KNO₃. These 24 hour samples still exhibited surface deterioration. Evidently the compressive layer caused from the exchange of potassium ions for lithium ions in the surface was thick enough for the 24 hour samples that the surface deterioration was overcome. In other words, there was still some weakening attributed to the chemically attacked surface of the samples, but the compressive layer produced allowed the samples to begin strengthening again.

Treatment B

The Weibull plot of samples treated with Treatment A at 580 °C for 30 minutes (preheated for 20 minutes at 580 °C) followed by Treatment B at 450 °C for times between 30 minutes and 24 hours (preheated for 5 minutes at 450 °C) can be seen in Figure 43. Table XII shows the Weibull moduli and the characteristic strengths of these samples as well as the untreated rods, and related 1-step treatment. The glass rods treated in the Treatment B 2-step process did not exhibit significant strengthening when compared to the 1-step process in Treatment A. The largest increase in characteristic strength occurred for the 1 hour, 2-step treatment. When compared to the untreated samples an increase of 104% , from 131 MPa to 267 MPa was recorded. But when compared to the strengths obtained with only Treatment A at 580 °C for 30 minute the strength increased only 10 %, from 242 MPa to 267 MPa. However, the samples treated in Treatment B compared to the related 1-step process exhibit increases in their Weibull moduli. Samples treated in this fashion for all times showed an increase in their Weibull moduli when compared to the relevant 1-step process. For shorter time treatments (30 minutes-2hours) had Weibull moduli between 10.6 and 13.2, where the 1-step samples had a Weibull modulus of 6.4. The 4 hour and 12 hour 2-step treatment samples both had a Weibull modulus of 8.0 before increasing to 13.0 for the 24 hour samples. This increase in Weibull modulus is due to more consistency in strength, even though the strengths for these samples had no significant increase from their 1-step counterpart.

The samples treated in this manner showed no signs of chemical attack. Increases in strengths for short time periods were expected for this 2-step treatment process since the exchange of sodium ions for lithium ions should have resulted in a surface compressive layer. However, when looking at the exchange profiles for these samples shown in Figures 9-14, it is

evident that the exchange of sodium ions in the bath for potassium ions in the glass surface is also happening. This exchange of $\text{Na}^+ \rightarrow \text{K}^+$ results in tension occurring in the glass surface, as well as defect generation caused from the rearrangement of ionic sites. Thus, there are exchanges that are both strengthening and weakening the glass rods at the same time. For short times, it would appear that both these effects are essentially cancelling each other out and causing no significant increase in strength. For long treatment times, the depletion of lithium ions in the surface slows down the exchange with sodium ions, but the rate exchange of $\text{Na}^+ \rightarrow \text{K}^+$ remains essentially constant. This causes the tensional stresses in the surface to increase with time, and allows for more defects to be made. Thus, the decrease in strengths for long time treatments in this process agrees with the concentration profiles of alkali ions. The increase in Weibull moduli in these samples could be attributed to the defects generated during this exchange. The defects made during this process could cause micro-cracks, or even nano-cracks to occur in the glass surface. These cracks allow for the glass to break at more consistent strengths and thus achieve a higher Weibull modulus.

Treatment C

Figure 44 shows the Weibull plot of glass rods treated with Treatment A at 580 °C for 30 minutes (preheated for 20 minutes at 580 °C) followed by Treatment C at 450 °C for times between 1 hour and 24 hours (preheated for 5 minutes at 450 °C). The calculated Weibull moduli and characteristic strengths for these samples, as well as the untreated samples and the related 1-step samples are shown in Table XIII. The largest increase in characteristic strength can be seen from the glass rods treated for 1 hour in this process. When compared to the untreated rods the 1 hour samples had a 160% increase in strength from 131 MPa to 340 MPa. The Weibull modulus of the 1 hour samples decreased from 11.7 to 6.4. Comparing the 1 hour samples to the related 1-step treatment the characteristic strength increased from 197 MPa to 340 MPa, a 73% increase in strength. A Weibull modulus of 6.4 was observed for both the 1 hour 2-step samples and the related 1-step samples.

No chemical attack on samples was observed in this 2-step process. Table XIII shows a trend of decreasing strength as the treatment time increases. However, Figures 12-16 indicate an increasing depth of $\text{K}^+ \rightarrow \text{Li}^+$ exchange between 1 hour and 4 hours, which would normally result in increased strengths. This is not the case. This suggests that the lithium ions in the glass are

exchanging with the sodium ions in the glass while trying to achieve an equilibrated state. These exchanges cause tensional stress deeper in the glass, as well as defects generated from the rearrangement of ionic sites. Evidently, these exchanges have a larger effect on the strength of the glass rods than expected. For longer exchange times (12 hour and 24 hour exchanges) the concentration profiles suggest that the compressive layer caused from the $K^+ \rightarrow Li^+$ exchange is actually thinner than the shorter time exchanges in this treatment. Although further studies are need to explain this phenomenon, this explains why the longer time treatment strengths are less than the smaller time treatments. Also for longer treatment times the amount of sodium ions approaches a constant throughout the glass rods. Thus, the sodium ions from within the glass rod could also be exchanging with the potassium ions at the surface layer of the rods. This exchange would also contribute to reduced compressive stress and defects, which would reduce the magnitude of strengthening.

Treatment D

Weibull plots are shown for glass rods treated in Treatment A for 30 minutes at 580 °C (preheated for 20 minutes at 580 °C) followed by Treatment D at 450 °C for times between 30 minutes and 24 hours (preheated for 5 minutes at 450 °C) in Figure 45. The Weibull modulus and characteristic strengths for these samples, as well as the untreated rods and related 1-step treatment samples were calculated and recorded in Table XIV. Compared to the untreated rods the 1 hour treatment showed the largest increase in characteristic strengths (131 MPa and 223 MPa respectively) of 70%, while the Weibull modulus decreased from 11.7 to 10.3. When compared to the 1-step Treatment A for 30 minutes at 580 °C rods the 2-step Treatment D samples decreased in strength, but had an increase in their Weibull moduli. For small times in this 2-step process the decrease in strength is insignificant, but still shows that there is no strengthening occurring during this process.

It is apparent from Figures 21-25 that the exchange of potassium and sodium ions from the bath for lithium ions in the surface is occurring, but rearrangement of ionic sites is happening simultaneously within the glass surface. These exchanges within the glass structure could include $Na^+ \rightarrow Li^+$, $Na^+ \rightarrow K^+$, $Li^+ \rightarrow Na^+$, $Li^+ \rightarrow K^+$, $K^+ \rightarrow Li^+$, and $K^+ \rightarrow Na^+$. If larger alkali ions are exchanging with smaller alkali ions then a compressive stress is produced. If smaller alkali ions are exchanging with smaller alkali ions then tensile stress (or reduced compression) are

produced and could account for the observed decrease of strengths during this process. These tensile stresses reduce the compressive stresses created at the surface layer during the ion exchange of sodium and potassium ions for lithium ions at short treatment times. Thus, the glass rods exhibit no strengthening during short times of exchange. As the treatment time lengthens the amount of defects and tensile stress' throughout the glass rods in the outer layer dominates the glass structure even though the compressive layer on the surface thickens.

Another possible explanation for the strengths of these glass rods is that during the exchange of ions throughout the rods experience a mixed alkali effect. This effect could lower the T_g of the surface layer, or layers at small distances in the glass rod. If the T_g is lowered to below 450 °C at any point within the glass rods then the structure is allowed to relax, and the build-up of stresses are annihilated. Thus, not allowing for compressive layers to form in the surface of the glass, and inhibiting the strengthening process caused by ion exchange.

SUMMARY AND CONCLUSIONS

Investigations into the first step high temperature ion exchange showed that the exchange of lithium ions in the bath for sodium ions in the glass surface diffused at a relatively constant rate. Schott AR-Glas® exchanged at 580 °C achieved depths of 45.5, 65, and 80 µm when exchanged with Treatment A for 10, 20, and 30 minutes respectively. The Treatment A high temperature exchange improved the glass' characteristic strengths by up to 86% when compared to the untreated samples, but decreased the Weibull modulus for all treatment times when compared to the untreated samples. The concentration profiles showed that the lithium ions in the Treatment A salt bath exchanged regularly with the sodium ions in the glass surface, but the potassium ions in the glass surface appear to have been effected minimally by the molten salt. This could be attributed to the mixed alkali effect, and high energy anion traps in which there is not enough energy for the lithium ions to exchange with the potassium ions.

The two-step ion exchange processes revealed the complex nature of ion exchange in mixed alkali silicate glasses. The two step exchange which used Treatment A at 580 °C for 30 minutes followed by Treatment C at 450 °C proved to provide the most significant increase in characteristic strength when compared to the untreated samples, with increases up to 160%. The two step exchange process described previously using Treatment B as the low temperature exchange also increased the characteristic strengths but only by up to 104% when compared to the untreated samples, and the Treatment D two-step process proved to be ineffective in strengthening rods any further than the first step process. The 100% NaNO₃ and 100% KNO₃ two-step exchanges proved effective for small times of exchange but as the rods were submerged longer showed signs of chemical attacking of the surface, and thus weakened the rods. These studies show, that although the rods did not show drastic changes in strengthening for longer times in the baths that included diatomaceous earth, It was confirmed that the addition of D. E. did help eliminate attacking of the glass surface.

The two-step concentration profiles provide adequate information to help decipher what is happening during the diffusion process. During the Treatment B two-step process investigated in these studies, it can be seen that the lithium and potassium ions are being exchanged for the sodium ions in the bath. The $\text{Li}^+ \rightarrow \text{Na}^+$ exchange results in a compressive stress in the surface,

and the $K^+ \rightarrow Na^+$ exchange resulted in tensile stresses in the surface. During small exchange times the compressive stress outweighed the tensile stresses and resulted in some strengthening of the glass rods. However, for longer exchange times the tensile stresses in the surface due to the exchange of sodium ions for potassium ions dominates the stress profile at the surface and causes the samples to weaken.

The concentration profiles for the Treatment C two-step exchange reveal a strange anomaly. The concentration profiles for potassium ions appear to follow a normal trend for smaller treatment times, where the depth of potassium increases with length of treatment time. However, for longer times, the exchange depth decreases. This is most likely caused by some sort of mixed alkali effect, and perhaps has something to do with the formation of high energy anion traps forming within the glass structure which do not allow for the potassium ions to travel any further into the glass. Also, the for long treatment times the sodium concentration reaches an equilibrium value which, as expected, is lower than the concentration in an untreated glass sample. The high concentration of potassium at the surface produces a high compressive layer in the surface which is shown by the strengthening of the glass rods during this exchange. But, the complex exchange of multiple alkali ions produces a multitude of compressive and tensile stresses, as well as defects in the glass, which halts the strengthening process for longer treatment times.

The Treatment D two-step concentration profiles show that the $Na^+ \rightarrow Li^+$ and $K^+ \rightarrow Li^+$ diffusion process appears regular. However, the strengths of the samples do not significantly increase during the process. This implies that the alkali ions are exchanging with each other in the surface of the glass, and that some structural defects are being formed. These defects result in tensile stresses that apparently overcome the expected compressive stress at the surface. Also, the mixed alkali effect may have some impact on the T_g of the glass surface, which may allow for some thermal relaxation to occur.

Ion exchange in mixed alkali glasses becomes amazingly complex. This study allows us to explain the first step high temperature exchange fairly well, although the mixed alkali effect on the exchange could still be further studied. Stress profiles, and concentration profiles of lithium in the surface of the glass would help further understand what is happening during this exchange. When studying the second step during the two-step exchanges, the concentration

gradients, and stress gradients in the surface make a proper assessment of the process near impossible. Once again stress profiles, and concentration profiles of lithium ions in the surface of the glass would help to explain what is truly happening during these exchanges. Also, studying the effect of different composition mixed alkali ions on the T_g , may help to show when and where in the glass is relaxing during the second step exchange.

In conclusion, the diffusion of alkali ions in mixed alkali glasses becomes a complicated system to study. However, the use of concentration profiles, and mass change of samples allows us to decipher some of the kinetic information of the system. There appears to be some phenomena occurring in these processes that can only be explained by the mixed alkali effect. Thus, the study of defects formed from the mixed alkali effect, as well as high energy anion traps in mixed alkali silicate glasses is needed to help aid in creating an exchange process that is successful in strengthening commercially available glasses effectively.

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