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Ion exchange glass strengthening using microwave processing

by

Ra’uf Tailony

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Master of science Degree in

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An Abstract of

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Current methods used for glass strengthening such as ion exchange processing have not been able to reach the maximum glass strengthening potential. Soda lime silicate glass has the potential to be strengthened to high levels exceeding 600 MPa of compressive stress on its surface. Applying ion exchange glass strengthening using microwave processing allowed us to reach compressive stress values exceeding 450 MPa in a short processing time of less than 30 minutes. Further comparison and optimization as well as combination between this method and old methods are studied in this thesis. We are trying to push the research of glass strengthening to a new level of fast, precise and efficient ion exchange strengthening method.
This work is dedicated to the mankind who are waiting the wind of change, to the scientists who are driven by curiosity and enthusiasm, to the researchers who can’t sleep well because of the questions waking them up in the midnights, for the people who are searching for the truth, who sacrificed their lives and times to build a better understanding of the world for the coming civilizations and generations.
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Table of Contents

Abstract iii
Acknowledgements v
Table of Contents vi
List of Figures viii
List of Symbols and Abbreviations x

I. Introduction 1
   1.1 Glass history 1
   1.2 Mechanical properties of glass 1
   1.3 Flashing and solution combustion 3
   1.4 Strengthening by ion exchange 4
   1.5 Motivation 6
   1.6 Objective 8

II. Literature review 9
   2.1 First successful ion exchange process 10
   2.2 Ion exchange process technique 10
   2.3 Pros and cons of ion exchange glass strengthening 11
   2.4 Factors affecting ion exchange efficiency 12
      2.4.1 Salt bath impurities 12
      2.4.2 Glass chemical composition 15
   2.5 Multistage ion exchange 16
   2.6 Stress relaxation 18
2.7 Diffusion
2.8 The physics of ion exchange process
2.9 The chemistry behind ion exchange process

III. Procedures and techniques

3.1 Silicate glass samples characteristics
3.2 Flash combustion thermodynamics
3.3 Salt bath chemical and thermal properties
3.4 Experimental procedures and techniques
  3.4.1 Salt bath impurities
  3.4.2 Salt bath impurities
  3.4.3 Salt bath impurities
  3.4.4 Salt bath impurities
3.5 Results and discussion
  3.5.1 Immersion in potassium nitrate results
  3.5.2 Clay coating effects on treated samples strength
  3.5.3 Microwaving of Coated potassium nitrite results
  3.5.4 Hybrid method results
3.5 Conclusions

References
List of Figures

Figure 1  Ion exchange process schematic. .................................................................11
Figure 2  Intensity of secondary ions - depth profiles. ...............................................14
Figure 3  Bend strength-concentration(mol%). ..........................................................15
Figure 4  Na, Li and K radii illustration. .................................................................17
Figure 5  Cation induced relaxation of (CIRON) network. .......................................22
Figure 6  Variation of the interdiffusion coefficient as a function of the mixed-alkali
          ratio covering the ion exchanged region. .......................................................25
Figure 7  Coordinate axis for stress development and diffusion during ion exchange. .27
Figure 8  Stress profile vs. concentration profile(10 Bars=1Mpa). ............................29
Figure 9  Subsurface compression maximum in ion exchanged soda-lime silicate
          glass. ........................................................................................................31
Figure 10 Alkali ions stuffing by ion exchange. .........................................................32
Figure 11 EDS line scan of sample(8) with with K ion exchange depth of 27.2 µm. ....35
Figure 12 Stress profiles for 23Na₂O.77SiO immersed in KNO₃ composition. ..........37
Figure 13 Float glass production line. ......................................................................38
Figure 14 Experimental glass cup dimensions. .........................................................40
Figure 15 Experimental sample dimensions. ............................................................40
Figure 16 Glass rod dimensions. .............................................................................41
Figure 17 Chemical structure of components in eq. (6). .........................................43
Figure 18 Chemical structure of components in eq. (7). .........................................44
Figure 19 Chemical structure of components in eq. (9). .........................................46
Figure 20 Glass cup immersed up side down in the glass beaker and solution. .......52
Figure 21  Glass cup fixed for polariscopic distribution and retardation testing using 
(S3/30) strain scope. .................................................................53
Figure 22  Clay coated glass cup for experimentation. ........................................55
Figure 23  Ceramic box covered with alumina foam for testing purposes. ..............56
Figure 24  Glass cup polarization analysis using strain scope. ..............................60
Figure 25  Preferable stress distribution along the sample surface. ..........................61
Figure 26  Light direction through sample surface in strain scope. ...........................63
Figure 27  Ca(NO₃) square glass sample after ion exchange treatment. ..................66
Figure 28  XRD result of Calcio-olivine created on sample after ion exchange process. 67
Figure 29  Clouding due to over treatment of KNO₂. ............................................69
Figure 30  Stress distribution of sample (11) in table (13), using polariscope. ..........69
Figure 31  K⁺ ions concentration for KNO₃ salt bath. ............................................70
Figure 32  K⁺ concentration – depth for KNO₃ salt bath. ........................................71
Figure 33  K⁺ ions concentration for KNO₂ salt bath. ............................................71
Figure 34  K⁺ concentration – depth for KNO₂ salt bath. ........................................72
Figure 35  Weibull plot for data in Table 15. ..........................................................73
Figure 36  Clay coated glass square and glass rod after microwaving treatment. .......75
List of Symbols and Abbreviations

MPa…………Mega Pascal
µm…………Micrometer
°C…………Degrees centigrade
°F…………Fahrenheit
pm…………Pico meter
mol %……..Molar percentage of material
γ………………The fractional exchange coefficient
α………………Thermal expansion coefficient
Ca^{+2}……Calcium ion
Sr^{+2}……Strontium ion
Ba^{+2}……Barium ion
KNO_3……..Potassium nitrate
KNO_2……..Potassium nitrite
Lb./Sq.In……Pound per square inches
CaO…………Calcium oxide
MgO…………Magnesium oxide
Tg…………..Glass transition temperature
CIRON……..Cation induced relaxation of the network
ESP…………Engineered stress profile
SLS………..Soda-lime silicate glasses
Chapter One

Introduction

1.1 Glass history

Glass is one of the most ancient materials found in nature dating back to 5,000 B.C. According to archeological evidence, the first glass made by man was in the eastern Mesopotamia and Egypt around 3500BC. In another 500 years, Egypt, Syria and other countries along the Mediterranean Sea coast became centers of glass manufacturing. The primary methods of manufacturing glass were slow and hard, due to the usage of the primitive furnaces. Glass production was focused on water storage bottles and water glass cups, and later expanded to reach the building aesthetics using stained and colored glass. It was a long journey for the glass until it developed to the way we see it today, but this journey did not end there. Modern glassmaking techniques still depend on energy to operate the glass melting furnaces. Current methods utilize gas and coal furnaces that are both time and energy consuming.

1.2 Mechanical properties of glass

Studying the glass in a systematic and scientific way started about 1880. The first attempts to study glass was based on the glassy nature, rather than the physical or chemical behavior. Scientist like Faraday and Kistler found it hard to define the state of the glass. The difficulty of understanding the state of glass is due to its brittle property [2,21]. The current theories describing glass properties focus on the glass in the solid state in studying it’s chemical and physical properties. The complexity of describing the glass
characteristics as a solid material is derived from the glass formation. By melting silica, alumina and other oxides using heat treatment. Heat treatment has a direct effect on the glass properties when it gets back to solid state after cooling down, the heat treatment and cooling down forms a glass with default internal flaws which become the starting point of fracture and glass structure failure under different loads [10]. The thermodynamical changes in the glass structure during meting process has an impact on the produced glass chemical properties. Researchers understand the effects of the heat treatment method used in glass processing on the properties of the produced glass, for example glass modulus of rupture and the expansion coefficient differ when treating a glass of the same composition and in the same experimental conditions, which emphasize on the study of the glass properties during forming [22]. Reaching the point of expressing and predicting the glass stress profile during forming and based on the glass treatment method gives us the ability to control the end product detailed properties of the glass as maximum surface compression, expansion coefficient, scratch depth and impact durability, these properties are formed during glass transition into solid state.

During glass solidification it’s structure rebuilds, resisting the forming stresses and the chemical compounds trying to reach the equilibrium position, which makes the glass solidify in a non uniform manner.

Griffith studied the relation between the defects and the brittle material strength (e.g. glass), and the effects of surface energy on defects propagation [25]. Glass strength depends on the flaws concentration and distribution along the surface, and based on Griffith conclusions, current chemical strengthening processes try to cover these flaws and prevent them from expansion, hence increasing glass strength.
Throughout this thesis we will focus on the chemical strengthening of glass using the ions exchange method, by applying a novel technique to enhance ion exchange diffusion time and efficiency, subsequently we will investigate the properties of the treated glasses and try to make reverse exploration of the stress formation behavior and suggesting the chemical and physical reasons that made the stress to behave the way it does. By studying the glass properties using electron microscopy, polariscopy, and other tests that helps in better understanding of the soda-lime silicate glass behavior related to chemical strengthening ions exchange process.

1.3 Flashing and solution combustion

This thesis is about investigating the possibility to replace the oven treatment of glass samples and performing the ion exchange process using microwave processing of glass. Even though the oven is a popular heating source in the ion exchange treatment of glass but it extends the processing time required to reach the activation temperature of the ions and waiting the samples to cool down after finishing the treatment. Microwave usage as a heating source is faster in reaching the activation temperature of ions which reduces the over all time of the process. Since the oven is used for 12 hours in average as an overall time of pre and post heating, which consumes a lot of power, and cost the glass manufacturers more money, side by side with the large containers of expensive salt baths used in this method. The microwave treatment of samples reduces the time of heat treatment because of the flashing phenomenon, while we are using KNO$_3$ as a salt bath, nitrates are working as oxidizers which leads to a combustion reaction, combining KNO$_3$ with auxiliary agents as Carbohydrazide leads the combustion reaction to reach higher adiabatic temperature($T_{ad.}$)
and reduces the treatment time required to complete the ion exchange process. Adiabatic temperature is known as maximum ignition temperature or flashing temperature, this temperature is controlled by balancing the valences of the oxidizer and the auxiliary agent (e.g. KNO$_3$ and Carbohydrazide).

Flash is achieved by combusting the solution by increasing its temperature using a heating source. Article temperature should be uniformly distributed in order to prevent any thermal shock to the sample during the process, but a controlled article heating near to the transition temperature heal the flaws on the glass surface leading to an increased strength of glass article.

The experimental method is performed by treating the glass in a microwave furnace. Optimizing the microwave treatment protocol, and understanding the chemical stoichiometry are two important parameters in optimizing the process of strengthening. Comparing the results we got in this optimization with the referenced results we got from the basic repetition of the old ion exchange method helped us in determining the level of success in our new flash combustion using microwave ion exchange glass strengthening.

1.4 Strengthening by ion exchange

Since the glass manufacturing is developed to meet the various needs of the daily use. There are always attempts to ensure that there is no premature fracture of glass. One strategy used in glass strengthening is glass tempering. This method depends on processing the glass in a thermally controlled treatment to increase its strength in comparison to normal glass, tempering changes the outer surface into compression and
the inner surface into tension, this method gives the glass the property to be stronger than the normal glass due to keeping flaws under compression.

Tempered glass is used in the automobile windows, different type of plates and cookwares, shower doors and refrigerator trays, this process can be performed on a glass with a minimum thickness of 0.3175 mm and a maximum thickness of 12.7 mm, in heat tempering process, glass substrate passes through a furnace, and heating up the glass for a temperature higher than its annealing point up to nearly 720 °C, and then quickly cool it down with a forced air drafts.

The second general method for glass strengthening is the chemical strengthening. Glass surface has a large number of flaws that are generated depending on the method used for glass manufacturing. These flaws can be observed when the glass is tested in the micro or nano scale, the flaws under tensile load become the start of crack propagation leading to glass fracture eventually, and the chemical strengthening of glass techniques are based on filling up these flaws or keeping them in compressive state in order to make the crack propagation slower and harder under different types of loads or impacts.

Chemical strengthening is basically an ion exchange process. Ion exchange is based on certain concepts, which are related to the ion behavior in certain chemical solutions. First condition for the ion exchange is that the pristine glass surface should contain a relatively large number of at least one type of alkali components as sodium, lithium, calcium or potassium.
Second condition is that the glass and the diffusing ions are both in a molten salt bath, at a temperature around the glass transition temperature and higher than the salt melting temperature in order for the ions to diffuse into the pristine glass surface.

Third condition is that when the reaction temperature is higher than glass transition temperature, larger diffusing alkali ions replace the smaller alkali ions in the glass structure (e.g. potassium ions replacing sodium ions). When the reaction temperature slightly lower than the glass transition temperature the smaller ions of the diffusing alkali ion replace the larger ions in the glass structure (e.g. lithium ions replacing sodium ions).

The scientific explanation of the ion exchange glass strengthening can be summarized as the following: When the larger ions replace the smaller ions in the glass surface, glass structure expands which makes the surface in compression state and as a result, tensile state is generated in the interior of the glass to balance the compression at the outer surface. In this thesis, we focused on strengthening of soda-lime-silicate glass using the ion exchange technique, because it has enough alkali ions in its composition.

1.5 Motivation

Ion exchange glass strengthening came as a substitution to the drawbacks of the glass tempering, since the glass tempering method have limitations to the type of glass that can be treated and limitations on the shape and thickness of glass needed to be strengthened, for example, thermal strengthening method has a mandatory condition for the glass geometry to be $\geq 2$mm in thickness, and for the mechanical properties of the glass to have a thermal expansion coefficient ($\alpha$) $\geq 4.5 \times 10^{-6} \, ^{\circ}C^{-1}$, on the other hand ion exchange glass strengthening method has almost no limitations, whereas it accepts all glass
compositions with alkalis, and can be applied for glass sheets with thickness < 2mm or glasses with large thickness values, it also can be applied to glasses with any shape, it doesn’t require to have the glass in a certain shape before starting the treatment, ion exchange can be done for glasses with thermal expansion coefficient almost zero; specially with the treatment of bulk glasses.

All the previous advantages of the ion exchange strengthening forced the industry to pay attention to it and make more research on the ions exchange method, and employing researchers to do reports and scientific models of a feasible and successful optimization of ion exchange method to be able to totally replace the thermal treatment from the industry and manufacturing processes or at least reduce it.

This thesis is concerned about the industry development of glass strengthening, which needs the ion exchange strengthening of glass using microwave processing to replace the heat treatment processes or reduce it, current research is focusing on the methodology used to make an efficient ion exchange process in a short time table, and getting the results equal to or better than the strength reached using regular thermal strengthening methods.

The importance of the microwave based ion exchange glass strengthening is in the reduction of cost of the strengthening processes, processing time needed, and the reduction of the power consumption using ovens, the new method of strengthening using the microwaves is durable and easy to be implemented in manufacturing processes.
1.6 Objective

In this thesis we are seeking to develop the strengthened glass using ion exchange technique. It is intent to reduce the process time and yet achieved enhanced strengthening by reducing the treatment time compared to the time used in other techniques, and in the same time enhancing the values of the glass strength compared to the values obtained by other researchers whom working on enhancement of this technique.

we have used the microwave treatment as a heating source for the flash reaction to take place, to reduce treatment time and enhance glass strength, and also using a hybrid microwave\oven technique to reduce the treatment time and increase the maximum compressive stress on the glass surface.

Ion exchange activation using the microwave power is not introduced in the prior art, which makes it a competitive field to study, specially because of the fast microwaves heating compared to the regular induction slow heating used in traditional ovens for glass manufacturing and treatment.
Chapter Two

Literature Review

Strengthening using chemical method is divided into four techniques:

a. **Etching technique:**

In this technique surface flaws and damaged areas are removed using chemical etching, chemicals used to form the etching solution are a dilution of aqueous solution of hydrogen fluoride, hydrochloride or Sulfuric acid. The solution leads to a reaction between hydrogen fluoride and glass, leading to removal of flaws from the glass surface or increasing the cracks tips radii [2]. Bulk glasses can be processed by this method and produce a mechanical strength over 1000 MPa.

b. **Thin coating technique:**

Thin coating is based on covering the glass surface with a chemical layer that has the ability to stick on the surface and protect it against any scratches or indentation. This makes the glass stronger. Some of the coating materials that are used for this method are Titania and tin oxide [4].

c. **Cladding technique:**

Coating the surface with a material that has lower expansion coefficient, put the surface under compression, and enhance glass strengthening.
d. Ion exchange technique:

As noted previously this thesis focuses on this technique in order to reach a higher strengthening values of the glass samples treated in our custom methodology. Hence this subject is described in details in the following.

2.1 First successful ion exchange process

“Chemical Strengthening” and nonspecifically “Ion Exchange Glass Strengthening”, was described as a successful strategy by Kistler [2] in 1962. The scientific paper described a detailed process of glass strengthening, and the main subject described was the inter-diffusion of ions effects on glass strengthening. It was reported that the glass strength is doubled and sometimes tripled, depending on the processing time of the glass article.

2.2 Ion exchange process technique

Ion exchange is performed in the industry using a large stainless steel container of molten salt at a temperature higher than melting point of the salt used in the reaction and lower than the glass transition temperature. As soon as the salt (e.g. potassium nitrate) reaches the glass surface at the high temperature of the oven, the potassium ions start to exchange with sodium ions on the glass surface as shown in Figure1. Potassium nitrate is one of the most common salts used by the industry in the ion exchange process. The glass articles are processed inside the stainless steel vessel for several hours (e.g. 2 hours to 12 hours), and the most widely used type of glass is the glass containing sodium or lithium silicates. This glass is dipped in the molten potassium nitrate at a temperature below the glass strain point [4,5].
2.3 Pros and cons of ion exchange glass strengthening

The drawbacks of the ion exchange glass strengthening was discussed in several papers [23,21], from different perspectives. The common drawbacks reported for the ion exchange process is the long processing time of the glass, which varies from 1 to 12 hours depending on the strength needed to be achieved and the types of alkalis involved in the exchange process. On the other hand researchers around the globe reported advantages of ion exchange process. Those include the independence on the shape of glass to be treated, no limitation on the thickness of glass, as well as no limitation on the thermal expansion coefficient. This led many companies in the industry getting involved in the field. They translated the technology in manufacturing air craft cockpit windshields, photocopiers glass, high strength-to-weight ratio glass containers and thin screens in the current communication devices [3].

1 source: PRELCO™ company website
2.4 Factors affecting ion exchange efficiency

2.4.1 Salt bath impurities

The efficiency of ion exchange process has a direct effect on the glass strengthening. The purity of the salt bath has a direct effect on the ion exchange process. Some researchers reported results showing the effect of the salt bath impurities on the surface glass network leads to unwanted outcome out of the strengthening process [7].

One of the reported solutions for the salt bath impurities in the prior art is the use of a very pure with high concentration salt in an ultra-clean stainless steel vessel which reduces the salt bath impurities and doubling the ion exchange efficiency, but these pure salts are economically not feasible, which pushed the researchers to find other solutions with low cost and the same efficiency.

Some researchers claimed salt impurities enhance the ion exchange efficiency, but this claim is not supported with a well defined experimental results or any measurable quantitative information about the mechanical and chemical methods used to reach that result [8].

The existence of certain alkalis and specially alkaline earths block and efficiency reduction of ion exchange is known in the prior art as a process poisoning. Zhang et al. discussed in depth the effects of impurities on ion exchange process in potassium nitrate molten solution, and they considered some alkaline earths as impurities since they block or reduce the ion exchange efficiency, Figure 2, specifically, the presence calcium ions in
the solution block the exchange process. Zhang et al. made a comprehensive test on the effect of different ions of alkaline earths on the ion exchange of potassium and sodium. They determined that the molar percentages of the alkaline earth at which the blocking effect starts, and their study had the conclusion that for calcium ions (Ca$^{2+}$) the effective percentage of blocking starts in the molten salt is (0.01 mol %). Other impurities that had blocking effect on the chemical glass strengthening process were Strontium (Sr$^{2+}$) and Barium ion (Ba$^{2+}$) but their required molar percentage needs to be higher, which means there should be more concentration of barium and Strontium in the salt bath to have a blocking effect, which is important to mention here (0.1 mol % for Sr and Ba ions, Figure(3)) [9].
Figure 2 above illustrates different compositions of NaO.4SiO glass and the profiles of different molar percentage of impurities on different depths and the related effect on potassium ions mobility. It is concluded that the ions of impurities with larger radius can strongly affect the diffusion even with small molar percentage as Ca, Ba and Sr ions as shown in Figure 3 below.

Figure 2: Intensity of secondary ions -depth profiles [9].
The calcium impurities affect the glass strength with a big reduction in strength compared to strontium and barium ions on the same molar percentage value, because the calcium ions block the diffusion of the potassium ions and divalent diffusion from taking place on the glass surface.

2.4.2 Glass chemical composition

Chemical composition of the treated glass has a direct effect on the ion exchange process itself, this phenomenon is reported by many researchers. They tried many different glass compositions with different percentage to evaluate the effect of each composition on the glass strengthening process.
2.5 Multistage ion exchange

Knowing that each ion exchange process has its own unique results depending on the properties of the ions being exchanged, researchers tried to do multistage ion exchange, combining the ions that gives best properties for the glass being treated [8,9].

One approach succeeded in glass strengthening using multiple alkalis ion exchange. This method is applied for Lithia-soda glass and for Soda-lime silicate glass. Sodium and potassium ions exist in the composition of the soda-lime silicate glasses. Glass composition have great importance and always considered a main factor for the ion exchange process success [8]. The alkalis being exchanged should be relatively in a high concentration with comparison to other glass compositions, this concentration determines how successful the ion exchange process will be. An exception to this rule when there are ions with high diffusivity, they can diffuse into the glass surface through the salt bath even with low concentrations. Specifically, ions with smaller atomic diameter are able to exchange easier even with lower energy, and providing deeper penetration in the surface of the glass than the ions with larger atomic diameter [8].

Multistage ion exchange is conducted in two steps. In the first, lithium nitrate(LiNO3) and potassium nitrate(KNO3) are melted in the same container and then the soda-lime-glass sample is dipped to the melted bath at a temperature lower than glass strain point. This leads to the exchange of lithium ions and potassium ions with sodium ions on glass surface. In the second step, treating the glass in the lithium salt bath and waiting until the glass is slowly cooled down. In this case lithium exchanged with the sodium ions, and subsequently dipping of the glass in a potassium nitrate bath results in the exchange of
potassium ions with the sodium ions on glass surface. It is noted that when we exchange the lithium ions with sodium, only the sodium ions on the glass surface are exchanged. Since the lithium ions ionic radii (0.076 nm) are relatively smaller than the sodium ions ionic radii (0.102 nm), Figure 4, the penetration and the case depth of the lithium ions is relatively high (about 50 microns). This means that the ion exchange occurs with the sodium ions on the deeper surface ions and replacing it with lithium ions, but the sodium ions on the top of the surface are going to be exchanged with the potassium ions which may double the glass strength by replacing a relatively large amount of sodium ions from the surface in order to reach the goal of leaving the glass surface in compression state.

Figure 4: Na, Li and K radii illustration.
Although most multi stage ion exchange is made for lithium based glass (e.g. Lithia-soda glass) by replacing the smaller lithium ions by a larger ions of sodium and potassium, but this method is still valid for other types of glass containing alkalis in their composition by doing the ion exchange process by changing one type of ions at a time, and doing the second level exchange after the glass surface is getting cold. The main factor in the experimental part of this exchanging process is the process temperature. If it is lower than strain temperature of glass, ions with larger ionic radius replace the ions with relatively smaller radius, and smaller ions replace relatively larger ions when the process temperature is slightly higher than the strain temperature [8].

Saunders et al. in their patent described a new conclusion that there is a customized glass composition that needs to be made before making the multistage ion exchange process and this customization enhances the ion exchange efficiency significantly and the glass strength as a result. One of the recommended compositions of the invaded glass by Saunders et al. are illustrated in the following table:

<table>
<thead>
<tr>
<th>Oxide component</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>44.38</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>26.61</td>
</tr>
<tr>
<td>Li₂O</td>
<td>5.04</td>
</tr>
<tr>
<td>Na₂O</td>
<td>11.0</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>9.96</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The author reported that this glass composition is used to make 4 inches by 4 inches by 1/10 of an inch thick glass samples, which are later dipped in a mixed alkali metal molten salt baths, consists of four molten salt types using one at a time, and the result was as described in the following table:
As seen in Table 2, the customized glass composition is treated with potassium nitrate molten salt bath at a temperature of (496 °C), and the treatment time is 30 minutes. This treatment led to a total compression layer depth of 18 microns, and surface compression value of 660 MPa. This result shows how important to keep the layer depth as low as possible. Since its known in the prior art that the large value of layer depth does not necessarily lead to a higher compression value but most of the time leads to stress relaxation. The reasons of having successful glass strengthening in this experiment was the potassium nitrate precise stoichiometry calculations, and reasonable treatment time, together leads to a high surface compression ratio.

Table 2: Four ion exchange treatment of customized glass samples [8].

<table>
<thead>
<tr>
<th>Molten Salt</th>
<th>Temperature of Ion Exchange, °F</th>
<th>Treating Time</th>
<th>Total Compression Layer Depth</th>
<th>Surface Compression, Lbs. per Sq. In.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO3</td>
<td>850</td>
<td>30 minutes</td>
<td>200 microns</td>
<td>60,000</td>
</tr>
<tr>
<td>KNO3</td>
<td>925</td>
<td>do</td>
<td>18 microns</td>
<td>96,600</td>
</tr>
<tr>
<td>KNO3+NaNO3, 8=1</td>
<td>875</td>
<td>do</td>
<td>215 microns</td>
<td>92,000</td>
</tr>
<tr>
<td>KNO3+NaNO3, 20=1</td>
<td>875</td>
<td>do</td>
<td>185 microns</td>
<td>98,900</td>
</tr>
</tbody>
</table>
2.6 Stress relaxation

The goal of glass strengthening is to reach as much high strength as the glass can withstand. However, as the researchers treated the glass at a higher temperatures and longer times, they tried to optimize the process by trying to find the perfect temperature and time ratio of treatment to get the highest strength of the glass. During the tests, they observed that the glass strength values reach a peak and then the strength goes down rapidly. This is known as stress relaxation. Stress relaxation is a non-uniform property that happens in a random fashion and at different extents. The fact that this relaxation does not happen in a certain constant manner makes it hard to explain the reason leading to this phenomenon, since the relaxation happens near the stress peak values and directly after the ion exchange process completion. The first explanation assumed that when the larger ions diffuse into the glass surface. The glass network restructures to create sites for the new ions. This restructuring process leads to elastic deformations caused by the departure of smaller ions and the arrival of larger ions on the glass surface. Other researchers added that the continuous plastic deformation taking place because of restructuring and readjustment of non bridging oxygens as well as displacement and bond bending of bridging oxygens causes these relaxations. This process of network relaxation is known as CIRON (Cation induced relaxation of the network). CIRON starts when the large ions invasion gets slower and the network relaxation begins, Figure 5 [10]. Stress profile is the descriptive tool for the glass strength, by increasing exchange time the surface compression decreases, but at the same time increasing the exchange time increases the depth of penetration for the diffused ions [10]. Since compressive layers are also generated by the difference in thermal expansion coefficient of the glass
composition, the thermal history of glass affects the possibility to have stress relaxation. The best procedure adopted by researchers to stay away from stress relaxation was by performing the ion exchange process relatively far from the transition temperature of glass and in the same time doing the exchange in a reasonable process time, in order to get the best results out of the strengthening process.
Figure 5: Cation induced relaxation of (CIRON) network [11].
As shown in Figure 5, in the microscopic region in the area of ion exchange, the bonds have the ability to stretch or bend in their elastic regions in order to contain the newly presented ions in the glass structure trying to make permanent stable place for these ions. Physically with this modification, the volume will increase but the glass structure adjust to change the volume to absorb the new ions but keeping the shape unchanged, and knowing that each component of the glass structure has its own elastic limit which is different than others, we can imagine how complicated is the prediction of the place of the new ions in the glass structure geometry.

2.7 Diffusion

The phenomenon of diffusion of ions and its kinetics inside the glass surface determines how deep ions can penetrate in the glass. Diffusion is the main factor of the ion exchange process. It is a measure of the ions mobility and interaction with the different constituents of the glass structure components.

Interdiffusion is the specific topic of diffusion and its mainly related to chemical strengthening of glass and more specifically in ion exchange chemical strengthening. Interdiffusion happens between the incoming ions and the ions on the glass surface and at the same time the diffusion of the landed ions in the glass structure. When the glass sample is immersed in a melt or a solution containing monovalent ions, these ions exchange with sodium ions in the glass. To understand the ion exchange and diffusion we should study the diffusion control of the rate at which exchange process takes place of ions on the glass surface [12].

In order to have a full descriptive explanation of the diffusion process, quantitative equations such as Fick’s equation, are important tools. When different species of atoms
participate in diffusion, an equivalent diffusion coefficient can be written as per the following formula:

\[
\bar{D} = \frac{D_1 D_2}{N_1 D_1 + N_2 D_2}
\]  

(1)

where, \( \bar{D} \): is interdiffusion coefficient, \( N \): is local ionic fraction.

Na-K ions interdiffusion coefficients in soda lime glasses during ion exchange are found to be nearly constant and independent of local concentration and exchange time [10]. Hence, equation (1) can be written as Na-K system :

\[
\bar{D} = \frac{D_{Na} D_K}{D_{Na} N_{Na} + D_K N_K}
\]  

(1')

where \( N_i \): is the fractional concentration of alkali ion i, and \( D_i \): is diffusion coefficient in mixed-alkali glass composition. Equations (1) and (1’) are known as Fick’s diffusion law and Nernst-Plank equation respectively.

It is known in the prior literature that the interdiffusion accelerates by the interior tension and slows down by surface compression. It is possible to have a relation between ions diffusion on glass surface and the stress relaxation.

Many researchers did experiments on different glass compositions and presented the results of the diffusion as figures in order to show different diffusion behaviors for
different ions being exchanged, as illustrated in Figure 6, [13]. The figure is describing the relation between the fractional exchange (\( \gamma \)) and the diffusion coefficient, where it is clear that there is a difference between the diffusion of the sodium (Na) and the potassium (K) ions and the interdiffusion between the exchanged ions.

![Figure 6: Variation of the interdiffusion coefficient as a function of the mixed-alkali ratio covering the ion exchanged region [13].](image)
This figure is generated by measuring the data of customized glass samples, some of them are mainly soda-lime silicate glass samples and others are sodium borosilicate glass samples.

2.8 The physics of ion exchange process

Stress is a physical property expressed as the main reason for the glass failures and cracks, in order to describe what strengthens the glass and what causes the glass fracture in the way it happens, we need to start from the physics of the glass structure and specifically from the stress build up and stress profiles related to manipulation of the glass with different glass strengthening processes.

Since the stress is a vector quantity in physics, we need to assume that we have an infinitesimal three dimensional cube that receives stress generation in three dimensions and strain effects in three dimensions in the same time, after that we use a mathematical model which has a descriptive equations to define the stress generation and behavior in a precise and repeatable way.

Let us assume that, we have a thin semi-infinite (in y and z dimensions) glass plate of thickness 2L, and the stress field at location x of the glass plate, as shown in Figure 7:
where, \( x \): is diffusion direction, \( E \): is young’s modulus, \( \nu \): is Poisson’s ratio, \( B \): is linear network dilatation coefficient. Where, \( B = \frac{1}{3V} \left( \frac{\partial V}{\partial C} \right) \).

The equation (2) assumes that \( (\sigma_{xx})_x = 0 \), we observe that the stress main factors affect the stress value in the direction assumed are \( B \) and \( C \). Recalling the equation of \( B \) and the

\[
(\sigma_{xx})_x = 0 \\
(\sigma_{zz})_x = (\sigma_{yy})_x = -\frac{BEC_x}{(1-\nu)} + \frac{1}{L} \int_0^L \frac{BEC_x}{(1-\nu)} \, dx 
\]

Figure 7: Coordinate axis for stress development and diffusion during ion exchange [14].
definition of $C$, we can say that the main factors affecting the stress distribution are the partial change of volume per unit exchange of concentration, and the ions concentration of the assumed direction [14].

After the assumption that $(\sigma_{xx})_x = 0$, the strains at location $x$ are given by:

$$\left(\varepsilon_{zx}\right)_x = \left(\varepsilon_{yx}\right)_x = 0 \quad (3)$$

where $(\varepsilon_{zx})_x$ is the strain in the $z$-$x$ plane in the $x$ direction, and $(\varepsilon_{yx})_x$ is the strain in the $y$-$x$ plane in the $x$ direction.

And

$$\left(\varepsilon_{xx}\right)_x = -\frac{v}{E} \left[\left(\sigma_{yy}\right)_x + (\sigma_{zz})_x\right] + BC_x = -\frac{2v}{E} \left[\left(\sigma_{yy}\right)_x\right] + BC_x \quad (4)$$

$$\left(\varepsilon_{zz}\right)_x = \left(\varepsilon_{yy}\right)_x = \frac{1-v}{E} (\sigma_{zz})_x + BC_x \quad (5)$$

The average elastic strain in $y$ and $z$-direction can be computed by integrating eq. (5) over the specimen width, which will be:

$$\frac{1}{L} \int_0^L BC_x dx$$

and in the same manner the net expansion in the $x$-direction from eq. (4) will be:

$$\int_0^L BC_x dx$$
After this physical review of the stress behavior in equations forms, we can comment that there is a relation between the stress magnitude and direction and the concentration of the ions in the salt bath or the glass surface. Varshneya et al. described the measured stress profile with the concentration profile as a function of depth in a sodium borosilicate glass, as shown in Figure 8:

![Stress profile vs. concentration profile](image)

Figure 8: Stress profile vs. concentration profile (10 Bars=1MPa) [13].

The Figure 8 shows that in the top compression area, the calculated stress profile has a relatively small shift from the concentration profile and differs largely in the tension area, so the stress profile can almost coincide with the concentration profile if we made a higher ions concentration and lower case depth for the ion exchange process with high
compressive stress value, which deserves to spend sometime on optimizing these parameters in the lab.

Concentration variation between the the measured and the calculated value (Figure 9) prevents scientists and lab experimenters from rising the level of the highest compression that could be reached in a short period of time. This difference prevents us from giving a fixed physical or mathematical model of the process, which keeps us away from the ultimate ratios for the best ion exchange results.
2.9 The chemistry behind ion exchange process

The process of ion exchange is related to chemical strengthening, using chemical molten salt baths with glass of a different compositions in order to enhance the strength of these glasses. Our focus is on the soda-lime silicate glass and trying to discuss the chemistry involved in the ion exchange strengthening by dipping a glass sample in the KNO$_3$ bath in an averaged temperature of 450 °C for a different periods of time.

As mentioned previously, chemical strengthening of glass depends on the compression magnitude and case depth generated during ion exchange process and in the same time depends on the initial flaws condition of the glass. The strengthening values presented by
compression magnitude and case depth can be controlled by the glass chemistry and the chemistry of the ion exchange medium, Figure 10. That means it is very important to carefully choose the chemistry of the bath used for the ion exchange process and the composition of the glass used to enhance its strengthening [14].

Silica glasses are difficult to be strengthened due to the low concentration of alkali ions exist in the glass composition, the soda-lime silicate glasses can achieve surface compression in the range of 350-700 MPa with case depth of nearly 50 µm using specially designed compositions, the case depth for soda-lime silicate glass is considered to be very small. In the case that the potassium ions diffuse into the surface to a deeper penetration of ions deeper than the case depth will result to compressive stress relaxation, for certain applications the case depth increase could be desirable, and this can be done
for the soda-lime silicate glass by replacing the CaO by MgO which could increase the case depth to 90 µm with a little sacrifice of the total strength [15].

Sinton et al. reported experimental data for many experimental compositions and the average depth achieved, and the impact of reducing the MgO or CaO percentage on the depth achieved (Table 3).

Table 3: Experimental compositions and the average depth of ions [15].

<table>
<thead>
<tr>
<th>Experimental Compositions</th>
<th>67.00</th>
<th>69.75</th>
<th>69.00</th>
<th>70.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td>CaO</td>
<td>4.50</td>
<td>5.25</td>
<td>5.75</td>
<td>5.75</td>
</tr>
<tr>
<td>MgO</td>
<td>7.50</td>
<td>8.00</td>
<td>7.50</td>
<td>7.75</td>
</tr>
<tr>
<td>Na₂O</td>
<td>17.00</td>
<td>15.25</td>
<td>14.50</td>
<td>15.50</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.75</td>
<td>1.50</td>
<td>3.00</td>
<td>0.50</td>
</tr>
<tr>
<td>Avg. depth (µm)</td>
<td>89.4</td>
<td>67.4</td>
<td>70.6</td>
<td>57.4</td>
</tr>
<tr>
<td>SD</td>
<td>1.3</td>
<td>0.4</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Number of analyses</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>

*24-hour treatment at 450°C.

Table 3 above describes that increasing the percentage of MgO and CaO together in the glass composition reduces the case depth, but the increase of the MgO percentage with the reduction of CaO percentage increases the case depth significantly.

In order to have a wide picture of comparison we need to include the float glass molar percentages and the average depth for that glass compositions, Table 4, describes the basic compositions and their related depth values, as follows:
for example, we consider glass number 8 from Table 4, CaO molar percent is 8.77 and MgO molar percent is 5.21, the average depth was 27.7 µm, considering the samples number 5 and 16 we observe that when the MgO molar content is reduced to almost zero and the CaO molar percent is increased around 10, it becomes clear that the average depth increases to around 40 µm, which confirms the assumption made before: that the increase of case depth is relative to the increase in CaO molar percent and the decrease of MgO molar percent in the glass composition.
In this thesis we are focusing on soda-lime silicate glass, and the most popular glass composition commercially used by weight percent as follows:

Table 5: Soda-lime silicate glass popular composition wt.%.

<table>
<thead>
<tr>
<th>Composition component</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>74</td>
</tr>
<tr>
<td>Na₂O</td>
<td>13</td>
</tr>
<tr>
<td>CaO</td>
<td>10.5</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.3</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.04</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Figure 11: EDS line scan of sample(8) with K ion exchange depth of 27.2 µm [15].
Industry usually goes from this basic composition and try to modify some components mass or molar percentage in order to get new and better properties for the glass produced. For example, increasing or reducing the alkalis percentage in the soda-lime silicate glass and studying the maximum strength that can be achieved by the chemical strengthening, or tuning the percentage of CaO and MgO and observing the diffusion depth of ions, or sometimes adding new constituents to the composition and observing the glass bioactivity or transparency or optical properties. These optimization efforts in the glass chemistry leads to innovative solutions for the glass uses in the daily life applications.

For the reason of having a better understanding of the ion exchange effects on the glass properties, scientists knew the importance of understanding the chemistry of the glass composition in details, the departure from the target compositions, and the ion exchange bath chemistry.

Experiments showed that glasses with low alkali concentration in their compositions such as pure silica or high silica glasses don’t reach acceptable strengthening values. This is because alkalis are the modifiers of the glass structure and the reason of the development of surface compression, in the same time glasses with low expansion have a poor strengthening ability [16].

Soda-lime silicate glasses are popular among glass scientisits due to their high tendency to strengthen exceedingly in the chemical strengthening treatment. This is because of having the content of Na2O molar percent of 13 to 15%, and because the composition of
glass allows exchange with invading K\(^+\) ions from KNO\(_3\) bath. Soda-lime silicate glasses have 350 MPa surface compression, and this value can reach 700 MPa in the customized composition designs, but the only drawback is the short case depth as mentioned previously, which makes it important to control the diffusing ions penetration depth, since deeper penetration than case depth leads to stress relaxation. Subsurface compression maximum always found in alkali silicate and soda lime silicate glasses, Figure 12.

![Stress profiles for 23Na\(_2\)O.77SiO immersed in KNO\(_3\) composition](image)

Figure 12: Stress profiles for 23Na\(_2\)O.77SiO immersed in KNO\(_3\) composition [18].

The chemistry difference that happens between the molten glass and the phase in contact with the glass have a strong effect on the overall glass properties, for example, the glass surface facing the air in the production line has different properties than the molten glass facing the container side [17], which is tin bath in some of the floating glass processes. If we take 23Na\(_2\)O.77SiO glass as an example and the tin bath as the medium for the ion exchange process of K\(^+\) and Na\(^+\) then there is a difference in the properties of the glass between the air side and the tin side which will eventually lead to wrap in the glass as shown in Table 6.
Table 6: Ion exchange strengthened SLS air versus tin surface compression and case depth measured by ellipsometry [18].

<table>
<thead>
<tr>
<th>Exchange Temperature</th>
<th>1.1 mm Substrate</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface Compression (MPa)</td>
<td>Case Depth (micron)</td>
</tr>
<tr>
<td></td>
<td>Tin</td>
<td>Air</td>
</tr>
<tr>
<td>A</td>
<td>488</td>
<td>501</td>
</tr>
<tr>
<td>B</td>
<td>453</td>
<td>466</td>
</tr>
<tr>
<td>C</td>
<td>382</td>
<td>394</td>
</tr>
</tbody>
</table>

Float glass processes are used to produce thin glasses for mobile screens applications and TV screens. The wrapping formation is a main problem in the manufacturing which makes the product useless for the applications designed for. As mentioned in Table 6, the surface compression of glass is varying between the air direction and tin direction and hence causing wrapping of the glass, Figure 13.

Figure 13: Float glass production line [19].
Chapter Three

Procedures and Techniques

3.1 Silicate glass samples characteristics

We used in our research and experiments soda-lime silicate glass composition, as supplied by Libbey glass Company, as shown in Table 7. We used glass samples of square shape Figure 14, glass rods, Figure 15, and glass cups, Figure 16, a more representative illustration of the samples can be extracted from the Figures 14, 15 and 16.

Table 7: Chemical composition of tested glass samples.

<table>
<thead>
<tr>
<th>Composition component</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>74</td>
</tr>
<tr>
<td>Na₂O</td>
<td>13</td>
</tr>
<tr>
<td>CaO</td>
<td>10.5</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.3</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.04</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Figure 14: Experimental glass cup dimensions.

Figure 15: Experimental sample dimensions.
3.2 Flash combustion thermodynamics

Successful ion exchange experiments require a correct stoichiometry calculations of used reactions. Glass composition has to be alkali based with sufficient alkali ions concentration in the glass composition. Glass transition temperature has to be determined since the exposure of a temperature higher than transition temperature leads to the relaxation of compression layer created on the glass surface as discussed in the literature review, part (2.6). Another important part in glass strengthening reactions is related to the chemical and thermal calculations of the salt bath. In all the following experiments we use mainly two salt baths, Potassium Nitrate (KNO₃) with Carbohydrazide (CH₆N₄O) and Potassium Nitrite (KNO₂) with Carbohydrazide (CH₆N₄O), and in the same time we introduce two new experiments in which we used the Calcium Nitrate(CaNO₃)₂ with Carbohydrazide (CH₆N₄O), as well as Lithium Nitrate (LiNO₃) with Carbohydrazide (CH₄N₂O), (CaNO₃)₂ and (LiNO₃) salt baths are introduced because of the large ionic
radius of $\text{Ca}^{2+}$ and the small ionic radius of $\text{Li}^+$. Comparing the behavior of diffusion for these two ions helps us predicting the behavior of the $\text{K}^+$ ions in treatment process, as it is discussed in results section.

Potassium Nitrate salt bath is popularly used by researchers and the industry in the glass strengthening field. The method is the same but the stoichiometry and salt baths used differ, based on the glass composition and the application of the glass. In our experimentation we use Carbohydrazide ($\text{CH}_6\text{N}_4\text{O}$) as an auxiliary factor (reaction fuel) with the Potassium Nitrate ($\text{KNO}_3$). The basic balanced equation of the reaction of Potassium nitrate and Carbohydrazide is shown in eq. (6).

$$8 \text{KNO}_3 + 5 \text{CH}_6\text{N}_4\text{O} \rightarrow 4 \text{K}_2\text{O} + 5 \text{CO}_2 + 14 \text{N}_2 + 15 \text{H}_2\text{O} \quad (6)$$

eq(6) interpretation and materials phases:

Potassium Nitrate (solid) + Carbohydrazide (solid) $\rightarrow$ Potassium Oxide (aqueous) + Carbon Dioxide (gas) + Nitrogen (gas) + Water (liquid)

Based on balanced equation (6), molar ratio of Potassium Nitrate to Carbohydrazide are 8:5. The mass ratios in grams of Potassium Nitrate to Carbohydrazide are 808.8 : 450.4.

Molar ratios and mass ratios are determined depending on the scale of the experiment, in our case the standard mass of the reactants depending on the molar ratios, as illustrated in Table 8.
Table 8: molar and mass ratios of reactants in eq. (6).

<table>
<thead>
<tr>
<th></th>
<th>KNO₃</th>
<th>CH₆N₄O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar ratio</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Mass ratio (grams)</td>
<td>808.8</td>
<td>450.4</td>
</tr>
<tr>
<td>Molar ratio²</td>
<td>0.0297</td>
<td>0.019</td>
</tr>
<tr>
<td>Mass ratio (grams)</td>
<td>3</td>
<td>1.7</td>
</tr>
<tr>
<td>Tₐd.(°C)</td>
<td></td>
<td>605</td>
</tr>
</tbody>
</table>

Both reactants in eq.(6) are soluble in water, and the solubility in water of the reactants, specially KNO₃ is important because we need to free the potassium ions K⁺ in order to be able to invade the glass structure and accomplish the ion exchange successfully, as shown in the chemical structure of eq.(6), Figure 17.

![Chemical structure of components in eq. (6).](image)

K⁺ ions and NO₃⁻ ions in water are free to make a new bonds with other components, as we observe in the products in eq. (6), the K⁺ ions made a new two monovalent bonds with oxygen, which is more satisfactory for the mobility of the K⁺ ions in the ion exchange.

² ratios are based on 100ml of water as a reaction medium.
process temperature, so its easy for potassium ions to break the monovalent bond and have high mobility to invade the glass surface.

Another salt bath used in our experiments is the Potassium Nitrite (KNO₂) and Carbohydrazide (CH₆N₄O), since both reactants have a good solubility in water at room temperature, some of the experiments we run was made in water medium in order to assure that all ions has a carrying medium to pass through it to the glass surface making the ion penetration. The stoichiometry of the KNO₂ with CH₆N₄O are shown in the balanced equation (7).

\[
8\text{KNO}_2 + 3\text{CH}_6\text{N}_4\text{O} \rightarrow 4\text{K}_2\text{O} + 3\text{CO}_2 + 10\text{N}_2 + 9\text{H}_2\text{O}
\]  

(7)

interpretation and material phases are similar to the reaction of KNO₃ with Carbohydrazide, and its as following:

Potassium Nitrite (solid) + Carbohydrazide (solid) \(\rightarrow\) Potassium Oxide (aqueous) + Carbon Dioxide (gas) + Nitrogen (gas) + Water (liquid)

The only different thing is the molar and mass ratios, as well as the over all melting point for the salt bath in the ion exchange process.

Reactants and products chemical structures described in Figure 18. The products have two potassium ions bonded in monovalent manner with O₂.

![Figure 18: Chemical structure of components in eq. (7)](image-url)
The molar ratios and molar masses of the reactants are used to determine the amount of reactants required to have a complete reaction, Table 9.

<table>
<thead>
<tr>
<th></th>
<th>KNO₂</th>
<th>CH₄N₄O</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molar ratio</strong></td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td><strong>Mass ratio (grams)</strong></td>
<td>680.8</td>
<td>270.3</td>
</tr>
<tr>
<td><strong>Molar ratio /100ml H₂O</strong></td>
<td>0.0353</td>
<td>0.0132</td>
</tr>
<tr>
<td><strong>Mass ratio (grams) /100ml H₂O</strong></td>
<td>3</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>T_{ad}(°C)</strong></td>
<td></td>
<td>620</td>
</tr>
</tbody>
</table>

The goal of these reactions stoichiometry is to find the optimum optimization of the mass ratios compatible with the glass composition to have the highest compression layer on the glass surface with out having any relaxation in the stress, since the compression layer is developed because of the structure modifiers (Alkalis) introduction in the glass composition based on the alkalis ion radii, we tried to determine the peaks of the experiment by using relatively large alkali ions penetration in the glass surface (as Calcium) as well as relatively small alkali ions penetration (as Lithium), in this case we have the maximum and minimum point of compressive stress which our glass can withstand regardless to the efficiency of the process. Following is the balanced chemical equations of Calcium Nitrate with Carbohydrazide, and Lithium Nitrate with Carbohydrazide, eq.(8) and eq.(9).
\[ 8\text{Ca(NO}_3\text{)}_2 + 11\text{CH}_6\text{N}_4\text{O} \rightarrow 4\text{CaO} + 11\text{CO}_2 + 30\text{N}_2 + 33\text{H}_2\text{O} \]  \hspace{1cm} (8)

\[ 8\text{LiNO}_3 + 5\text{CH}_6\text{N}_4\text{O} \rightarrow 4\text{Li}_2\text{O} + 5\text{CO}_2 + 14\text{N}_2 + 15\text{H}_2\text{O} \]  \hspace{1cm} (9)

The molar and mass ratios of reactants in equations (8), (9), are illustrated in Table 10, these data will be a reference to the ion exchange process thermal properties when discussed in the following section (3.3).

\[ \]

**Table 10: Molar and mass ratios of reactants in eq. (8,9).**

<table>
<thead>
<tr>
<th></th>
<th>(\text{Ca(NO}_3\text{)}_2)</th>
<th>(\text{CH}_6\text{N}_4\text{O})</th>
<th>(\text{LiNO}_3)</th>
<th>(\text{CH}_6\text{N}_4\text{O})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic molar ratio</td>
<td>8</td>
<td>11</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Experimental molar ratio</td>
<td>0.006</td>
<td>0.008</td>
<td>0.015</td>
<td>0.009</td>
</tr>
<tr>
<td>Experimental mass ratio(g)</td>
<td>1</td>
<td>0.75</td>
<td>1</td>
<td>0.82</td>
</tr>
</tbody>
</table>

The chemical structure of equation (9) is in Figure 19, indicating the bonds formed between lithium ions and oxygen compound.

\[ \]

**Figure 19: Chemical structure of components in eq. (9).**
3.3 Salt bath chemical and thermal properties

After determining the stoichiometry, the salt bath preparation needs some thermal estimations. These thermal estimations are based on the thermal properties of each compound participating in the ion exchange process (e.g. the melting point of the reactants, transition temperature of glass, ions radii, ions mobility and the oven set temperature). These factors determine the melting temperature of the salt bath system. In the case of using microwave heating, the determination of the microwave power and radiation flux determine the final heat on the treated glass surface.

Table 11, includes all the chemical and thermal properties needed for the determination of the range of temperatures used to make successful ion exchange.

<table>
<thead>
<tr>
<th></th>
<th>Melting point(°C)</th>
<th>Boiling point(°C)</th>
<th>Solubility in water @ 20 °C</th>
<th>Transient temperature(Tg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO₃</td>
<td>434</td>
<td>400</td>
<td>316g/L @ 20 °C</td>
<td>-</td>
</tr>
<tr>
<td>KNO₂</td>
<td>440.02</td>
<td>537</td>
<td>312g/100 ml @ 25 °C</td>
<td>-</td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>561</td>
<td>132</td>
<td>1212 g/L @ 20 °C</td>
<td>-</td>
</tr>
<tr>
<td>LiNO₃</td>
<td>255</td>
<td>600</td>
<td>52.2g/100ml @ 20°C</td>
<td>-</td>
</tr>
<tr>
<td>CH₆N₄O</td>
<td>154</td>
<td>-</td>
<td>very soluble</td>
<td>-</td>
</tr>
<tr>
<td>Glass(customized)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>560 °C</td>
</tr>
</tbody>
</table>
The first technique used in ion exchange, by immersing the glass cup up side down in a glass beaker filled with 100 ml of water, and the first stoichiometry used was Potassium nitrate with Carbohydrazide, eq. (6), and the decision of the set temperature of the oven to start the ion exchange process was based on the data extracted from Table 10, and in the same time based on the understanding of ion exchange itself, where the invading ions of potassium need to released from the bond with nitrate, and it’s done by reaching the melting point of the potassium nitrate. Since potassium nitrate and Carbohydrazide melting points are 434 °C and 154 °C respectively, and the transient temperature of the used customized glass is 560 °C, then the most convenient temperature at which salt bath melts and below the glass $T_g$ is 500 °C, Table 12 summarizes the oven chosen temperature for all of the salt baths used in our experimentation based on this logic.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T_{oven}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{KNO}_3 + \text{CH}_6\text{N}_4\text{O}$</td>
<td>500</td>
</tr>
<tr>
<td>$\text{KNO}_2 + \text{CH}_6\text{N}_4\text{O}$</td>
<td>509</td>
</tr>
<tr>
<td>$\text{CA(NO}_3)_2 + \text{CH}_6\text{N}_4\text{O}$</td>
<td>580</td>
</tr>
<tr>
<td>$\text{LINO}_3 + \text{CH}_6\text{N}_4\text{O}$</td>
<td>470</td>
</tr>
</tbody>
</table>

Since some of these reactions are highly exothermic, before doing any experiment with these salt baths we made adiabatic temperature calculations using (HSC-Chemistry) software, these calculations of $T_{ad}$ was a useful tool to predict how aggressive the reaction will be, before we actually start it.
One note about Table 12 values, the melting temperature of Calcium nitrate is slightly above the $T_g$ of our glass, even though we proceeded to do the experiment on 580 °C to study the behavior of glass surface with Calcium Nitrate.

As mentioned previously we kept in our consideration the ionic radii and the mobility of the invading ions, which helped us massively in deciding and predicting the best ion that can invade and penetrate the glass surface successfully, related data extracted from SEM analysis of the treated samples, presented in Table 13.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Effective ion radius(nm)</th>
<th>Max. depth(µm)</th>
<th>Mobility (Relatively)$^3$</th>
<th>Min. Penetration time(min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$^+$</td>
<td>0.138</td>
<td>30</td>
<td>slow</td>
<td>60</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.100</td>
<td>40</td>
<td>intermediate</td>
<td>45</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.760</td>
<td>60</td>
<td>fast</td>
<td>20</td>
</tr>
</tbody>
</table>

As mentioned in section (2.5) in chapter 2, the smaller the ion the higher the mobility in the melted salt bath [8], but in some cases the behavior of the ion inside the glass structure and the modifications in the chemical structure leads to unsatisfactory results on the glass sample. After comparing the results of the exchange of each of these ions with the glass sample, we could decide to keep using this ion for exchange and optimize the process or trying another ion diffusion.

$^3$ Mobility is compared between K$^+$,Ca$^{2+}$ and Li$^+$ relative to each other.
3.4 Experimental procedures and techniques

Many procedures and techniques are used during the research in order to reach the optimum compressive stress on the surface of the glass, the compressive stress on the glass surface is measured using strain scope (ilis S3/30 strain scope) as a function of retardation (nm). Optical retardation is another representation of stress, it is a method of finding stress using light behavior observation while passing through stressed sample, the conversion of optical retardation (nm) to stress (MPa) can be done using the following equation:

\[ \sigma = \frac{\delta}{t \times C_B} \]  

(6)

Where, \( \sigma \) is stress in MPa, \( \delta \): Optical retardation (nm), \( t \): sample thickness (cm), \( C_B \): Stress optical constant (brewsters).

For Soda lime silicate glass \( C_B = 2.83 \) brewsters, and illumination wave length = 596 nm, using these values and eq. (6) we can find the stress values in MPa corresponding to the optical retardation, by using eq. (6) the maximum compressive stress value is 58 MPa.

We used the ultrasonic cleaner (KENDAL HB-48248T) with ionized water for samples cleaning. For heating treatment, we used a (FISHER SCIENTIFIC) oven with a maximum temperature of 1500 °C. In our experiments we focused on the treatment of the glass rim (3cm from the glass top) since the strain scope can provide the stress generated on that area.
3.4.1 Direct immersion of samples in salt bath-water solution

This is the first method we used to treat the glass samples by immersing the glass cups, glass rods and glass squares in the solution, as in the following detailed steps:

(a) Measure (3 grams) Potassium Nitrate and Carbohydrazide (1.7 grams).
(b) Pour the powder mix of potassium nitrate and carbohydrazide in a glass beaker with 100 ml of water.
(c) Place the glass beaker on the stirrer at room temperature at Stirring speed of 120 RPM for 15 minutes.
(d) Make sure that the powders are totally dissolved in water, and clean up the glass cup with ionized water and in the ultrasonic cleaner then Place the glass cup, Figure 14, up side down in the solution, Figure 20.
(e) Place the glass beaker in the oven after making sure its temperature is (500°C) for 1 hour.
(f) Set the oven temperature back to (100°C) and wait until the sample cools down.
(g) Clean up the sample with ionized water and let it dry in the oven at (100°C), then make the stress tests.
This method can be used for any powder salt bath which is soluble in water. However, there are two drawbacks. First, since the water starts to evaporate from the solution, the steam pushes up the cup violently, by the accumulated water vapor which makes the cup jumps tens of times, thus if the cup temperature is high we found many samples broken after the ion exchange process is finished. Second, this method makes the oven a pressurized container which could damage the oven if there is no pressure relief in the oven setup.
The testing method for the glass retardation and stress using strain scope is done by fixing the glass cup upside down over a sensory rod immersed in thick photo reflective liquid to enhance the polar results, Figure 21.

![Figure 21: Glass cup fixed for polariscopic distribution and retardation testing using (S3/30) strain scope.](image)

### 3.4.2 Clay coating of glass samples

This method is more reliable because there is a problem in placing the sample in the oven in a stable position. Coating the sample with a clay that is saturated with salts assures the ion exchange in the area of the coating, and thin coating of clay will stay on the sample surface even with high treatment temperatures which holds the ionic mix at the right place to start the penetration in the glass surface. In this method we used commercial clay (5grams), then mixed it with (15 ml) of salt bath-water solution, where salt bath-water solution is made highly saturated. The detailed steps are as the following:
(a) Clean the samples in ionized water and ultrasonic cleaner.

(b) Prepare (3 grams) of Potassium Nitrate powder and (1.7 grams) of Carbohydrazide.

(c) Pour the powder mix in (15 ml) of water and leave it on the stirrer for 15 min.

(d) Mix (5 grams) of clay with the solution until it looks homogeneous and a little thick.

(e) Coat the area of interest of the sample (glass cup rim or sample surface) with a thin layer of clay, Figure 22.

(f) Place the coated sample in the oven at (500 °C) for 1 hour.

(g) Turn the oven off and wait for the sample to cool down.

(h) Clean up the dry clay on the sample surface, then clean it again with acetone and dry it in the oven at (100 °C).

(i) Test the sample in a mechanical testing machine.
This method is an improvement over the immersion method. It is more precise than the immersion method and applicable for all the previously mentioned salt baths in eq.(6,7,8). The only drawback of this method is the difficulty to clean the clay if the sample is treated at a high temperature. Which could cause surface scratch during the hard cleaning of the sample.

3.4.3 Ion exchange using microwave processing

This method is not popular in the prior art, we are generating a new way of glass treatment with ion exchange process that is using microwave furnace as a heating source. Flash combustion is new, but microwave processing is even better when combined with flashing, it is fast, safe and time efficient. The average time needed to reach the set
temperature of the process is between 1 to 3 minutes with exposure time of the sample between 10 to 15 minutes, this method is designed by our research team, and most likely will be the future of the ion exchange processing.

The microwave which is used for samples treatment in this method is (Panasonic 1200) with a power of 1200 Watt, and with customizable microwave power in a scale from 1-10, we also used our customized ceramic box that is covered with aluminum foam for keeping the sample safe from a thermal shock during testing the sample temperature, Figure 23.

Figure 23: Ceramic box covered with alumina foam for testing purposes.
Treatment initial steps are the same as the clay coating method, and they are as the following:

(a) Clean the sample in ionized water and ultrasonic cleaner.

(b) Prepare (3 gram) of Potassium Nitrate powder and (1.7 grams) of Carbohydrazide (or following mass ratios in tables (8,9) for other salt bath usage).

(c) Pour the powder mix in (15 ml) of water and leave it on the stirrer for 15 min.

(d) Mix (5 grams) of clay with the solution until they look homogeneous and a little thick.

(e) Coat the area of interest of the sample with a thin layer of clay.

(f) Place the coated sample in the ceramic box and put them in the microwave and set the timing to 10 minutes, after 2 continuous minutes stop the microwave and make sure the glass surface is reaching the process designed temperature, after 15 seconds run the microwave again with pausing every 15 seconds for 2 seconds, and so on until you finish the 10 minutes.

(g) When the microwave exposure is finished keep the sample in the microwave at least 3 hours to make sure that the sample is cooled down.

(h) Clean up the dry clay on the sample, then clean it again with acetone and dry it in the oven on (100 °C).

This method is fast and reliable. But as seen in step (f) above, turning the microwave on and off every certain time is a manual way. To have a better control and sustainability of the sample temperature. This method would make a better results if it has a full controlled
microwave system, so the experimenter will be sure that the glass sample exposure to the same pre designed temperature during the treatment. Another issue about this method is the flashing of the exchange process. During the microwave exposure of the sample we observed flashing happens every time we treated sample in the microwave, and this flashing is because of arcing between microwaves and evaporating substances, so a better understanding of microwave based exchange process is based on a better involvement in the concept of the microwaving technologies and systems.

3.4.4 Treatment using hybrid heating source

We gave the nomenclature of hybrid for the samples treatment in the oven for a certain time and in the microwave after that or vise versa. For a few samples we used this method, which is based on heating the sample after salt bath treatment using a combination of microwave and oven. This method consists of two steps. First, we heated up the coated samples in the microwave for 3-5 minutes at the ion exchange set temperature (Table 11), and then transferring the sample into the customized box with pre wrapped alumina foam (Figure 23) to protect the sample from thermal shock, and put in the oven at the exchange temperature for a time 50% shorter than the time of exposure used when the sample is treated with oven only.

Another way we followed to apply this hybrid method, by heating up the sample in the oven for 40% of the treatment time using the microwaving box covered with foam (Figure 23) and transferring the setup to the microwave and treating the sample in microwave for 6 minutes.
The fact that some samples have a strain history caused by the manufacturing process of the glass, some samples needed longer times in the heating source to have a relatively high compressive stress value. Therefore, the microwave accelerates the exchange process, and modify the sample surface stress to the required value within a reasonable time period.

This method a solution to the problem of uneven distribution of the microwaves over the sample, so transferring the sample from the microwave to a uniform heating source as the oven distributes the stress evenly on the glass surface.

3.5 Results and discussion

In this section we present the data gathered from different testing protocols and compare the results of the samples treated using the previously discussed methods and techniques, in order to have a better understanding of the best method that should be used and applied in the industry to make a better and more reliable glass products in the near future.

We tested samples on different testing instruments. Our goal was to compare the maximum stress that can be gathered using our technique and finding the best optimization of time-temperature-stress relations to have higher value of compressive stress on the glass surface. The goal is to evaluate either to continue using this method or switching to another method or adjusting our technique in the same method.

3.5.1 Immersion in potassium nitrate results

After the preparation of the Potassium Nitrate with Carbohydrazide in 100 ml of water and immersing the glass samples in it. Following the detailed procedure discussed in
section (3.4.1), we need investigate the stress distribution on the glass sample as a quantitative value in a comprehensive manner rather than precise numbers of stress. In order to do so we used Strain Scope to give us the polarization of the glass surface and measuring the optical retardation with respect to sample thickness, and an example of the result is shown in Figure 24.

![Glass cup polarization analysis using strain scope.](image)

In Figure 24, the blue line represents the tension on the surface and yellow line represent the compression, in this sample its obvious that the result we obtained is not satisfactory because the tension is massively concentrated on the outer side of the glass and continues to reach the inner side of the glass as we go toward the glass cup base. At the same time only a small portion on the top layer on the inner side of the glass rim has tensile stress and the over all stress distribution is not in equilibrium. This means that the glass is not
strengthened. The value of retardation for this sample was (46nm) which is relatively low as expected from the polariscopic stress analysis.

The optical retardation of glass sample is an optical reading of the stress. In our case we are seeking a higher compressive stress on the surface, subsequently a higher negative retardation value. We are trying to achieve equilibrium between the compressive stress and tensile stress by blocking the tensile stress in the middle of the glass cup between two compressive stress layers on the maximum outer surface of the glass cup and on the minimum of the inner surface which leads to higher glass total strength, as illustrated in Figure 25.

![Figure 25: Preferable stress distribution along the sample surface.](image)

The results of retardation values for the samples treated using the immersion method are represented in Graph 1. The overall result of using KNO₃ as a salt bath was not
reasonable, usually this method is used in the glass industry for average treatment time of 12 to 48 hours in order to reach an acceptable stress value.

Graph 1: Optical retardation-thickness of sample perpendicular to light path.

Optical retardation is the main representation of stress being tested using strain scopes and polariscopic devices, where it is a reflection of light behavior through the target sample, which exposed to light that passes perpendicular to its surface, Figure 26. The delay and scattering of the light is due to the stress built up in the surface. Graph 1 represent the values of 10 samples being averaged based on the stress position in the sample surface.
The main focus of this thesis is on the methods of strengthening glass using clay coating, microwave processing and the combination of these two methods (Hybrid method). As we discussed earlier in this chapter, the method of sample immersion in the salt bath is not time efficient, so when used for processing time of 2 hours or less, the resultant compressive stress will not be fulfilling, the samples results shown previously in Graph 1 confirms this conclusion.

3.5.2 Clay coating effects on treated samples strength

Clay is a convenient choice for treatment. When it is mixed with the salt bath it acts as a carrier and holder for the salt on the surface of the sample during treatment. We applied clay coating method on KNO₃, KNO₂, Ca(NO₃)₂ and LiNO₃ using the method steps described in sec 3.4.2 , and we optimized the process time and oven temperature +/- 50
°C based on the feedback of the retardation values in order to avoid the relaxation temperature.

Table 14, shows the salt bath used, oven temperature and the retardation related to each salt bath treatment.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Salt Bath</th>
<th>Water(ml)</th>
<th>Clay(g)</th>
<th>Process Time (min.)</th>
<th>Oven T(°C)</th>
<th>Retardation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KNO₃+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>20</td>
<td>470</td>
<td>-27</td>
</tr>
<tr>
<td>2</td>
<td>KNO₃+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>-78</td>
</tr>
<tr>
<td>3</td>
<td>KNO₃+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>500</td>
<td>-41</td>
</tr>
<tr>
<td>4</td>
<td>KNO₃+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>-50</td>
</tr>
<tr>
<td>5</td>
<td>KNO₃+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>120</td>
<td>470</td>
<td>-87</td>
</tr>
<tr>
<td>6</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>500</td>
<td>-68</td>
</tr>
<tr>
<td>7</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>-78</td>
</tr>
<tr>
<td>8</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>-87</td>
</tr>
<tr>
<td>9</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>-106</td>
</tr>
<tr>
<td>10</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>120</td>
<td>470</td>
<td>-117</td>
</tr>
<tr>
<td>11</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>120</td>
<td>470</td>
<td>-132</td>
</tr>
<tr>
<td>12</td>
<td>LiNO₃+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>-39</td>
</tr>
</tbody>
</table>

We learned from Table 14 that changing the process time slightly, changes the stress value significantly, we treated tens of samples but, in this table we present the samples with representative values, and the samples which has impact on our optimization for the ultimate successful exchange process. The first two values of KNO₃ salt bath are treated 20 minutes and 1 hour respectively, we can see the value of retardation and stress build up is doubled in a non linear way, mean while Graph 2, shows the retardation values, where it is larger using the clay for KNO₃ than using the immersion method, even the

4 Optical retardation (-) sign is a directional sign representing stress compression.
experiment conditions as processing time and salt bath ratios are the same specially for
samples number(2) and (5). Having retardation value larger than 80 nm in treatment time
less than 2 hours is promising to the success of clay method in increasing the efficiency
of the ion exchange process.

![Graph 2: KNO₃ retardation values representation.](image)

On the other hand, when we treated Lithium Nitrate, the retardation values of LiNO₃ did
not exceed 50 nm (compression) in 5 treated samples between 1 and 2 hours and caused
clouding on the sample surface after 30 minutes of treatment. Such a salt is not pursued
further. Any salt bath that exceeds 70 nm compression retardation after 1 hour treatment,
could have a potential to give a better compressive stress value with more optimization in
the process, otherwise the salt bath can not be successful in the current setup we are using
in our testing and experimentation.
As expected previously Ca(NO$_3$)$_3$ excluded from our treatment salts versus KNO$_3$ and KNO$_2$, since the Calcium Nitrates has a melting temperature higher than the T$_g$ of our glass, it will not lead to any good strengthening results, values of optical retardation did not exceed 40 nm in compression, but it worth to mention that the square glass samples treated using clay in oven at 580 °C had a crystalline material on part of the surface, Figure 27. We investigated this material using XRD device (Rigaku XRD with SAXS) and the result as shown in Figure 28.

![Figure 27: Ca(NO$_3$)$_3$ square glass sample after ion exchange treatment.](image-url)
XRD analysis shows a new material formed on the glass sample surface which means we exceeded the T_g of the glass, due to that calcium formed a crystalline material, this means glass surface is becoming crystalline composite, known as glass-ceramic formation.

Our choices on this stage of research are narrowed to either we choose KNO_2 or KNO_3 with Carbohydrazide, for a better comparison between the two salt baths we represented the retardation data with a graph representing the compressive stress values in nm produced by coating the glass with the mix of these salts with clay, each salt bath separately, Graph3.
The dominant values in Graph 3 are the values of KNO$_2$ salt bath, potassium nitrite has a large potential to increase the compressive stress on the glass surface over a short period of treatment time, the oven temperature used is 470 °C and the increase of temperature in an increment of 10 degrees increased the retardation value 5 nm. One limitation on using the KNO$_2$ as a salt bath on higher temperature is its ability to form a clouding on sample surface by exceeding 2 hours of treatment at 500 °C, where the ions reach a larger depth in the sample structure and causes optical dispersion in the glass, Figure 29. However, it is useful if the treatment time less than 2 hours. In our research we are trying to get higher strengthening values in lower treatment time, which means in less than 60 minutes of treatment time.
The best compressive result of KNO$_2$ treatment was from sample (11), Table 13, where the retardation value reached (-132) nm. The stress distribution through the glass cup of sample (11) was as the following:

Clearly, the stress distribution is forming a large tensile stress in the middle of the sample thickness and two narrow lines of compressive stress on the outer and inner surfaces, as
discussed before and illustrated in Figure 30, this is the optimum balanced distribution of stress that increases the strength of the glass, and this is the optimum stress distribution on successfully strengthened glass surface.

In order to have a better understanding about the successfulness of the ion exchange on the surface of the treated glass sample, we need to know the concentration of potassium ions on the invaded surface and the case depth of these ions, we made SEM testing (FEI Quanta 3D FEG Dual Beam Electron Microscope) for the KNO₃ and KNO₂ samples with the highest stress values, to understand the reason that leads some samples to have higher compressive surface stress values than the others, even all are treated in the same experimental conditions, Figures 31, 32, respectively represent the case depth and K⁺ ions concentration of the sample surface treated by KNO₃, Figures 33, 34, represent the K⁺ ion concentration on sample surface.

![Figure 31: K⁺ ions concentration for KNO₃ salt bath.](image)
Figure 32: $K^+$ concentration – depth for $\text{KNO}_3$ salt bath.

Figure 33: $K^+$ ions concentration for $\text{KNO}_3$ salt bath.
Figures 31-34, shows the distribution of ions on the surface of treated samples, KNO₂ concentration peaks starts (1) micron away from the glass top surface then decreases to the half concentration value by reaching 5 microns case depth, but the KNO₃ have a direct peak of concentration directly on the surface then vanishes after 3 microns away from the surface, this difference in ions distribution as going deep in the surface is the factor controlling the glass strengthening and stress profile equilibrium, KNO₃ peak concentration on the surface affects negatively on the glass structure producing one large compression layer on the surface and large tension layer along the glass thickness which actually weakens the glass, this profile is not desirable in ion exchange strengthening.

In the same experimental conditions we treated glass rods and tested the Modulus of rupture using 4-points bending test device (INSTRON 5569), the values are calculated using Ffracture substitution in eq. (7).

$$\sigma = \frac{16F \cdot L}{3 \cdot \pi \cdot D^3}$$

(7)

where; $\sigma$: Compressive stress (MPa), F: Absolute fracture force (N), L: Distance between roller support centers (mm), D: Glass rod diameter (mm).
For KNO₃ and KNO₂ salt baths samples, results are shown in Table 15:

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Salt Bath</th>
<th>Water(ml)</th>
<th>Clay(g)</th>
<th>Process Time (min.)</th>
<th>Oven T(°C)</th>
<th>MOR(MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KNO₃+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>186.4</td>
</tr>
<tr>
<td>2</td>
<td>KNO₃+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>192.1</td>
</tr>
<tr>
<td>3</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>283.7</td>
</tr>
<tr>
<td>4</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>356</td>
</tr>
<tr>
<td>5</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>462</td>
</tr>
<tr>
<td>6</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>500</td>
<td>486.4</td>
</tr>
<tr>
<td>7</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>170</td>
</tr>
<tr>
<td>8</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>275</td>
</tr>
<tr>
<td>9</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>175</td>
</tr>
<tr>
<td>10</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>468</td>
</tr>
<tr>
<td>11</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>462</td>
</tr>
<tr>
<td>12</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>360</td>
</tr>
<tr>
<td>13</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>413</td>
</tr>
</tbody>
</table>

The Weibull plot for the data listed in Table 15 are illustrated in Figure 35.

![Weibull Plot](image)

Figure 35: Weibull plot for data in Table 15.
3.5.3 Microwaving of coated potassium nitrite results

In this method we used the exact procedure described in section 3.4.3 but with the optimization of exchange process temperature to be 470 °C using KNO₂ with Carbohydrazide as a salt bath, but with glass rod treatment. Glass rods are tested using 4-points test device (INSTRON 5569). The fracture stress (MOR) values are combined in Table 16, as followed:

<table>
<thead>
<tr>
<th>Salt Bath</th>
<th>Water (ml)</th>
<th>Clay (g)</th>
<th>Process Time (min.)</th>
<th>Microwave Process T(°C)</th>
<th>Modulus of Rupture (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>20</td>
<td>470</td>
<td>162.1</td>
</tr>
<tr>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>20</td>
<td>470</td>
<td>235</td>
</tr>
<tr>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>20</td>
<td>470</td>
<td>243.2</td>
</tr>
<tr>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>20</td>
<td>470</td>
<td>348.6</td>
</tr>
</tbody>
</table>

The modulus of rupture of treated samples results are promising, and encouraging for keep using this method. The fluctuation of stress values from low to high are mainly due to not controlling the process, and opening the microwave from time to time to test the sample temperature, this leads to minor thermal shock caused by inefficient process setup, it can be solved by establishing a fully controlled system of microwaving as mentioned previously.

Samples being microwaved after coating are observed by their unique dry coating shape, since microwaving process involves flashing and fast water evaporation, N₂ and CO₂ gases evaporation (eq.(7)) out of the coating mix leading to holes in the dry coating, Figure 35.
3.5.4 Hybrid method results

processing using the microwave as a standalone heating source still needs more development and control on the heating process, since the microwaving has its own thermal equations, in the regular oven it’s a well known and well defined process based on the convection of heat to the samples inside the oven, but in the case of microwave we need a more complex control and sensory system in order to understand the heat distribution over the glass sample surface, as we observed the Microwave processing is the future of short time strengthening processes. It is capable of developing the compressive stress on the glass surface in a short time schedule, in this method we will
combine the microwave treatment efficiency with the oven heat distribution using our optimized stoichiometry and technique.

Samples results of hybrid heating of oven and microwave preheating are gathered from strain scope and averaged in Table 17, the observation concluded from this table is that, when we heated the samples in microwave then transferred to the oven by increasing the microwave treatment time 30 seconds, we could reduce the oven process time by 15 minutes while the final retardation values stayed in the range of the values reached with using the oven only.

Table 17: Averaged retardation values at different hybrid processing times.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>MW Time (sec.)</th>
<th>Salt Bath</th>
<th>Water (ml)</th>
<th>Clay (g)</th>
<th>Process Time (min.)</th>
<th>Oven T(°C)</th>
<th>Retardation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>-80</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>60</td>
<td>470</td>
<td>-84</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>45</td>
<td>470</td>
<td>-87</td>
</tr>
</tbody>
</table>

This method is considered the best method to be used by the current lab tools. The mission was to increase the microwaving time to 10 minutes with a controlled process temperature, and reducing the oven exposure time to 10 minutes and as a total producing the compressive stress equal to the value of 1 hour oven treatment, in 20 minutes hybrid treatment. Averaged results of modulus of rupture for 10 samples in 3 peak values was as the following, Table 18.
Table 18: Averaged MOR values at different hybrid processing times.

<table>
<thead>
<tr>
<th>Average Number</th>
<th>MW Time (min.)</th>
<th>Salt Bath</th>
<th>Water (ml)</th>
<th>Clay (g)</th>
<th>Oven Treatment Time (min.)</th>
<th>Oven T(°C)</th>
<th>MOR (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>10</td>
<td>470</td>
<td>348</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>7</td>
<td>470</td>
<td>361</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>KNO₂+CH₆N₄O</td>
<td>15</td>
<td>5</td>
<td>5</td>
<td>470</td>
<td>480</td>
</tr>
</tbody>
</table>

3.6 Conclusions

Ion exchange chemical strengthening of glass is a method with many variables affecting the final strengthening of the glass and process success, some of these variables are related to thermodynamics. For example, the behavior of the salt bath used in the process depends on the process temperature and others depend on the chemical bonds between the compounds of the glass itself, as alkalis concentration and non bridging oxygen ions in the glass structure, while some are depending on the type of heating source of the process where the activation of ion exchange and invading ions energy is dependent on the reaction temperature. Even the geometry of the ions and salt bath purity has it is remarkable effects on the ion exchange process as discussed in the literature review.

Ion exchange using immersion method is not efficient enough and results compressive stress less than (100MPa), and the problem of the accumulated water vapor inside the oven makes it a non desirable strengthening method.

Coating the samples with clay mixture of salt bath solution is a smart choice, because of it is ability to focus the ion exchange on a certain area of the glass sample, and using less water which means less water vapor in the heating compartment, sticking the invading ions to the glass surface until the activation energy of the ions is reached, hence, making
more concentration of possible invading ions, this method has a higher compressive stress values and optical retardation, which makes it a better technique for ions exchange by Oven treatment, Microwave or hybrid method.

KNO₂ and KNO₃ where nominated to be the carrier salt bath of the K⁺ ions before invading the glass surface, but as discussed in section (3.5.2), KNO₃ results didn’t reach as high as the ions carried by the KNO₂, that results eliminated the KNO₃ and raised the KNO₂ to be the dominant choice of salt bath used in the chemical processing of ions exchange, after a few optimizations of the chemical stoichiometry and process temperature KNO₂ led to compressive stress of 480 (MPa) in less than one hour treatment in the oven and in the microwave as well.

Ion exchange using microwave processing method gave a good compressive stress results with comparison to the treatment time. Modulus of rupture for the treated samples reached 348 MPa in 20 minutes exposure time, which has a lot of potential to be developed with a fully controlled system in order to eliminate the other effects from the samples final stress results.

Soda lime silicate glass is a popular glass in the market, and has the ability to reach very high compressive stress values, this can be achieved by further research efforts in the field of glass around the world, more directive research is needed on the nature of the glass itself in the solid and liquid states and in between, where a lot of intrinsic and fundamental questions are still waiting to be answered, in the same time many phenomena are involved in the glass chemistry and bonds, between its atoms in the dynamic transformation of glass from liquid to solid phase, and no one claims he understand it very well.
References


