The Corrosion of Float Glass

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ABSTRACT

The corrosion of float glass is a big problem in the glass industry. It manifests itself during exposure of glass to humid conditions or when in contact with water. The corroded surface impairs the adhesion of coatings and causes optical defects at the glass surface. Glass corrosion is a complex phenomenon involving diffusion and ion exchange accompanied by silica network dissolution and the formation of corrosion products. Treatment of the glass surface with zinc ions has been proposed to inhibit the corrosion process, however little rigorous study on the inhibition of glass corrosion using zinc has been published.

In this current work the corrosion of float glass in contact with humid air has been studied by a gravimetric technique. This has also been investigated by surface analysis techniques (SIMS, ion-beam analysis, XPS and AFM). A numerical simulation of water uptake due to glass corrosion has also been developed, based on a Cellular Automaton approach.

The gravimetric analysis was performed on crushed float glass, enabling direct quantification of corrosion in real time by running experiments that last for several days. The primary assumption for the measurement of corrosion is that the mass uptake by the sample is purely a result of water adsorption to the surface, where the water adsorbed is replacing the water that has diffused into the bulk glass. Results of the gravimetric studies showed increased corrosion for higher temperatures and higher relative humidity values. Corrosion flux values were obtained by evaluating the specific surface area of the samples from BET analysis of water sorption isotherms. A striking effect of zinc treatment was observed. The corrosion flux value for an untreated sample was 11.8 times higher that of a zinc treated sample exposed to 15°C, 9.25 times higher at 20°C and 2.85 times higher at 30°C. The effectiveness of zinc treatment therefore appears to decrease with increasing temperature.

From the three temperatures studied, it appears that the corrosion flux follows an Arrhenius relationship with temperature, consistent with the published behaviour of water diffusion through glass. Values of the activation energy \(E_a\) were obtained. For
untreated glass the value of $E_a$ recorded in this present work was 50.9 kJ.mol$^{-1}$, comparing favourably with previously published values for float glass. The value of $E_a$ obtained for zinc-treated glass was 122.3 kJ.mol$^{-1}$. This increase in activation energy gives further quantification of the effectiveness of zinc treatment. The beneficial effects of zinc treatment were also apparent from the significant reduction in water mass uptake for zinc-treated samples when measuring water adsorption isotherms. Furthermore, SIMS surface analysis of an untreated glass surface showed much more sodium depletion after exposure to saturated air, compared to zinc-treated glass. Previous work has attributed the effectiveness of zinc treatment to zinc ions blocking the silica interstices, thus inhibiting the ion-diffusion process. However the current work reveals that zinc treatment effectively reduces the amount of water adsorbed. It is therefore proposed that zinc ions combine with the surface hydroxyl groups thus rendering the surface less hydrophilic.

Gravimetric analysis suggests that zinc treated glass surfaces lose their corrosion protection with time. This ageing effect is supported by data from surface analysis studies, indicating that zinc ions diffuse into the glass over long periods of time. Further work is recommended to characterise this effect.

During routine water adsorption isotherm measurement for zinc-treated glass, an anomalous decrease in mass was observed at a relative humidity of between 30 and 40%. No explanation can currently be offered to explain this phenomenon and further work is therefore required.

A Cellular Automaton numerical simulation technique has been applied to model float glass corrosion. This technique was found to give simulation results that compared favourably to experimental data for mass uptake of water. The CA technique can readily be adapted to include other mechanisms and therefore it is recommended for further use in the field of glass corrosion. A sensitivity analysis revealed that the CA model was mostly influenced by parameters relating to the gas phase and surface reaction. The model was insensitive to parameters relating to the bulk glass phase, including diffusivity. Further development of the model is recommended.
DECLARATION

I declare that this dissertation is my own work unless it is specifically stated in the text.

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# TABLE OF CONTENTS

**TABLE OF CONTENTS**

TABLE OF CONTENTS.................................................................vi

**LIST OF FIGURES**................................................................ix

**LIST OF TABLES**.................................................................xiii

**NOMENCLATURE**...................................................................xv

1  **INTRODUCTION**.................................................................1

1.1  Aims and Objectives.................................................................3
   1.1.1  Aims.................................................................................3
   1.1.2  Objectives.......................................................................3

1.2  Contents map of report............................................................3

2  **LITERATURE SURVEY**.........................................................5

2.1  Introduction...........................................................................5

2.2  Production of Float Glass....................................................5

2.3  Glass Structure.................................................................7

2.4  Glass Corrosion ...................................................................9
   2.4.1  Ion Exchange.................................................................9
   2.4.2  Network Dissolution.......................................................11

2.5  Weathering........................................................................13
   2.5.1  Adsorbed Water Layer ................................................15
   2.5.2  The Gel Layer..............................................................16

2.6  Factors Affecting Corrosion................................................19
   2.6.1  Time Dependency..........................................................20
   2.6.2  Diffusion Mechanism....................................................21
   2.6.3  Glass Surface Area to Solution Volume Ratio (A/V).........24
   2.6.4  Specific Surface Area....................................................25
   2.6.5  Effect of Temperature..................................................26
   2.6.6  Solution pH.................................................................27
   2.6.7  Effect of Relative Humidity..........................................28
   2.6.8  Glass Composition.......................................................30

2.7  Corrosion Prevention..........................................................31
   2.7.1  Interleaving Materials..................................................32
   2.7.2  Corrosion Inhibitors.......................................................33
   2.7.3  Other Methods.............................................................40

2.8  Summary of Experimental Techniques.................................41
   2.8.1  Surface Analysis..........................................................41
   2.8.2  Summary of Techniques...............................................41

2.9  Numerical Methods............................................................44
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9.1</td>
<td>Partial Differential Equation Solution Techniques</td>
<td>44</td>
</tr>
<tr>
<td>2.9.2</td>
<td>Statistical Mechanics</td>
<td>44</td>
</tr>
<tr>
<td>2.9.3</td>
<td>Cellular Automaton</td>
<td>46</td>
</tr>
<tr>
<td>2.10</td>
<td>Concluding Comments</td>
<td>47</td>
</tr>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>48</td>
</tr>
<tr>
<td>3.2</td>
<td>System description and assumptions</td>
<td>48</td>
</tr>
<tr>
<td>3.3</td>
<td>Theory</td>
<td>50</td>
</tr>
<tr>
<td>3.4</td>
<td>Cellular Automaton</td>
<td>55</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Automaton Representation of Current Problem</td>
<td>55</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Diffusion in a cellular automaton</td>
<td>58</td>
</tr>
<tr>
<td>3.4.3</td>
<td>Equilibration at the Glass Surface</td>
<td>60</td>
</tr>
<tr>
<td>3.4.4</td>
<td>Reaction in the Solid</td>
<td>63</td>
</tr>
<tr>
<td>3.4.5</td>
<td>Parameter Estimation</td>
<td>63</td>
</tr>
<tr>
<td>3.5</td>
<td>Concluding Comments</td>
<td>68</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>69</td>
</tr>
<tr>
<td>4.2</td>
<td>IGAsorp (Intelligent Gravimetric Analyser)</td>
<td>69</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Preparation of Materials</td>
<td>71</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Data Analysis</td>
<td>73</td>
</tr>
<tr>
<td>4.3</td>
<td>Surface Analysis Techniques</td>
<td>74</td>
</tr>
<tr>
<td>4.3.1</td>
<td>AFM (Atomic Force microscopy)</td>
<td>75</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Ion Beam Analysis (IBA)</td>
<td>76</td>
</tr>
<tr>
<td>4.3.3</td>
<td>XPS (X-ray Photoelectron Spectroscopy)</td>
<td>78</td>
</tr>
<tr>
<td>4.3.4</td>
<td>SIMS (Secondary Ion Mass Spectrometry)</td>
<td>80</td>
</tr>
<tr>
<td>4.4</td>
<td>Concluding Comments</td>
<td>83</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>84</td>
</tr>
<tr>
<td>5.2</td>
<td>Gravimetric Analysis</td>
<td>84</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Mass Uptake as a Function of Relative Humidity</td>
<td>85</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Mass Uptake as a Function of Temperature</td>
<td>87</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Corrosion Kinetics</td>
<td>90</td>
</tr>
<tr>
<td>5.2.4</td>
<td>Isotherms</td>
<td>96</td>
</tr>
<tr>
<td>5.2.5</td>
<td>BET Analysis</td>
<td>99</td>
</tr>
<tr>
<td>5.2.6</td>
<td>Layer Thickness</td>
<td>107</td>
</tr>
<tr>
<td>5.2.7</td>
<td>Thermodynamics</td>
<td>108</td>
</tr>
<tr>
<td>5.2.8</td>
<td>Correlating Mass uptake per Unit Surface Area</td>
<td>110</td>
</tr>
<tr>
<td>5.2.9</td>
<td>Determination of Corrosion Flux</td>
<td>112</td>
</tr>
<tr>
<td>5.2.10</td>
<td>Data Reproducibility and Ageing</td>
<td>116</td>
</tr>
<tr>
<td>5.3</td>
<td>Cellular Automaton Simulation Results</td>
<td>121</td>
</tr>
</tbody>
</table>
list of figures

Figure 2-1; Pilkington Float Glass Process adaptation from British Glass (2009)........................................ 6
Figure 2-2; Silica structure where the small atoms represent the oxygen and the large atoms represent the silica, Hill and Petrucci (1999)................................................................. 7
Figure 2-3; A modified random network (MRN) for a "2-dimensional" oxide glass. The nominal composition is $M_2O_3(SiO_3)$, where $M$'s are modifying cations and $G$'s are network forming cations. Covalent bonds are shown by the solid lines and ionic bonds by the dotted lines. The shaded regions are defined by the boundary conditions which run through the $G-O$ (non-bridging) bonds. These highlight the percolation channels of $M_2O_3$ that run through the network. Greaves (1985). The small open circles can be taken to be silicon, the large open circles are oxygen, and the small black circles are network modifying cations shown with 3-fold coordination for convenience e.g. $Al^{11+}$ or $Fe^{11+}$ ........ 8
Figure 2-4; SEM image of milled float glass exposed to dry and saturated conditions for a 7 day period, respectively (LeCourt 2006).............................................................................. 14
Figure 2-6; Five types of glass surfaces conditions resulting from glass-water interactions (Hench et al. 1980) ........................................................................................................................................................................................................ 18
Figure 2-7; Surface condition of a Type III B glass surface resulting from glass-environment interactions, Hench (1982).................................................................................................... 19
Figure 2-8; Short time and long time water leaching of 15 Na$_2$O 85 SiO$_2$ glass grains at different temperatures (Douglas and El-Shamy 1967) ................................................................. 21
Figure 2-9; Na$_2$O on surface after weathering of moderately resistant borosilicate glass at 98% RH and 50°C, Walters and Adams (1975). .................................................................................. 26
Figure 2-10; Depth profiles obtained by SIMS analysis of sodium ion concentration on a fabricated glass at ambient conditions. The glass sample was examined straight after production (as made), and after submission to 37% and 55% RH, Fearn et al. (2004)..................................................... 29
Figure 2-11; H$_2$O adsorbed on several glasses as a function of RH after 7 days (Walters and Adams 1975) ........................................................................................................................................... 30
Figure 2-12; Haze pattern on lightly weathered float glass samples which had been interleaved by paper and exposed to 80% RH and 60 °C for 40 days, Staunton (2007)................................. 32
Figure 2-13; Graph showing the change in pH of an adipic and boric acid solution (0.2 g of stain inhibitor in 200 ml of water) against millilitres of added 0.1 M sodium hydroxide Holmes (2007a).... 35
Figure 2-14; Haze pattern on lightly weathered float glass samples which had been interleaved by adipic and boric acid respectively, the samples were exposed to 60°C, 80% RH for 40 days, Staunton (2007).......................................................................................................................................................... 36
Figure 2-15; Adipic acid interleaved sample exposed to cyclic conditions (Smith and Pantano 2008)37
Figure 2-16; Boric acid interleaved sample exposed to cyclic conditions (Smith and Pantano 2008). 37
Figure 2-17; Figure showing the ratio of hydrogen released ($H^+$) with zinc adsorbed (Zn$^{11+}$) as a function of solution pH and corresponding individual amounts are also shown, Kosawa (1961)........ 39
Figure 2-18; Schematic representation of CA, 'Game of Life'. Five subsequent steps are shown. Gray filled squares represent 'living' nodes, while empty squares are 'dead' nodes. In each time step, the following rule is applied to each square simultaneously: A 'living' node surrounded by less than three or more than three 'living' nodes amongst its eight neighbours dies of isolation or overcrowdedness. On the other hand, a 'dead' cell will come to 'life' if there are exactly three 'living' cells amongst its eight nearest neighbours, (Deutsch and Dormann 2005).................................................................................................................. 46
Figure 2-19; Automaton diagram for the glass-water-air system shown in Figure 3-1................................. 56
Figure 2-3; Flow chart for CA calculation steps involved in generating mass uptake profiles................. 57
Figure 4-1; Image of the IGAsorp gravimetric water sorption analyser ......................................................... 69
Figure 4-2; Schematic of the inside of the IGAsorp (Hiden Isochema 2003). .............................................. 70
Figure 4-3; Picture of the IGAsorp pan in which samples are loaded.......................................................... 70
Figure 4-4; Mass trace of an empty pan as a function of time at 25°C and 70% RH for a 4 day period. ........ 71
Figure 5-1; Fractional mass uptake at 20°C for Batch 1 (untreated) float glass samples with a particle size < 90 μm, exposed to 30%, 50% and 70% RH....................................................... 86
Figure 5-2; Fractional mass uptake at 20°C for Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 30%, 50% and 70% RH. Note the change of uptake scale from Figure 5-1 ........ 86
Figure 5-3; Fractional mass uptake over time for Batch 1 (untreated) float glass samples with a particle size < 90 μm, exposed to 15°C, 20°C and 30°C at 70% RH.

Figure 5-4; Fractional mass uptake over time for Batch 2 (zinc-treated) float glass samples with a particle size less than < 90 μm, exposed to 15°C, 20°C and 30°C at 70% RH.

Figure 5-5; Fractional mass uptake over time for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 15°C and 70% RH.

Figure 5-6; Fractional mass uptake over time for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 20°C and 70% RH.

Figure 5-7; Fractional mass uptake over time for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 30°C and 70% RH.

Figure 5-8; Log of fractional mass uptake as a function of the log of time, for samples from Batch 1 (untreated) float glass samples with particle size < 90 μm, exposed to 15°C, 20°C and 30°C. Regions of linearity are shown for determination of the time index (a) and the corrosion constant (k_r) as depicted in Equation (5.1).

Figure 5-9; Log of fractional mass uptake as a function of the log of time for samples from Batch 2 (zinc-treated) float glass samples with particle size < 90 μm, exposed to 15°C, 20°C and 30°C. Regions of linearity are shown for determination of the time index (a) and the corrosion constant (k_r) as depicted in Equation (5.1).

Figure 5-10; Values for the time index parameters (a) at 15°C, 20°C and 30°C for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm.

Figure 5-11; Mean values for the corrosion constant (k_r) at 15°C, 20°C and 30°C for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm.

Figure 5-12; Fractional mass adsorbed and desorbed as a function of percent relative humidity for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 15°C.

Figure 5-13; Fractional mass adsorbed and desorbed as a function of percent relative humidity for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 20°C.

Figure 5-14; Fractional mass adsorbed and desorbed as a function of percent relative humidity for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 30°C.

Figure 5-15; BET plots of p/x(p/p_o) vs. p/p_o for the data from the water adsorption isotherms for float glass samples with particle size < 90 μm, exposed to 15°C for fractional pressures between 0.1-0.3.

Figure 5-16; BET plots of p/x(p/p_o) vs. p/p_o for the data from the water adsorption isotherms for float glass samples with < 90 μm, exposed to 20°C for fractional pressures between 0.1-0.3.

Figure 5-17; BET plots of p/x(p/p_o) vs. p/p_o for the data from the water adsorption isotherms for float glass samples with a particle size < 90 μm, exposed to 30°C for fractional pressures between 0.1-0.3.

Figure 5-18; BET plots of p/x(p/p_o) vs. p/p_o for the data from the water desorption isotherms for float glass samples with a particle size < 90 μm, exposed to 15°C for fractional pressures between 0.1-0.3.

Figure 5-19; BET plots of p/x(p/p_o) vs. p/p_o for the data from the water desorption isotherms for float glass samples with a particle size < 90 μm, exposed to 20°C for fractional pressures between 0.1-0.3.

Figure 5-20; BET plots of p/x(p/p_o) vs. p/p_o for the data from the water desorption isotherms for float glass samples with a particle size < 90 μm, exposed to 30°C for fractional pressures between 0.1-0.3.

Figure 5-21; Layer thickness (l) and number of molecular layers (n') plotted as a function of % RH for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 30°C during adsorption. The dashed horizontal lines correspond to monolayers.

Figure 5-22; Polynomial fit to data of mass uptake per unit surface area as a function of time for Batch 1 (untreated) float glass samples with a particle size < 90 μm, exposed to 15°C, 20°C and 30°C at 70% RH.

Figure 5-23; Polynomial fit to data of mass uptake per unit surface area as a function of time for Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 15°C, 20°C and 30°C at 70% RH.

Figure 5-24; Corrosion flux values for every 100 minutes up to 6000 minutes for Batch 1 (untreated) float glass samples with a particle size < 90 μm.

Figure 5-25; Corrosion flux values for every 100 minutes up to 6000 minutes for Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm.
Figure 5-26: Arrhenius plot for Batch 1 (untreated) and Batch 2 (zinc treated) float glass samples with a particle size < 90 μm, showing the logarithm of the flux values as a function of the inverse of temperature for a time t = 3000 minutes.

Figure 5-27: Fractional mass adsorbed and desorbed as a function of relative humidity for Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 30°C.

Figure 5-28: BET plots of p/2 (p/p0) vs. p/p0, for the data from the water desorption isotherms for Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 30°C.

Figure 5-29: Fractional mass uptake vs. time for two samples from Batch 1 (untreated) float glass samples with a particle size < 90 μm, exposed to 30°C and 70% RH. These samples were stored in a desiccator for 63 and 103 days at dry conditions prior to sample analysis.

Figure 5-30: Fractional mass uptake vs. time for two samples from Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 20°C. These samples were stored in a desiccator for 12 and 150 days at dry conditions prior to sample analysis.

Figure 5-31: Log of fractional mass uptake as a function of the log of time for Batch 2 (zinc-treated) samples with a particle size < 90 μm, exposed to 20°C. Regions of linearity are shown for determination of the time index and the corrosion constant as depicted in Equation (5.1).

Figure 5-32: Mass uptake as a function of time at 15°C and 70% RH from gravimetric experiments. Here ζ is the intercept of the final mass uptake region.

Figure 5-33: Gravimetric adsorption isotherm for a Batch 1 (untreated) float glass sample with < 90 μm. q_wrepresents the amount adsorbed at 70% RH and at 15°C in this instance.

Figure 5-34: Mass uptake curve from simulation for glass exposed to 15°C when diffusion and reaction occurs in the glass. Diffusion only is also shown in the same graph.

Figure 5-35: Comparison of mass uptake on untreated float glass at 15°C for simulation and gravimetric experimental data reproduced from Figure 5-3.

Figure 5-36: Comparison of mass uptake on untreated float glass at 20°C for simulation and gravimetric experimental data reproduced from Figure 5-3.

Figure 5-37: Comparison of mass uptake on untreated float glass at 30°C for simulation and gravimetric experimental data reproduced from Figure 5-29, for the sample stored at dry conditions for 63 days prior to sample analysis.

Figure 5-38: Comparison of mass uptake on zinc treated float glass at 15°C for simulation and gravimetric experimental data reproduced from Figure 5-4.

Figure 5-39: Comparison of mass uptake on zinc treated float glass at 20°C for simulation and gravimetric experimental data reproduced from Figure 5-30, for the sample stored at dry conditions for a 12 day period prior to the sample analysis.

Figure 5-40: Comparison of mass uptake on zinc treated float glass at 30°C for simulation and gravimetric experimental data reproduced from Figure 5-4.

Figure 5-41: Comparison of mass uptake on untreated float glass at 20°C for simulation and gravimetric experimental data reproduced from Figure 5-3.

Figure 5-42: Comparison of mass uptake on zinc treated float glass at 15°C for simulation and gravimetric experimental data reproduced from Figure 5-4.

Figure 5-43: Comparison of mass uptake on untreated float glass at 20°C for simulation and gravimetric experimental data for a sample stored for 103 days as shown in Figure 5-29.

Figure 5-44: Comparison of mass uptake on zinc treated float glass at 20°C for simulation and gravimetric experimental data for sample stored for 150 days as shown in Figure 5-30.

Figure 5-45: AFM images after exposure of two float glass sheet samples to 30% and 90% RH at 20°C for a 12 hour period in the IGAsorp.

Figure 5-46: Edge of crater formed by SIMS etching. The spotted SIMS etching region on the right hand side of the image represents the sample with gold coating on the surface. Note the faint vertical line in the middle of the image indicates the edge of the etched crater. The horizontal lines represent the positions taken for the line scan analysis.

Figure 5-47: Line profile for the individual lines corresponding to Figure 5-46. The figure labels a, b and c correspond to the respective labels in Figure 5-46.

Figure 5-48: Depth profile of gold (Au) and silicon (Si) for an untreated sample etched for 500 s. It can be seen that both depth profiles cross each other at around 88 time units, this value was taken to be the point at which the glass starts being etched.

Figure 5-49: PIXE spectrum of the air side of an untreated sheet float glass sample. The red line in this figure represents the fit to the data (from the software GUPiX) and the dots represent the raw data.

Figure 5-50: Logarithmic plot of amount detected for different float glass elements by ion-beam analysis.
LIST OF TABLES

Table 2-1: Illustration of variation in specific surface area as a function on pore size and particle size for Davistil silica, obtained by nitrogen adsorption, Collins et al. (2005) ................................................................. 26
Table 2-2: Summary of relevant spectrometry and spectroscopy techniques ................................................................................................................................. 42
Table 2-3: Summary of relevant imaging techniques ............................................................................................................................................................................. 43
Table 2-4: Summary of other relevant techniques .............................................................................................................................................................................. 43
Table 3-1: Summary of diffusion coefficient values and respective mass transfer coefficient values ............................................................................................................ 66
Table 3-2: Summary of known simulation parameters ........................................................................................................................................................................ 67
Table 3-3: Summary of unknown simulation parameters ................................................................................................................................................................. 68
Table 4-1: Composition of float glass used in this dissertation, Staunton (2007) ........................................................................................................................................... 72
Table 4-2: Summary of ground float glass samples used in this study .................................................................................................................................. 72
Table 5-1: Summary of exposure conditions and sample description for the IGAsorp gravimetric experiments, see Table 4-2 in Chapter 4 for the description of the individual batches including their production and preparation date. The letter R denotes repeated experiments .......................................................................................................................... 85
Table 5-2: Summary of time index (a) and corrosion constant (k,) in Equation 5.1 obtained from Figure 5-8 and Figure 5-9 ................................................................. 94
Table 5-3: Data from the BET analysis for water adsorption on ground float glass samples relating to Figure 5-15, 5-16 and Figure 5-17 ...................................................................................................................... 102
Table 5-4: BET specific surface area (S) from adsorption isotherm for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm ........................................................................................................................................................................... 103
Table 5-5: Summary of particle size diameter for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm particle size calculated from data at different temperatures ................................................................................................................................. 104
Table 5-6: BET parameters from desorption data for the isotherms shown in Figure 5-12 to Figure 5-14 at 15°C, 20°C and 30°C for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples ........................................................................................................................................................................... 106
Table 5-7: Summary of saturated vapour pressure (p_v) values obtained using the Antoine equation (see Equation 3.2 in Chapter 3) at 288.15, 293.15 and 303.15 K ................................................................................................................................................................................................. 108
Table 5-8: Summary of thermodynamic parameters obtained for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples of particle size < 90 μm from desorption isotherms ........................................................................................................................................................................... 110
Table 5-9: Summary of corrosion constant (k,) values for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 15°C, 20°C and 30°C .................................................................................................................................................................................................. 111
Table 5-10: Summary of corrosion flux equations for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples exposed to 15°C, 20°C and 30°C ........................................................................................................................................................................... 113
Table 5-11: Summary of corrosion flux (J') values at t = 3000 minutes for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples exposed to 15°C, 20°C and 30°C .................................................................................................................................................................................................. 114
Table 5-12: BET parameters from desorption data for the isotherms at 30°C shown in Figure 5-27 for two Batch 2 (zinc-treated) float glass samples with a particle size < 90μm .................................................................................................................................................................................................. 118
Table 5-13: Summary of reaction parameters obtained from Figure 5-31, for the Batch 2 (zinc-treated) float glass sample. Note that the value of the corrosion constant was considered to be the logarithm of the intercept value in Figure 5-31 ................................................................................................................................................................. 120
Table 5-14: Summary of simulation parameters and their description, (Table 3-2 reproduced shown in Chapter 3) ........................................................................................................................................................................... 122
Table 5-15: Summary of unknown parameters, Table 3-3 reproduced from Chapter 3 ........................................................................................................................................................................... 123
Table 5-16: Summary of parameters from Equation 5.2 for both untreated and zinc-treated glass exposed to 15°C, 20°C and 30°C .................................................................................................................................................................................................. 124
Table 5-17: Summary of predicted %RH and adjusted %RH values based on q_a from Equation 5.2 at 15°C, 20°C and 30°C for untreated and zinc-treated glass .................................................................................................................................................................................................. 125
Table 5-18: Summary of BET data as a function of temperature from isotherms shown in Figure 5-12 to Figure 5-14. These results were also previously shown in Table 5-3 but now the monolayer value has been converted to units of mol kg⁻¹ .................................................................................................................................................................................................. 126
Table 5-19: Summary of estimated reaction rate constant values for untreated glass samples for the temperatures used in the gravimetric experiments .................................................................................................................................................................................................. 127
Table 5-20: Relative results of sensitivity analysis for a 5% perturbation in the simulation parameters for untreated glass exposed to 15°C .................................................................................................................................................................................................. 135
Table 5-21: Relative results of sensitivity analysis for a 5% perturbation in the simulation parameters for zinc-treated glass exposed to 15°C .................................................................................................................................................................................................. 136
NOMENCLATURE

\%RH  Percent relative humidity (-)

\( A \)  Surface area of the sample (m²)

\( a \)  Reaction rate constant (s⁻¹)

\( A' \)  Antoine constant (-)

\( a' \)  Rate of matrix corrosion (m s⁻¹)

\( a_1 \)  Interfacial area (m² kg⁻¹)

\( A_m \)  Cross-sectional area of molecule (m²)

\( b \)  Reaction rate constant (s⁻¹)

\( B' \)  Antoine constant (-)

\( C \)  Concentration (mol m⁻³)

\( c \)  BET constant (-)

\( C' \)  Antoine constant (K)

\( c_d \)  Etch crater depth (m)

\( D \)  Diffusion coefficient (m² s⁻¹)

\( D_{gl} \)  Diffusion coefficient in glass (m² s⁻¹)

\( d_e \)  Erosion depth (m)

\( d_{pan} \)  Pan diameter (m)

\( d_{particle} \)  Sauter mean particle diameter (m)

\( D_R \)  Relative diffusion (-)

\( E_l \)  Energy of adsorption in the first layer (J mol⁻¹)

\( E_a \)  Activation energy (J mol⁻¹)

\( f \)  Conversion factor (-)

\( \text{gas}_dz \)  Distance step length in gas (m)

\( J \)  Mass uptake (kg m⁻²)

\( J' \)  Corrosion flux (kg m⁻² s⁻¹)

\( K \)  Equilibrium constant (mol m⁻³)

\( k' \)  Reaction rate constant (s⁻¹)

\( k \)  Reaction constant (mol m⁻³ s⁻¹)

\( k_g \)  Mass transfer coefficient (m s⁻¹)

\( k_0 \)  Frequency factor (mol m⁻³ s⁻¹)

\( k_T \)  Mass transfer coefficient (mol s⁻¹ Pa⁻¹ m⁻²)

\( K_p \)  Partition coefficient (m³ kg⁻¹)

\( k_r \)  Corrosion constant (kg kg⁻¹ s⁻¹)

\( k_r' \)  Corrosion constant (kg m⁻³ s⁻¹)

\( h \)  Layer thickness (m)

\( L_v \)  Latent heat of vaporisation (J kg⁻¹)

\( L_{n,b} \)  Latent heat at normal boiling point (J kg⁻¹)

\( M \)  Molecular weight (g mol⁻¹)

\( N \)  Flux (mol m⁻² s⁻¹)

\( n \)  Amount of material (mol)

\( N' \)  Avogadro’s constant (mol⁻¹)

\( n' \)  Number of molecular layers (-)

\( N_n \)  Number of nodes (-)

\( p \)  Total pressure (Pa)

\( p_0 \)  Saturated vapour pressure (Pa)

\( p_{\infty} \)  Partial pressure in the gas bulk (Pa)

\( P_{ka} \)  Acid ionisation constant (-)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_s$</td>
<td>Partial pressure at the glass surface (Pa)</td>
</tr>
<tr>
<td>$q$</td>
<td>Amount adsorbed (mol kg$^{-1}$)</td>
</tr>
<tr>
<td>$Q$</td>
<td>Quantity of alkali extracted (kg kg$^{-1}$)</td>
</tr>
<tr>
<td>$Q_d$</td>
<td>Amount of alkali extracted per unit surface area (mol m$^{-2}$)</td>
</tr>
<tr>
<td>$q_m$</td>
<td>BET monolayer capacity (mol kg$^{-1}$)</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant (J K$^{-1}$ mol$^{-1}$)</td>
</tr>
<tr>
<td>$r$</td>
<td>Reaction rate (m$^3$ mol$^{-1}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Regression coefficient (-)</td>
</tr>
<tr>
<td>$R_c$</td>
<td>Reaction capacity in bulk glass (mol m$^{-3}$)</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds flow number (-)</td>
</tr>
<tr>
<td>$S$</td>
<td>Specific surface area (m$^2$ kg$^{-1}$)</td>
</tr>
<tr>
<td>$Sc$</td>
<td>Schmidt number (-)</td>
</tr>
<tr>
<td>$Sh$</td>
<td>Sherwood number (-)</td>
</tr>
<tr>
<td>$S_R$</td>
<td>Sputtering rate (m s$^{-1}$)</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>$t$</td>
<td>Time (s)</td>
</tr>
<tr>
<td>$T_b$</td>
<td>Temperature at normal boiling point (K)</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Critical temperature (K)</td>
</tr>
<tr>
<td>$t_t$</td>
<td>Duration of simulation experiment (s)</td>
</tr>
<tr>
<td>$t_s$</td>
<td>Number of time steps (-)</td>
</tr>
<tr>
<td>$t_f$</td>
<td>Total etch time (s)</td>
</tr>
<tr>
<td>$u$</td>
<td>Velocity (m s$^{-1}$)</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume of solution (m$^3$)</td>
</tr>
<tr>
<td>$w$</td>
<td>Amount adsorbed (kg)</td>
</tr>
<tr>
<td>$w_a$</td>
<td>Mass adsorbed (kg)</td>
</tr>
<tr>
<td>$w_{dry}$</td>
<td>Dry weight (kg)</td>
</tr>
<tr>
<td>$w_T$</td>
<td>Total sample weight (kg)</td>
</tr>
<tr>
<td>$x$</td>
<td>Fractional mass uptake (kg kg$^{-1}$)</td>
</tr>
<tr>
<td>$x_m$</td>
<td>BET monolayer (kg kg$^{-1}$)</td>
</tr>
<tr>
<td>$X$</td>
<td>Relative humidity (-)</td>
</tr>
<tr>
<td>$z$</td>
<td>Position (m)</td>
</tr>
<tr>
<td>$\Omega_D$</td>
<td>Collision integral (-)</td>
</tr>
<tr>
<td>$\pi$</td>
<td>3.142 (-)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity (N m$^{-1}$ s)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Time index constant (-)</td>
</tr>
<tr>
<td>$\delta t$</td>
<td>Time step length (s)</td>
</tr>
<tr>
<td>$\delta z$</td>
<td>Distance step length in the solid (m)</td>
</tr>
<tr>
<td>$\delta z_g$</td>
<td>Thickness of gas node (m)</td>
</tr>
<tr>
<td>$\delta z_s$</td>
<td>Thickness of glass node (m)</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Mass uptake at long time intervals (mol kg$^{-1}$)</td>
</tr>
<tr>
<td>$\rho_{sample}$</td>
<td>Density of sample (kg m$^{-3}$)</td>
</tr>
<tr>
<td>$\sigma_{AB}$</td>
<td>Characteristic length (m)</td>
</tr>
</tbody>
</table>
1 Introduction

Glass has been known to civilisation for thousands of years. In prehistoric times natural glasses (amorphous silica) were formed when siliceous lava was expelled from volcanic eruptions and cooled rapidly. This type of glass is called obsidian glass. One of the early uses of glass is believed to have been for hunting purposes (Davison 2003).

As human kind evolved, glass production processes also evolved and other uses for glass were found. Traditionally for the current society, glass is part of daily life, from drinking glasses and bottles to decorative glassware and reading glasses.

Currently, there is an increase in glass demand from the building industry due to tighter legislation on energy saving, safety and noise attenuation. There is also an increase in demand for glass in photovoltaic panels. For the automotive industry the demands are focused on car glazing, adding style and individuality to the car design and noise attenuation (Pilkington 2005).

Glass corrosion is a well established phenomenon that involves the degradation of the glass surface when in contact with water, either as a bulk liquid or as an adsorbed film. The degradation can involve leaching of components from within the glass and dissolution of the glass structure, Bacon (1968). The durability or corrosion resistance of glass has been an area extensively studied in literature, for a number of years. Glass durability is usually assessed after this material has been exposed to the environment (weathering) for a length of time, e.g. during glass storage. Under certain exposure conditions a water layer forms at the glass surface, and glass starts to degrade by changes in the chemical and physical structure. Therefore, it is of importance that glass is stored in warehouses at appropriate conditions of %RH and temperature.

Glass manufacturers have to pay particular attention to the durability of glass and the prevention of corrosion because this can cause optical defects on the glass surface,
prevent functional coatings adhering, and affect the glass mechanical properties, (Hayashi et al. 2002). Furthermore, glass durability is also a concern for glasses used for nuclear waste storage (borosilicate glasses), because it is important that these can withstand extreme conditions for very long periods of time, approximately $10^4$ years (Bodanski 2006). It is also an area of interest in the dating and preservation of antique glasses in museums, (Fearn et al. 2004). Furthermore, glass corrosion is also a concern for the consumer. This is illustrated by an increase in opacity of drinking glasses due to the repetitive cleaning over time in dishwashers, (Sharma et al. 2003).

The primary focus of this thesis is the corrosion of soda lime float glass. This type of glass constitutes 63% of the global flat glass market. The remaining market proportion includes sheet glass, rolled glass and lower quality float glass. Europe, Japan and North America account for more than 70% of the overall global flat glass demand (NSG 2008). Flat glass supplies constitute 47% of the building industry, 43% of the automotive industry and 10% of the speciality industries including glass fibre and information technology, (Holmes 2009).

In extreme cases, glass corrosion results in surface damage (staining) due to high solution pH of the contacting solution. In an effort to prolong glass durability, manufacturers commonly coat the freshly formed glass with various compounds termed ‘stain inhibitors’. Many of these are weak acids which counteract damaging high pH values. Stain inhibitors tend to be applied by scattering the particles in air with air blowers and letting them settle on the glass surface, (Smith and Pantano 2008). The literature on corrosion inhibitors is scarce and sometimes contradictory. In this thesis the float glass was treated with zinc nitrate and its inhibition effect was quantified by comparison with untreated samples. This compound was chosen because there is some evidence to suggest that it is a very effective stain inhibitor. However the evidence relating to its application to float glass is scarce.

Glass corrosion costs an estimated £100,000 per float line per year. NSG has around 40 float lines so the company’s annual loss due to glass corrosion is approximately £4 million. Assuming other manufacturers experience similar losses, the annual global loss is approximately £25 million (Holmes 2009).
1.1 Aims and Objectives

1.1.1 Aims

The aims of this work are to undertake an experimental study into the parameters that influence the corrosion of float glass, when exposed to air with a fixed relative humidity and temperature. The effectiveness of zinc nitrate as a corrosion inhibitor will also be investigated. The work also aims to test the application of a cellular automaton (CA) computer simulation method to model glass corrosion kinetics.

1.1.2 Objectives

The objectives of the study can be summarised as follows:

- To measure directly the corrosion rate of float glass, using gravimetric analysis.
- To quantify the influence of zinc nitrate in the reduction of corrosion by comparison with untreated samples.
- To use surface analysis techniques to characterise the extent of corrosion by depth profiling.
- To develop a cellular automaton model for the simulation of glass corrosion.
- To test the suitability of the model by comparison with experimental data.

1.2 Contents map of report

This dissertation is divided into seven main chapters including this chapter. These are Literature Survey, Theory Chapter, Experimental Methods, Results, Discussion and Conclusion and Recommendations for future work.

The literature survey chapter includes an introduction to the production of float glass, the structure of silica glasses and properties of glasses due to the addition of certain compounds. The general mechanisms known to occur in glass corrosion are shown and discussed. The main experimental results found in literature and the experimental techniques used are described, and the prevention of glass corrosion will be addressed.
The theory chapter covers the development of a theoretical simulation model for the kinetics of glass corrosion, using a cellular automaton (CA) approach. The assumptions and parameters involved are presented in detail.

The experimental methods chapter gives details of gravimetric analysis, surface analysis and imaging techniques used in this work for the generation of data. Details of sample preparation and application of the zinc treatment to the glass surface are also included.

The results chapter will be divided into three main sub-sections: gravimetric results, simulation results, and surface analysis results. Significant trends in the data are identified.

In Chapter 6 the results will be discussed in the context of the reported findings from the published literature. The main area of interest will be to assess the influence of environmental parameters on the corrosion rate of float glass, the effectiveness of zinc treatment and the suitability of the CA simulation method to model the experimental results.

In the conclusions and recommendations for future work chapter the main findings will be summarised together with recommendations for future experimental and theoretical work.
2 Literature Survey

2.1 Introduction

This chapter addresses the key areas which are considered to be relevant to the phenomenon of glass corrosion and also its prevention. Before the mechanism of glass corrosion is explained, a brief introduction to the molecular structure of glass is presented. The glass corrosion section includes an explanation of water film adsorption, gel layer and pore formation as these are important issues in glass corrosion. Work related to the prevention of glass corrosion by the application of chemical agents known as stain inhibitors is addressed. In the last section the use of modelling techniques to describe glass corrosion is also explored.

2.2 Production of Float Glass

The glass used in this work is Pilkington’s soda-lime-silica float glass. The mixture of materials used in this glass production has a general composition of silica sand (72.6%), sodium oxide Na₂O (13%), lime CaO (8.4%), dolomite (4%) (which is a type of limestone containing magnesium carbonate as well as calcium carbonate), alumina (1%) and cullet (1%). The latter is the term used for recycled glass, (Pilkington 2009).

The general chemistry of soda-lime glass formation according to Harding et al. (2002) is shown by Equation (2.1), below:

\[
Na_2CO_3 + CaCO_3 + 2SiO_2 \rightarrow CaO \cdot SiO_2 + Na_2O \cdot SiO_2 + 2CO_2 \uparrow \quad (2.1)
\]

Sodium and calcium carbonates i.e. Na₂CO₃ and CaCO₃ are mixed with silica sand (SiO₂) and melted at a temperature of around 1500°C. Sodium and calcium metasilicate form and carbon dioxide is released. More silica sand is added to sodium and calcium metasilicates and the mixture is left for a length of time (Pilkington 2009). Note that sodium oxide is added to reduce the glass melt viscosity but can also weaken the durability of the glass. This will be discussed later in Section 2.3.
The float glass process developed in 1953 by Sir Alastair Pilkington, was motivated by the desire to create a cheaper and less wasteful process than the plate process. The latter involved “casting” a plate of glass and flattening it down by the use of rollers. This would leave marks on the surface and require polishing, Pilkington (2009). In the float glass production process (see Figure 2-1, below) the raw materials are weighed and mixed before being melted in a furnace. The melted glass floats on a bath of molten tin where the melted glass spreads, forming a so-called glass ribbon (Ban et al. 2004). The speed at which the glass ribbon is dragged from the bath defines the thickness of the final glass. The glass ribbon then goes through an annealing stage (controlled cooling), cutting and application of stain inhibitors (organic acids applied to protect the glass surface from corrosion) and interleavant materials (materials used to physically separate the glass sheets during storage e.g. PMMA powder). The application of stain inhibitors and interleaving materials will be further discussed in Section 2.7.

![Pilkington Float Glass Process](image)

Figure 2-1; Pilkington Float Glass Process adaptation from British Glass (2009)

The float glass produced has two chemically different sides; a tin side and an air side. The air side only contains an average of 0.1% tin oxide content with a gradient extending 10-30µm down to the glass surface (Sieger 1975). This is due to the transport of the tin in the vapour phase during the production of float glass according to Feldmann and Weibmann (1997). The tin side is believed to contain elements such as silicon, sodium, calcium, magnesium, tin and oxygen, (Holmes 2008). The tin amount is not always the same and depends on the conditions of production and the
cleanliness of the tin bath. However a typical value for the SnO$_2$ concentration would be 2% on the tin side (Sieger 1975). The composition of the tin side of float glass was studied by Lamouroux et al. (1997) using ion beam analysis. This combined PIXE (Particle induced X-ray emission) with RBS (Rutherford backscattering spectrometry). These techniques are further explained in Section 4.3.2.

### 2.3 Glass Structure

Glass is defined as 'the fusion product of inorganic materials which have been cooled to a rigid condition without crystallising' Paul (1982). It therefore follows that glass has an amorphous structure, which is defined by the random arrangement of the silica (silicon oxide) groups in glass, shown in Figure 2-2 (Hill and Petrucci 1999).

![Figure 2-2; Silica structure where the small atoms represent the oxygen and the large atoms represent the silica, Hill and Petrucci (1999)](image)

In 1932 Zachariasen described glass as being an extended molecular network without symmetry and periodicity. This was further confirmed by the X-ray diffraction results of Warren in 1933, Vogel (1985). Furthermore, Zachariasen classified oxides in glass into network formers, network modifiers and intermediates. Network formers relate to oxide groups such as SiO$_2$. Network modifiers include alkali oxides such as Na$_2$O, and CaO Vogel (1985). When sodium oxide (Na$_2$O) and lime (CaO) are introduced to the basic silica structure, oxygen bridges are broken and the addition of these cations to the structure makes the network less interconnected. Non-bridging oxygen ions (oxygen atom bound to only one silicon atom, Jiang 2002) are created after the addition of alkali causing the network to have regions of unbalanced negativity. Intermediates are minor components in glass which restrict the movement of alkali ions and therefore increase the glass resistance to dissolution. These include
compounds such as $\text{Al}_2\text{O}_3$, $\text{P}_2\text{O}$ and $\text{Fe}_2\text{O}_3$, (Davison 2003). The theory described above is called the Zachariasen-Warren network theory.

In 1985 Greaves introduced the concept of percolation channels. These develop in the glass due to the presence of unbalanced regions and provide paths for ionic diffusion as shown in Figure 2-3, below (Greaves 1985). Greaves theory is now known as the modified random network theory and is the most currently used, Robinnet (2006).

![Figure 2-3; A modified random network (MRN) for a “2-dimensional” oxide glass. The nominal composition is $M_3\text{O}_x(G_2\text{O}_3)$, where $M$'s are modifying cations and $G$'s are network forming cations. Covalent bonds are shown by the solid lines and ionic bonds by the dotted lines. The shaded regions are defined by the boundary conditions which run through the $G$-$O$ (non-bridging) bonds. These highlight the percolation channels of $M_2\text{O}_3$ that run through the network. Greaves (1985). The small open circles can be taken to be silicon, the large open circles are oxygen, and the small black circles are network modifying cations shown with 3-fold coordination for convenience e.g. $\text{Al}^{3+}$ or $\text{Fe}^{3+}$]

Besides the addition of sodium oxide and lime to the basic silica structure, oxides of other metals have been added such as zinc, which increases the glass durability by reducing the number of non-bridging oxygen sites in the glass, causing alkali to be less readily exchanged with $\text{H}_3\text{O}^+$ as a result of a stronger bonding with oxygen, (Tait and Jensen 1982). Boron has also been added to the silica structure; sodium borosilicate glasses are the most commonly used glasses for the storage of nuclear waste, (Ledieu et al. 2004).
2.4 Glass Corrosion

Glass corrosion is a general term used to describe the degradation of a glass surface due to two main reactions; an ion exchange between the alkali metals at the glass surface with the hydrogen ions in solution, and a network dissolution which occurs if the contacting solution pH becomes higher than a value of 9, (Clark et al. 1979). These reactions are discussed individually in Section 2.4.1 and Section 2.4.2 below.

Two main types of glass corrosion have been generally established; aqueous corrosion in which the glass surface is in direct contact with an aqueous solution, and weathering in which the glass surface is contacted by water from the surrounding air, either in the form of an adsorbed film or water droplets. In principle the two reactions i.e. ion exchange and network dissolution are applicable to both types of corrosion, (Schmitz et al. 1995). Float glass corrosion is primarily related to weathering.

2.4.1 Ion Exchange

Equation (2.2) below describes the ion-exchange reaction between the sodium ions at the glass surface with the hydroxonium from solution which results in the formation of a silanol group (=SiOH) and the leaching of a sodium ion (Na⁺), (Jupille 2001). Note that the symbol ‘ ‘ in Equation (2.2), denotes a silicon bonding to another three oxygen atoms.

\[
= SiO^-Na^+H_3O^+ \rightarrow =SiOH + H_2O + Na^+
\]  

(2.2)

The basic assumption of the ion exchange mechanism is that the Na⁺ ions are the only mobile charge carriers within the glass. The Na⁺ ions are linked to the silica network in the form =Si-ONa⁺. The anions (≡Si-O⁻) to which the Na⁺ cations are connected do not allow migration of Na⁺ ions due to electrostatic charge. However, the introduction of another positive ion i.e. H⁺ or H₂O⁺ in the structure allows the Na⁺ ions to leach out of the structure. The presence of Na⁺ ions at the surface helps water dissociate according to Equation (2.3) thereby encouraging corrosion. This is known as the Doremus model of interdiffusing ions referred to by Lanford et al. (1979).
Douglas and Isard (1949) explained why the sodium ions diffuse out of the glass. According to these authors the protons in water need to achieve an energetically more favourable environment by exchanging positions with the sodium ions in the glass, therefore these are forced out by demands of the system to decrease its free energy.

Even though other forms of the ion-exchange mechanism have been found in literature where the glass reacts with a water molecule (Lanford c.f. Haller 1963, Ernsberger 1980, Bunker 1994) or as ions including $\text{H}^+$ and $\text{H}_3\text{O}^+$ (Doremus 1975), Lanford et al. (1979) demonstrated that the most likely species to diffuse at the glass surface is the hydroxonium ion. They measured hydrogen and sodium depth profiles using a resonant nuclear reaction to show that the proportion of hydrogen entering the material was a factor of 3 greater than that of the sodium being leached. This implies that the interdiffusing species in the ion-exchange mechanism is indeed the hydroxonium ion.

From Equation (2.2) it ensues that the glass surface layer will be depleted in $\text{Na}^+$; this region of depletion is known as the gel layer (see Section 2.5.2 for more details). Leaching results showed that silica can also be extracted as well as alkali metals including $\text{Ca}^{2+}$ from sodium-silicate glasses in solutions below a pH of 7. However, this constitutes a much smaller amount compared to the amount of $\text{Na}^+$ extracted at the same pH, Douglas and El-Shamy (1967).

The ion-exchange mechanism is believed to cause a strain on the glass surface due to the $\text{Na}^+$ being replaced by an ion with a smaller radius i.e. $\text{H}^+$, causing the glass melt to break on cooling. Holland (1964) referred to Kraus and Darby (1922) who studied the ion-exchange mechanism (Equation 2.2) with a range of fused salts on soda-lime silica glass to explain the above statement. Kraus and Darby (1922) concluded that silver ($\text{Ag}^+$) is the only ion which does not produce a strain on the glass surface due to the similarity of the radius size with sodium, from the range of fused salts studied.
The surface area of soda-glass in contact with an aqueous layer has been reported to increase due to the formation of micropores Clark et al. (1979). It is believed that pores form during the ion exchange mechanism, due to size dissimilarities between the exchanging ions Doremus (1973). The presence of pores has been proved experimentally by Bunker (1994) after exposure of a sodium silicate glass for 4 hours at 80°C in a solution at a pH value of 1.5 by considering the transmission electron micrographs of the former glass. The author found interconnected voids of 3 nm in space which would facilitate the diffusion of water.

2.4.2 Network Dissolution

The dissolution of the glass network is most commonly expressed by Equation (2.4), Carmona et al. (2005), Tourié et al. (2008). This equation shows the silicate network being attacked by a hydroxyl group which results in the formation of a silanol group and a non-bridging oxygen group (≡Si-O?):

\[
≡Si − O − Si ≡ +OH^- \leftrightarrow Si − OH^+ ≡ Si − O^-
\] (2.4)

According to Carmona et al. (2005) this mechanism is initiated in superficial surface defects. The local dissolution of the network gives rise to pits and craters at the glass surface.

Some authors such as Holland (1964), Clark et al. (1979) believe that network dissolution can only occur once the ion-exchange has been completed, whereas Bunker (1994) and Derosa et al. (2003) state that both mechanisms occur simultaneously. Network dissolution is believed to be viable in alkaline conditions only, and if the initial solution pH contacting the glass at the beginning is acidic then a large increase in the pH value will need to have taken place, induced by the leaching of alkali from the glass before the network dissolution can occur. Hence it would make sense to say that the ion-exchange and the network dissolution mechanisms do not take place at the same time.
The increase in solution pH can be caused by the contacting solution not being replenished which according to Clark et al. (1979) is termed static corrosion. Conversely, continual removal and replacement of the contacting solution is known as dynamic corrosion.

The reaction which follows network dissolution (Equation 2.4) is caused by the formation of the non-bridging oxygen group which is now available to react with another water molecule and form a silanol group and an hydroxyl ion (OH⁻) as shown by Equation (2.5). The OH⁻ ion can cause further network dissolution and Equation (2.4) is repeated again, Charles (1958), Carmona et al. (2005).

\[
\text{Si} - \text{O}^– + \text{H}_2\text{O} \rightarrow \text{Si} - \text{OH} + \text{OH}^–
\]

(2.5)

According to Doremus (1979) and Jupille (2001) silica reacts with water to form silicic acid (\(\text{H}_4\text{SiO}_4\)), as shown in Equation (2.6):

\[
\text{SiO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{H}_4\text{SiO}_4
\]

(2.6)

At a pH above 9, silicic acid ionizes due to the presence of OH⁻ in the solution see Equation (2.7), (Doremus 1979).

\[
\text{H}_4\text{SiO}_4 \leftrightarrow \text{H}_3\text{SiO}_4^– + \text{H}^+
\]

(2.7)

At an even higher solution pH values a second hydrogen ionizes Doremus (1979):

\[
\text{H}_3\text{SiO}_4 \leftrightarrow \text{H}_2\text{SiO}_4^{2–} + \text{H}^+
\]

(2.8)

The dissociation of silicic acid at a pH>9 justifies why a pH value lower than 9 is recommended for the preservation of the silica structure.

Network dissolution is the most commonly studied mechanism when long term glass durability is of importance, namely for glass used for radioactive waste encapsulation. This stage has been studied experimentally by a number of authors such as Perera et
al. (1991). Theoretical techniques including Molecular Dynamics and Monte Carlo simulation have also been applied, (Aertsens and Ghaleb 2001). These are discussed further in Section 2.9.

2.5 Weathering

The main concern of this current work is corrosion by weathering. The weatherability of ancient glasses has been an area extensively studied by glass researchers in order to better understand how exposure to the environment affects their surfaces. In some museums atmospheric control systems (Bernardi et al. 2006) are used in order to protect glasses exposed to ambient conditions. Weathering has also been used as a means for dating ancient glass by measuring the extent of hydration at the glass surface and for determining the long-term glass durability of glasses used for consolidation of nuclear waste, (Lanford et al. 1979 citing Lanford 1977, Readey and Cooley 1977 respectively). Understanding weathering is also a foundation for the understanding of how corrosion can be prevented, Clark et al. (1979). It has been found in literature that weathering is strongly dependent on the relative humidity to which glass is exposed, as well as the glass composition (Walters and Adams 1975). Other factors such as the temperature of exposure and the so-called geometric effects which include orientation and distance of separation of glass surfaces Clark et al. (1979) during storage, are also of importance.

The term weathering is used when the glass is in contact with water vapour from the ambient atmosphere, causing a water layer to adsorb at the glass surface. This is sufficient to initiate the ion-exchange mechanism and the formation of insoluble salts termed "corrosion products". Figure 2-4 below is an SEM image showing the presence of corrosion products at the surface of a milled float glass sample after sample exposure to dry and saturated conditions for 7 days, (LeCourt 2006).
It is believed that weathering initially shares the same corrosion mechanism as aqueous corrosion i.e. an ion-exchange mechanism. This has been shown by Schmitz et al. (1995) with the use of SEM (scanning electron microscopy) combined with EDX (energy dispersive X-ray analysis) and SIMS. However, Isaard and Patel (1981) exposed a soda-lime-silicate glass to water at 60°C in an aqueous solution and to air at 80%RH and 60°C for the same time and concluded that aqueous corrosion and weathering were two different mechanisms because the quantity of alkali leached in each experiment did not agree. This could have been because the ratio of glass surface area to volume (A/V) was not taken into account. This is discussed further in Section 2.6.3.

According to Carmona et al. (2005) and Garcia-Heras et al. (2005) water can penetrate more deeply into the glass and reach the calcium ions after local network dissolution has occurred, see Equation (2.9).

\[
\text{(Si-O...Ca}^{2+}...O-Si =)+2H_2O \rightarrow Si-OH + HO-Si = +Ca(OH)_2 \quad (2.9)
\]

If carbon dioxide (CO\textsubscript{2}) is present in the surrounding environment it will dissolve in the adsorbed film at the surface and react with calcium hydroxide (CaOH\textsubscript{2}) to form a calcium carbonate precipitate (see Equation 2.10), Carter et al. (1997) and Carmona et al. (2005).
Two types of weathering can be identified; condensation run-off and condensation evaporation. In condensation run-off an amount of moisture collects on the glass surface which then runs off due to the action of gravity washing away any reaction products that have formed. In condensation evaporation a layer of fog is formed but it evaporates before the formation of droplets. The first type of weathering is usually due to extreme climatic changes and the second type is usually due to mild humidity and temperature changes during storage, shipment or use, Clark et al. (1979).

2.5.1 **Adsorbed Water Layer**

During weathering a layer of water adsorbs on the glass surface by both chemisorption and physisorption. Figure 2-5 below, describes the interfacial structure of a soda-lime-silica glass exposed to water vapour (Pulker 1984). In the glass bulk and surface, ions of opposite charge are present to maintain the electrical neutrality of glass where bonds have been broken. Note that calcium ions are only shown in the bulk glass and not in the chemisorbed layer, presumably due to their lower mobility than sodium.

\[
Ca(OH)_2 + CO_2 \leftrightarrow CaCO_3 + H_2O
\]

(2.10)

![Figure 2-5; Schematic representation of the formation of a water film on glass by adsorption of water vapour, Pulker (1984)](image-url)
Water chemisorbs i.e. reacts with the glass surface by hydroxylisation and silanol groups are formed, (Young 1958, Pulker 1984). The newly formed silanol groups make the glass surface more polar which can then promote further physisorption of water (Schaut and Pantano 2005). In the physisorbed region the molecular water adsorbs on to the existing silanol groups by van der Waals forces, represented by the dotted lines in Figure 2-5.

### 2.5.2 The Gel Layer

The presence of an adsorbed water layer at the glass surface initiates an ion exchange between H\(^+\) ions and Na\(^+\) ions causing a gel layer to form within the glass surface. The gel layer has also been reported in literature as a silica-rich layer, a hydrogen glass or as a leached layer which will be rich in silica due to the preferential leaching of Na\(^+\) ions, Davison (2003). The definition of a gel layer according to Pulker (1984), illustrated by Figure 2-5 does not seem to correspond to the above definitions i.e. if a gel layer is considered to be a silica-rich layer, then the gel layer in Figure 2-5 should extend downwards into the bulk glass. The gel layer takes its name from the similar behaviour of silica gel which expands and contracts with water, Davison (2003), like a sponge.

It is thought that the gel layer progressively increases in thickness as corrosion proceeds due to the progressive removal of sodium ions from deeper in the glass, (Fearn *et al.* 2006). According to Müller *et al.* (1995), for historical glasses and antique glasses the presence of a gel layer at the surface can have a barely visible iridescence to a significant opacity. Over time the gel layer thickness in historical glasses can range from 10 to 100 \(\mu\)m or even reach millimetre dimensions for excavated glasses (Müller *et al.* 1995).

According to Hench *et al.* (1980) five types of surfaces can be representative of any silica glass at some stage of their life; these are shown in Figure 2-6, below.

Type 1 glass surfaces are known to be resistant to exposure to corrosive environments. No significant compositional changes occur by either of the main corrosion mechanisms hence the bulk and the surface have the same composition.
Vitreous silica exposed to neutral conditions is representative of a Type 1 surface (Hench et al. 1980).

For a Type 2 surface, corrosion has occurred by selective alkali leaching at the glass surface forming a silica protective layer (Hench et al. 1980). A Type 2 surface is durable at a pH below 9 and can be representative of silica glasses with a low alkali content. The mechanism through which alkalis leach is diffusion-controlled, hence according to Hench et al. the amount extracted is best represented by Equation (2.11), below:

\[ Q = at^{1/2} \]  

(2.11)

Here \( Q \) (g g\(^{-1}\)) is the quantity of alkali extracted with exposure time \( t \) (s), and \( a \) is a constant (g g\(^{-1}\) s\(^{-1/2}\)). Equation (2.11) will be further discussed in Section 2.6.1. This equation also applies to Type 3 surfaces. These surfaces are described by a dual-protective layer which can consist of an alumino-silicate or calcio-silicate layer due to the addition of Al\(_2\)O\(_3\) or CaO to the glass composition. Glasses included in the latter type are very resistant to corrosion in both alkali and acid environments, Hench et al. (1980).
Type 4 surfaces have low durability and include glasses such as binary-sodium silicate glasses and potassium silicate glasses that are rich in alkali. According to Clark et al. (1979) Type 4 glasses, have a silica concentration that is insufficient for a protective film to form at the glass surface, therefore the main corrosion mechanism is total network dissolution. These surfaces exhibit a linear time dependency of Q on time (see Equation 2.12) because the extraction is no longer controlled by diffusion, (Hench et al. 1980). The same applies for Type 5 surfaces.
\[ Q = bt \]  \hspace{1cm} (2.12)

Here \( b \) is a constant \((g \text{ g}^{-1} \text{s}^{-1})\).

A Type 5 surface is characteristic of a glass which is dissolving by losing equal amounts of silica and alkali; this is called congruent dissolution. This type of surface is representative of silicate glasses which have been exposed to high pH conditions Hench et al. (1980).

In 1982 Hench devised another type of glass surface the Type IIIIB surface, see Figure 2-7 below. This type of surface applies to alkali borosilicate glasses which develop multiple layers of oxides or hydroxides at the surface after exposure to water, Hench (1982).

![Figure 2-7; Surface condition of a Type III B glass surface resulting from glass-environment interactions, Hench (1982)](image)

### 2.6 Factors Affecting Corrosion

According to Clark et al. (1979) the extent of glass corrosion depends on the type of corrosion (aqueous or weathering) and the exposure conditions of the samples such as temperature, time and %RH. Other parameters such as the surface area to volume ratio and the solution pH are also of importance. These will be individually discussed next.
2.6.1 Time Dependency

The amount of alkali extracted in solution is commonly described in literature by the empirical equation, (see Equation 2.13) Douglas and El-Shamy (1967):

\[ Q = at^{\frac{1}{2}} + bt \]  

(2.13)

Here \( Q \) (g g\(^{-1}\)) is the amount of alkali extracted with exposure time \( t \) (s), and \( a \) and \( b \) are constants with units of g g\(^{-1}\)s\(^{-\frac{1}{2}}\) and g g\(^{-1}\)s\(^{-1}\) respectively.

Equation (2.13) has a gradient with the limiting values of \( \frac{1}{2} \) as \( t \to 0 \) and 1 as \( t \to \infty \), and increases slowly with time at intermediate values.

Differentiating the logarithmic form of Equation (2.13) gives Equation (2.14), (Douglas and El-Shamy 1967):

\[ \frac{d\log Q}{d\log t} = \frac{a}{2\sqrt{t}} + b \left[ \frac{1}{a\sqrt{t} + b} \right] \]  

(2.14)

Over limited times, approximately linear plots of log \( Q \) versus log \( t \) would be expected and the slopes of these would vary between \( \frac{1}{2} \) and 1 as the time increases (Douglas and El-Shamy 1967).

The dependency of extraction of alkali on the square root of time in aqueous solutions is generally attributed to a diffusion mechanism in which the alkali diffuses from the solid through a leached layer that is augmenting in thickness with time, e.g. Douglas and El-Shamy (1967) and Hench et al. (1980). After a given time a direct time dependency may be seen instead. This has been attributed to diffusion through a leached layer of constant composition and thickness, (Douglas and El-Shamy 1967, Tait and Jensen 1982). Alternatively the transition from square-root time dependent behaviour to linear dependency of sodium extraction with time has been attributed to an increase in the leaching solution pH, Duffer (1995). This is likely to be associated with the onset of network dissolution, Equation (2.4) which is known to occur above a pH of 9.
Douglas and El-Shamy (1967) studied aqueous corrosion of sodium silicate glasses in de-ionised water. Their results agreed with Equation (2.13). It is apparent from their results that the extraction of Na$_2$O in sodium silicate glasses at short times (up to 100 minutes) is linear with the square-root of time. For longer times (> 2000 min) the extraction of Na$_2$O is linear with time (see Figure 2-8). Furthermore it appears the amount of Na$_2$O extracted is strongly temperature dependent as shown by increasing amounts of sodium leached with increasing temperature.

The nature of the time dependency on the extent of corrosion therefore appears to give an indication of the corrosion mechanism. This principle is adopted as part of the experimental investigation in the current work.

2.6.2 Diffusion Mechanism

It has been generally agreed that diffusion of a substance in a planar surface can be expressed by the diffusion equation see Equation (2.16) below, (Doremus 1975,
Smets and Lommen 1981) which is derived by a mass balance on an element using Fick’s First Law in one dimension, see Equation (2.15).

\[ N = -D \frac{\partial C}{\partial z} \quad (2.15) \]

Here \( N \) is the flux (mol s\(^{-1}\)m\(^{-2}\)), \( C \) is the concentration (mol m\(^{-3}\)), \( z \) is the depth (m) and \( D \) is the diffusion coefficient (m\(^2\) s\(^{-1}\)).

\[ \frac{\partial C}{\partial t} = \left( \frac{\partial}{\partial z} \right) \left[ D \left( \frac{\partial C}{\partial z} \right) \right] \quad (2.16) \]

If the diffusion coefficient \( D \) is constant with respect to time and position then Equation (2.16) becomes Fick’s Second Law, as follows:

\[ D \frac{\partial^2 C}{\partial z^2} = \frac{\partial C}{\partial t} \quad (2.17) \]

Equation (2.17) is generally applied for the calculation of the variation of concentration with time due to diffusion, and it assumes that the medium of the system is stationary, (Crank 1976).

The conditions are often taken as follows:

\[ C = 0, \ z > 0, \ t = 0 \quad (2.18) \]

\[ C = 0, \ z = \infty, \ t \geq 0 \quad (2.19) \]

\[ C = C_0, \ z = 0, \ t \geq 0 \quad (2.20) \]

For a temperature dependent diffusion in solids such as the diffusion of molecules in silica, an Arrhenius type relationship is generally assumed to apply as shown below, (Doremus 1975, Holland 1964).
Here $E_a$ is the activation energy (kJ kmol$^{-1}$), $R$ is the universal gas constant (J K$^{-1}$ mol$^{-1}$), $D_0$ is a constant (m$^2$ s$^{-1}$) and $D_e$ is the effective diffusion coefficient (m$^2$ s$^{-1}$). The activation energies for diffusion are directly related to the size of the diffusing atom (Doremus 2002).

**Combining Ion-Exchange and Network Dissolution Mechanisms**

The ion-exchange at the glass surface and network dissolution in the glass have been combined in a diffusion model where the glass surface is gradually removed, Doremus (1979). At short times, the amount of alkali extracted can be expressed by Equation (2.22) from interdiffusion theory, Doremus (1979) as follows:

$$Q_d = 2C_0 \sqrt{\frac{Dt}{\pi}}$$

Here $Q_d$ is the amount of alkali extracted per unit surface area (mol m$^{-2}$), $C_0$ is the initial alkali concentration (mol m$^{-3}$), $D$ is the diffusion coefficient (m$^2$ s$^{-1}$), and $t$ is time (s).

At longer times the alkali extraction becomes linear with time suggesting this process is no longer controlled by diffusion and is instead dependent on the rate of network dissolution. Doremus (1979) suggests Equation (2.23) below for the amount of alkali leached during network dissolution, where $a'$ is the rate constant of matrix corrosion (m s$^{-1}$).

$$Q_d = C_0 (a't + D/a')$$

**Water Diffusion Mechanism in Silica**

Doremus proposed a diffusion-reaction model for the diffusion of water in silica in which the molecular water diffuses interstitially in glass and reacts to equilibrium with the silicon-oxygen lattice Doremus (2002), according to Equation (2.24).
\[ \equiv Si - O - Si \equiv +H_2O \rightarrow SiOH + HOSi \equiv \] (2.24)

From Equation (2.24), Doremus (2002) states that the hydroxyl ions are immobile because only the molecular water diffuses. This model implies that the two main stages of corrosion are combined into a diffusion model in which the surface of the glass is progressively removed (McVay and Buckwalter 1980).

From Equation (2.24), Doremus (2002) introduces an equilibrium constant which represents the concentration ratio between the silanol groups and the molecular water, see Equation (2.25).

\[ K = \frac{C_R^2}{C_i} \] (2.25)

Here \( C_R \) is the concentration of reactant e.g. silanol (mol m\(^{-3}\)), \( C_i \) is the concentration of interstitial water molecules (mol m\(^{-3}\)) and \( K \) is the equilibrium constant (mol m\(^{-3}\)).

### 2.6.3 Glass Surface Area to Solution Volume Ratio (A/V)

During glass storage, in warehouses for instance, an adjoining condensed liquid layer may form between the stacked glass sheets because the separation distance between the sheets is typically only 100 \( \mu \)m. This in turn can induce high pH values and local network dissolution may occur, caused by the high A/V ratio \( i.e \) the surface area of glass exposed to the volume of the condensed liquid layer (Clark et al. 1979, Duffer 1995).

In aqueous corrosion of powdered glass of high surface area in a small volume of solution, the high A/V ratio will cause the solution to become saturated with hydroxyl ions due to the ion exchange mechanism (Equations 2.2 and 2.3), causing the solution pH to increase. Whilst, if a small surface area is used with the same volume of solution, the \( OH^- \) in solution will be more diluted and the pH value will remain low. A direct comparison between the fraction of alkali leached per unit surface area for
powder and continuous samples was not presented by McVay and Buckwalter (1980) whilst studying a complex nuclear waste containment glass. However, it appears from their data that a different sample surface area to solution volume was used in either case which could make the results questionable.

If powder samples are being used then care will have to be taken that a consistent particle size distribution is being used for a glass of a given composition to ensure the same specific surface area when different surface area to volume ratios are used. The kinetics of corrosion are directly proportional to the surface area to volume ratio as shown by Ethridge et al. (1979). They modify the reaction equation (see Equation 2.13) for corrosion by incorporating a surface area to volume ratio term, see Equation (2.26).

\[
C = \left( \frac{A}{V} \right) k t^n
\]  

(2.26)

Here \( C \) (mol m\(^{-3}\)) is the concentration of a species in solution, \( A \) is the surface area of the sample (m\(^2\)), \( V \) is the volume of solution (m\(^3\)), \( k \) is the reaction rate constant, (mol m\(^{-2}\) min\(^{-n}\)) and \( t \) is the reaction time (min).

### 2.6.4 Specific Surface Area

The specific surface area of a crushed glass sample is commonly determined by application of the BET theory. Most commonly inert gases such as nitrogen are used, but the use of water has also been found in literature, Young (1958), Harkins and Jura (1944). This will be further discussed in Chapter 6. The specific surface area is dependent on the size of particles, the solid porosity, Collins et al. (2005) and the solid composition, Harkins and Jura (1944).

Table 2-1 below, shows that for a larger pore size and a constant particle size the specific surface area value decreases. The same trend is seen for a constant pore size and larger particle sizes, (Collins et al. 2005). The specific surface area of the sample will also influence the amount of alkali extraction and the rate at which equilibrium is reached.
Table 2-1; Illustration of variation in specific surface area as a function on pore size and particle size for Davisil silica, obtained by nitrogen adsorption, Collins et al. (2005)

<table>
<thead>
<tr>
<th>Pore Size (nm)</th>
<th>Particle size (μm)</th>
<th>S (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
<td>351</td>
</tr>
<tr>
<td>15</td>
<td>10</td>
<td>301</td>
</tr>
<tr>
<td>15</td>
<td>200</td>
<td>265</td>
</tr>
</tbody>
</table>

Walters and Adams (1975) studied the sodium released per unit surface area from borosilicate glass tubing which had been exposed to 98% RH and 50°C over 20 days. The alkali leached was measured by flame spectroscopy after the samples were washed in distilled water. Two types of borosilicate glass surface were used; one of which had been drawn whilst the other was fractured see Figure 2-9 below. For the fractured surface more alkali was generated showing more weathering compared to the drawn sample this could be due to the creation of a fresh surface due to fracture which has a higher propensity for corrosion.

Figure 2-9; Na₂O on surface after weathering of moderately resistant borosilicate glass at 98% RH and 50°C, Walters and Adams (1975)

2.6.5 Effect of Temperature

Temperature has been suggested in literature to affect the kinetics of corrosion and also the mechanism by which corrosion is occurring, Clark et al. (1979). According to Paul (1977) increasing the solution temperature increases the kinetics of alkali
extraction known as Stage 1, and he states that for the majority of silica glasses the amount of alkali extracted doubles for an increase in temperature from 8 to 15 °C. The work of Douglas and El-Shamy (1967) in Section 2.6.1 showed that the amount of Na₂O extracted effectively increased with temperature of solution at both short and long exposure times (see Figure 2-8).

In section 2.6.3 it was established that the effect of temperature on diffusion through solids can be effectively described by an Arrhenius-type relationship, (see Equation 2.21). Mazer (1991) successfully uses this to correlate the temperature influence on corrosion rate for a range of nuclear waste containment glasses. However he points out that the mechanisms are complex and therefore the activation energy parameter does not have any real significance in terms of an individual reaction. In the present study, an attempt is made to correlate the extent of corrosion with temperature.

### 2.6.6 Solution pH

The solution pH is the most significant parameter in aqueous corrosion as this can determine the corrosion mechanism. During corrosion the rate of change of the solution pH is controlled by the ratio of the surface area of the sample to the volume of solution, see section 2.6.2. It is generally accepted that alkali extraction to the leaching solution occurs mainly up to a pH of 9 where after network dissolution occurs because of the dissociation of silicic acid (see Section 2.4.2 for equations). This leads to a higher effective solubility and a higher dissolution rate of the silicate lattice, (Paul 1977). If neutral or acidic conditions prevail instead, the rate of dissolution of the silicate lattice is not influenced by the pH, because the dissolving species, un-ionised silicic acid, has nearly constant solubility, (Paul 1977).

The solution pH is strongly dependent on the test conditions used i.e. whether these are static or dynamic. For the former the solution is not replenished which leads to a pH increase over time because hydroxyl ions have leached into solution. El-Shamy and Douglas (1972) studied the effect of the replenishment frequency of the leaching solution. Their results showed that the final solution pH value decreased with increasing number of solution replenishments. Further discussion on the effect of the solution pH is given in Section 2.7.
2.6.7 Effect of Relative Humidity

The identification of suitable RH conditions is of importance for glass storage in museums, for instance. This was sometimes determined by the stability of the corrosion products such as sodium and potassium carbonate, Robinnet (2006). Other methods have been used to study the extent of glass corrosion after exposure to a given %RH, *i.e.* by measurement of the Na⁺ depletion in the glass, Fearn *et al.* (2004), or by measuring the amount of water sorbed (Walters and Adams 1975) by the glass. These will be further discussed below.

The percent relative humidity (%RH) is determined by the ratio of the partial pressure \( p \) (Pa) of water vapour to the saturated vapour pressure value \( p_0 \) (Pa), see Equation (2.27). The \( p_0 \) value can be determined from the Antoine equation see Equation (2.28), below. The %RH can therefore be expressed as Equation (2.27), Coulson *et al.* (1999):

\[
%RH = \frac{p}{p_0} \times 100
\]  

(2.27)

The Antoine equation is expressed by Equation (2.28) below, (Reid *et al.* 1987):

\[
\log p_0 = A' - \frac{B'}{T + C'}
\]  

(2.28)

Here \( T \) is the temperature (K) and \( A' \), \( B' \) and \( C' \) are the Antoine constants. \( A' \) and \( B' \) are dimensionless, and \( C' \) has units of K.

Fearn *et al.* (2004) studied the variation of sodium ion concentration with depth and as a function of %RH for a fabricated glass with low energy SIMS (Secondary Ion Mass Spectrometry), see Figure 2-10 below. Three different conditions were used: as made *i.e.* the glass sample was examined straight after production at ambient conditions, and after storage at a relative humidity of 35% and 55% for 91 hours. The depth profiles (Figure 2-10) show a progressive decrease in the sodium ion concentration in the first few nanometres. Lacharme and Léhuéde (1985), cited by
Lombardo *et al.* (2005), attributed the decrease in Na\(^+\) ion concentration to surface artefacts caused by the use of SIMS, while Fearn *et al.* (2004) considers the decrease in concentration to be due to the removal of leached corrosion products from the surface of the glass. A progressive increase of the Na\(^+\) concentration is then measured followed by its stabilization which according to Fearn *et al.* (2004) corresponds to the bulk glass composition. Note at 55%RH the concentration profile becomes an S-shape implying the occurrence of concentration dependent diffusion, (Smets and Lommen 1981).

Water sorption isotherms are also used as a method to study the influence of %RH. The water adsorbed per unit surface area over a relative humidity range from 30 - 90%RH, for glasses of different compositions has been studied by Walters and Adams (1975) on desorption at 25°C using a moisture analyser. The glasses studied included two soda-lime glasses (one of high durability and the other of low durability), lead glass and borosilicate glass. For the latter glass the mass uptake is considerably smaller as illustrated by an almost flat trace in Figure 2-11. This could be due to the formation of complex oxide layers at the glass surface as suggested by Hench (1982), see Figure 2-7.
2.6.8 Glass Composition

The glass durability has been shown in literature to be strongly dependent on the concentration of silica (El-Shamy 1973), lime (Paul 1977) and the presence of high valency elements such as zinc (Tait and Jensen 1982). Experiments determined for glasses with a silica concentration below 66 mol% in the glass composition allow the formation of interconnecting paths of neighbouring silicon oxide groups and as a result provide suitable sites for the movement of interchanging ions. Above a 66 mol% silica concentration, the SiO₂ groups are isolated by Si-O-Si groups which restrain the movement of the leaching ions, (El-Shamy 1973). The addition of lime (CaO) to the glass structure prevents glass crystallisation and enhances glass durability by reducing the soda extraction. This is valid when less than 10 mol% of lime is used; at concentrations above 15 mol% a decline in durability is seen instead, Paul (1977). The addition of other higher valency elements such as zinc has also been found to increase the durability of glass (Paul 1977, Tait and Jensen 1982). The increase in durability for zinc containing glasses is believed to be related to an increase in the pH at which network dissolution occurs, according to the zinc oxide solubility curve, (Paul 1977).
For float glasses the air side and the tin side have very different durabilities. From literature it was found that the tin side of float glass is more durable than the air side when exposed to humid conditions, (Feldmann and Weibmann 2007). Presumably the higher durability of the tin side is for one of two reasons; there is a lower concentration of sodium compared to the air side, or because tin is less mobile under humid conditions because of its higher valency compared to sodium. Hayashi et al. (2002) linked the higher durability of the tin side to the concentration of Sn$^{2+}$, which restrains the ion-exchange between the sodium and the hydrogen ions. As a result thinner sodium leached layers are formed on the tin side compared to the air side.

2.7 Corrosion Prevention

In the previous sections the mechanisms by which glass corrodes were described. The two main stages of corrosion were seen to consist of an ion-exchange between the alkali in the glass and the hydrogen species from the solution (stage 1) and, if the pH of solution rose above 9 then network dissolution would occur (stage 2). When glass is exposed to humid conditions a water layer adsorbs on the glass surface. This is sufficient to initiate the ion-exchange mechanism and the formation of insoluble salts termed “corrosion products”, see Figure 2-4. If the adsorbed water becomes alkaline then the glass silicate network is attacked and staining (also termed haze) of the surface can occur (Smith and Pantano 2008, Holmes 2007a, b). Figure 2-12 below, shows a weathered float glass surface which was interleaved with paper and exposed to 60°C and 80% RH for 40 days in a humidity cabinet. After this time period the sample was removed and washed with DI water at 50°C in a Benteler glass washing machine. The sample was then dried with an air knife. The sample was illuminated with a torch (Challenge model 2936, 6 V, 55 W halogen bulb) and a picture was taken, Staunton (2007).
The existing literature on corrosion inhibition is scarce and somewhat contradictory. This section reviews the existing literature on corrosion prevention including the application of interleaving materials, stain inhibitors and retardants of dissolution.

### 2.7.1 Interleaving Materials

Interleaving materials are used to physically separate glass sheets during storage and to minimise mechanical damage such as abrasion during transport caused by friction of stacked glass sheets. Acid free paper, coconut flour, wood flour or polymer beads which include Ultra High Molecular Weight Polyethylene (UHMWPE) and Polymethyl Methacrylate (PMMA) are some of the most common interleaving materials. They reduce corrosion by separating the glass sheets sufficiently to prevent the formation of an adjoining condensed liquid film, (Franz 1980, Franz 1997, Franz and Fortunato 1997, Feldman and Weibmann 1997, Holmes 2007a, b) or by absorbing part of the water present on the surface of the glass, (Holmes 2007a). Therefore the
amount of alkali leached and the extent of surface damage is reduced. Interleaving materials have been used on their own or in conjunction with weak acids to minimise the alkali leached, (Holmes 2007b).

The sole application of PMMA beads on the surface of a float glass sample was studied by Smith and Pantano (2008) after exposure of samples to 85% RH and 85°C. The extent of corrosion was measured by the samples' roughness. Techniques such as AFM and FT-IRRS (Fourier-transform infrared reflectance spectroscopy) were used by Smith and Pantano. These authors reported a four-fold increase in roughness for the sample surface with PMMA beads, in comparison to a pristine glass surface. The increase in roughness was accompanied by the formation of visible staining which couldn't be removed suggesting a weathering induced network dissolution, Smith and Pantano (2008). This implies that the sole application of PMMA beads does not protect the glass surface against corrosion. Smith and Pantano (2008) also exposed glass samples interleaved with PMMA to cyclic conditions; the temperature was varied between 5 and 60°C at 75 %RH at these conditions no sodium leached layer was measured at the glass surface over a total experimental time of 90 days.

Feldmann and Weibmann (2007) also studied the effectiveness of coating float glass samples with PMMA. The authors used ellipsometry to measure the refractive index of the glass surface which they then related to the extent of corrosion. An increase in the refractive index value over time was observed for samples exposed to 40°C and 100% RH, suggesting some corrosion occurred. These results appear to confirm the findings of Smith and Pantano (2008) who detected corrosion on float glass coated with PMMA and exposed to static conditions.

2.7.2 Corrosion Inhibitors

Stain inhibitors are compounds, usually weak acids that are added to the glass surface for their ability to inhibit corrosion by neutralising the alkali leached from the surface. Hence it is of interest that the surface pH is kept below a pH of 9 so that the glass bulk will not be attacked Holmes (2007a). The application of an acid to the glass surface seems counter-intuitive because this is likely to enhance the alkali-hydrogen ion exchange (Holmes 2007b) hence accelerating the first stage of glass corrosion. Stain
inhibitors are often added in powder form for convenience. However this does not give a homogeneous distribution of coverage over the surface, and large regions are exposed and presumably unprotected. The most commonly used stain inhibitors in industry are adipic acid and boric acid, Schaut and Pantano (2005), Holmes (2007), Smith and Pantano (2008). The suitability of adipic and boric acid for the prevention of glass corrosion is based on a number of the acid properties such as acid strength, neutralisation capability, amount of acid required to neutralize glass corrosion, glass visual appearance after application of the stain inhibitor, amount of haze at the glass surface after exposure to humid conditions (Holmes 2007a), cost (Schaut and Pantano 2005) and toxicity.

In the application of acids to the glass surface it is of interest to apply acids which are weak because the hydrogen ion concentration will be lower, hence lowering the amount of alkali leached. According to Holmes (2007a) and Schaut and Pantano (2005), adipic acid is stronger than boric acid as suggested by the acid ionization constant \( pK_a \), i.e 4.4 and 9.47 respectively. Figure 2-13 below, shows that the pH of a boric acid solution will increase sharply on the addition of very small amounts of alkali. On the other hand adipic acid solution will accommodate much more alkali before the solution pH rises towards the threshold for network dissolution. Therefore adipic acid would seem to be a more suitable stain inhibitor.
According to Schaut and Pantano (2005), 1 molecule of adipic acid is known to neutralise 2 moles of sodium leached. This has been explained in terms of the molecular structure of adipic acid (C$_6$H$_{10}$O$_4$) which has an acid group at each end of the carbon backbone. In comparison, 1 molecule of boric acid, B(OH)$_3$ only neutralises 1 mole of sodium even though it has 3 hydroxyl groups bound to the boron atom. Therefore the neutralisation capacity of an acid is best represented by a pH curve such as Figure 2-13. The latter authors also consider the neutralisation capability in terms of amount of acid needed. They report an extra 18% of adipic acid is needed in comparison to boric acid to neutralise 1 mol of sodium (g).

Figure 2-14 below, Staunton (2007), shows the haze pattern on the air side of two float glass samples after application of 100 mg m$^{-2}$ of adipic acid and boric acid and exposure to 60°C and 80% RH for 40 days in a humidity cabinet. After this time period the samples were removed and washed with DI water at 50°C in a Benteler glass washing machine. The samples were then dried with an air knife and illuminated with a torch (Challenge model 2936, 6 V, 55 W halogen bulb) so that a picture of the glass surface could be taken, Staunton (2007).
From Figure 2-14 it appears that staining is worse for the sample previously treated with boric acid. The development of so-called spotty corrosion is believed to be due to the creation of open capillary spacing between stacked flat glass sheets which allows penetration of moisture and its accumulation around stain inhibitors, Franz (1980).

Smith and Pantano (2008) measured the leached layer thickness for adipic acid and boric acid mixed with PMMA beads, after exposure of the samples to cyclic tests where the temperature conditions were varied between 5 and 60°C at 75% RH. From the sodium depth profile data in Figure 2-15 and Figure 2-16 it appears that the extent of depletion increases with time and the profile is of similar shape when the glass surface is treated with adipic acid or boric acid. Note however that at prolonged exposure (60 and 90 days) the sodium concentration profiles are very close giving an apparent final leached layer depth of approximately 60 nm. It can be assumed that no wash-off occurred in the experiments of Smith and Pantano (2008) i.e. the accumulation of the sodium ions at the surface will reduce the concentration driving force for diffusion. The main difference appears to be for the as-received samples
where the remaining sodium concentration is higher for the sample treated with adipic acid. Smith and Pantano (2008) do not make clear why this initial concentration difference arises.

Feldmann and Weibmann (2007) showed the combination of PMMA with adipic acid was more effective in inhibiting corrosion compared to mixtures of polystyrene with boric acid, from the corresponding refractive index values. The former authors measured for a float glass sample coated with polystyrene and boric acid, an increase of 25% in the refractive index value, after 21 days of exposure to 40°C and 100% RH, compared to a sample coated with a mixture of PMMA and adipic acid.
In view of the data available in literature for adipic and boric acid treatments on glass, it appears that adipic acid would be the preferred acid because of its ability to neutralise large amounts of alkali leached whilst keeping the solution pH below 9, Holmes (2007a).

2.7.2.1 Zinc

Other compounds such as zinc are also effective in reducing the extent of corrosion. Zinc is called a retardant of dissolution (Iler 1979) presumably because the network dissolution is delayed up to a pH of 13, according to the ZnO solubility shown by Paul (1977). One of the earliest applications of zinc for glass corrosion prevention was in the washing and sterilising of returnable beverage bottles, Hudson and Bacon (1958). The latter filled a soda-lime glass bottle with 3% caustic soda solution (NaOH) at 125°F (52°C) and left it for a period of time. The addition of 10 ppm of zinc chloride (ZnCl₂) resulted in a decrease in silica dissolution of 90%. The same experiment was repeated using 10 ppm of beryllium sulphate (BeSO₄). This reduced the quantity of silica dissolved by 98%. Other modifiers, such as strontium chloride (SrCl₂) and antimony trichloride (SbCl₃) reduced the weight loss by 75%. Even though BeSO₄ was the best compound to reduce the amount of silica dissolution, its application for sterilising glass bottles is not recommended due to its toxicity. No details on the inhibition mechanism are given in this paper.

At present zinc, either as a soluble salt, (Green 1967) or as an insoluble compound (Caraval and Hatfield 1990), is used in dishwashing machine detergents for protection against glass corrosion and prolonging glassware use. The application of zinc has also been suggested in a solid metallic form, (Rutowski and Harbor 1972). An advantage of using soluble zinc salts is that they will be evenly distributed giving a homogeneous coating whereas insoluble zinc might be present in a particle form (Keyes et al. 2000), giving heterogeneous coverage and poorer protection.
Zinc Mechanism

Phan et al. (2004) studied the adsorption of zinc cations on colloidal silica from a solution of zinc sulphate, and proposed Equation (2.29), below to be a possible mechanism for the adsorption of zinc at the silica surface.

\[ \text{Si} - \text{OH} + \text{Zn}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Si} - \text{O}^-(\text{ZnOH})^+ + 2\text{H}^+ \]

A relation between the amount of hydrogen released and zinc adsorbed was studied by Kozowa (1961), for different solution pH values. The mole ratio of H\(^+\) released per Zn\(^{2+}\) adsorbed as a function of pH was measured by Kozawa for powdered silica gel, see Figure 2-17, below. An apparent 3:1 mole ratio of the number of hydrogen moles released per mole of zinc adsorbed (see H\(^+\)/Zn\(^{2+}\) in Figure 2-17) seems to apply for a solution pH between 5.48 and 6.3. The 3:1 mole ratio measured by Kozawa (1961) appears to contradict Equation (2.29) proposed by Phan et al. (2004).

![Figure 2-17](image-url)

Figure 2-17; Figure showing the ratio of hydrogen released (H\(^+\)) with zinc adsorbed (Zn\(^{2+}\)) as a function of solution pH and corresponding individual amounts are also shown, Kozawa (1961)

The results of Kozawa (1961) shown in Figure 2-17 suggest the zinc adsorption is favoured with increasing solution pH values. The adsorption of zinc at silica-containing surfaces as a function of pH was found to be favoured at higher acidic conditions by Tait and Jensen (1982), Vsalova (2001), Miyasaki et al. (2003) and even neutral conditions, Phan et al. (2004).
The adsorption of zinc at silica surfaces has been reported to increase with increasing zinc concentrations, Kozawa (1961) and Miyazaki et al. (2003). Increasing amounts of zinc have proven to have greater effect on the inhibition of sodium leaching from sodium borosilicate glasses, Tait and Jensen (1982). This is presumably because with higher zinc concentrations, more zinc adsorbs and fills the interstitial voids of the glass. Changes in the reaction kinetics have also been reported, Oka and Tomozawa (1980), Tait and Jensen (1982). The zinc adsorption at the glass surface has been suggested to result in a protective barrier to the leaching of alkali to the glass surface, Wegst et al. (1948), Tait and Jensen (1982), Lewis et al. (1982), Caraval and Hatfield (1990). It appears from literature that the development of a protective barrier could also be a result of the precipitation of Zn(OH)$_2$ at the silanol sites, Miyazaki et al. (2003).

In this thesis the mass uptake by crushed float glass exposed to different temperatures and %RH was measured gravimetrically for both untreated and zinc-treated float glass samples. Zinc was chosen in this thesis as a corrosion inhibitor because its application has not been extensively studied in literature. Furthermore, the small amount of existing evidence suggests that zinc is a viable corrosion inhibitor.

### 2.7.3 Other Methods

Besides the application of interleaving materials and stain inhibitors at the glass surface other compounds such as esters and neutral buffers have also been suggested to counteract the sodium leached, Holmes (2007a) and Holmes (2007b) respectively. Film coating the glass surface is also another option, Holmes (2007a). It has become clear that the main culprit of corrosion in soda-lime-silicate glass is the presence of alkali metals (mainly sodium) at the glass surface. Hence in industry some glasses are produced in a SO$_2$ (sulphur dioxide) environment. According to Doremus (1973) and Douglas and Isard (1949) cited in Doremus (1979) Equation (2.30) below applies in furnace atmospheres containing sulphur:

$$2Na^+{\text{(glass)}} + SO_2 + \frac{1}{2}O_2 + 3H_2O \rightarrow 2H_2O^* + Na_2SO_4 \tag{2.30}$$
At the glass surface the sodium reacts with sulphur dioxide to form sodium sulphate in a crystalline form. According to Doremus (1979) sodium sulphate has a lower alkalinity than sodium carbonate, or sodium hydroxide.

2.8 Summary of Experimental Techniques

The choice of a measurement technique is usually driven by the type of information required as well as by the limitations and benefits of the method. The sensitivity of an instrument depends on its ability to respond to small changes in the relevant parameter e.g. for a gravimetric instrument this would be mass. The limitations of a technique can arise from external variables such as specimen homogeneity and surface roughness for instance during SIMS analysis, (Clark et al. 1979).

2.8.1 Surface Analysis

The depth at which a surface analysis instrument performs is dependent on the type of radiation used on the surface. For most techniques the radiation emitted corresponds to the radiation detected with the exception of XPS where photons are emitted to the surface but electrons are detected. The surface sensitivity of a technique is defined by the depth from which the information is gathered at. According to Vickerman (1997) there are 3 surface regimes:

- Top surface monolayer.
- First 10 atomic layers.
- Surface film no greater than 100 nm.

Surface analysis techniques are operated in vacuum because ‘electrons and ions are scattered by molecules in the gas phase’, (Vickerman 1997) and because ‘long mean free paths for particles used in studying surfaces’ are required, (Wilson 1997). Furthermore, the use of high vacuum keeps ‘a surface free from adsorbed gases during the course of a surface analysis experiment’, (Wilson 1997).

2.8.2 Summary of Techniques

The tables below summarise the techniques which were referred to in the current chapter as well their attributes and the corresponding author and finding. Note that
PIXE/RBS, XPS, SIMS and gravimetric analysis will be further discussed in Chapter 4.

Based on the techniques previously chosen for the study of glass corrosion, in this present study ion beam analysis i.e. PIXE/RBS was used for the identification of elements in the float glass composition, XPS was chosen for quantification of the amount of zinc deposited at the glass surface, and SIMS was used for the depth profiling of float glass. AFM was used for imaging the float glass samples exposed to dry and saturated conditions. For the in situ measurement of the glass corrosion kinetics a gravimetric technique was also used for different temperatures and %RH conditions for untreated and zinc-treated float glass samples.

### Table 2-2: Summary of relevant spectrometry and spectroscopy techniques

<table>
<thead>
<tr>
<th>Mass Spectrometry</th>
<th>Technique</th>
<th>Characteristics</th>
<th>Author</th>
<th>Finding</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIMS (Secondary Ion-Mass Spectrometry)</td>
<td>See Section 4.3.4 in Chapter 4 for more details on this technique.</td>
<td>Fearn et al. (2004)</td>
<td>Sodium depth profile of alkali at various %RH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tait and Jensen (1982)</td>
<td>Depth profile for glass dipped in zinc solution</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Schmitz et al. (1995)</td>
<td>Weathering and aqueous corrosion share the same mechanism</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spectroscopy</th>
<th>Technique</th>
<th>Characteristics</th>
<th>Author</th>
<th>Finding</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-IRRS (Fourier Transform Infrared Reflection Spectroscopy)</td>
<td>Quantitative technique used for characterisation of glasses both prior and after exposure.</td>
<td>Smith and Pantano (2008)</td>
<td>Thickness of sodium leached layer on float glass samples</td>
<td></td>
</tr>
<tr>
<td>XPS (X-ray Photoelectron Spectroscopy)</td>
<td>See Section 4.3.2 in Chapter 4 for more details on this technique.</td>
<td>Smith and Pantano (2008)</td>
<td>Sodium concentration depth profiles</td>
<td></td>
</tr>
<tr>
<td>AES (Auger Electron Spectroscopy)</td>
<td>Useful for routine ID of chemical species at surface, very good spatial resolution but subject to electron beam damage, Clark et al. (1979).</td>
<td>Clark et al. (1979)</td>
<td>Temperature dependence on corrosion mechanism</td>
<td></td>
</tr>
<tr>
<td>AAS (Atomic Absorption Spectrometry)</td>
<td>Detection of leached ion concentration in solution, usually choice of spectrometry technique is dependent on ion valency, Clark et al. (1979).</td>
<td>Tait and Jensen (1982)</td>
<td>Identification of Na⁺, Si⁴⁺, Zn²⁺ in leached solutions</td>
<td></td>
</tr>
</tbody>
</table>
Table 2-3: Summary of relevant imaging techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Characteristics</th>
<th>Author</th>
<th>Finding</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM (Atomic Force Microscopy)</td>
<td>See Section 4.3.1 in Chapter 4 for more details on this technique</td>
<td>Smith and Pantano (2008)</td>
<td>Measurement of surface roughness</td>
</tr>
<tr>
<td>TEM (Transmission Electron Micrograph)</td>
<td>Better resolution than SEM the sample does not need to be gold coated, Clark et al. (1979).</td>
<td>Bunker (1994)</td>
<td>Identification of surface pores in a sodium-silicate surface</td>
</tr>
</tbody>
</table>

Table 2-4: Summary of other relevant techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Characteristics</th>
<th>Author</th>
<th>Finding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric analysis</td>
<td>See Chapter 4 for more details on this technique</td>
<td>Walters and Adams (1975)</td>
<td>Desorption of water for glasses of different compositions</td>
</tr>
<tr>
<td>EMPA (Electron Microprobe Analysis)</td>
<td>Dealkalisation and early stages of corrosion can be followed routinely. Accuracy dependent on sample roughness, Clark et al. (1979)</td>
<td>Müller et al. (1995)</td>
<td>Identification of distinct corrosion layers in medieval glass</td>
</tr>
<tr>
<td>SEM/EDX (Energy Dispersive X-ray Emission)</td>
<td>Analysis of surface heterogeneities &lt;1µm, Clark et al.(1979)</td>
<td>Schmitz et al. (1995)</td>
<td>Weathering and aqueous corrosion share the same mechanism</td>
</tr>
<tr>
<td>PIXE (Particle Induced X-Ray Emission) / RBS (Rutherford Backscattering Spectroscopy)</td>
<td>See Section 4.3.2 in Chapter 4 for more details on this technique</td>
<td>Lamouroux et al. (1997)</td>
<td>Tin profiles in float glass</td>
</tr>
</tbody>
</table>
2.9 Numerical Methods

In this section a range of solution techniques will be presented that have been applied to the corrosion of glass. Computationally based solution methods derived from statistical methods will be shown for completeness. Particular emphasis will be given to the cellular automaton (CA) solution method because this is the method selected to simulate the glass corrosion studied in this present work.

2.9.1 Partial Differential Equation Solution Techniques

Three classes of partial differential equations (PDE) have been identified from literature; these are hyperbolic (e.g. one dimensional wave equations), parabolic (e.g. diffusion equations) and elliptic (e.g. Poisson equations). The hyperbolic and parabolic equations usually describe a time evolution problem (also known as an initial value problem) where a given variable \( u \) varies with position and time \( u(x,t) \). An elliptic equation is considered to be a static solution problem (also known as a boundary value problem) in which the region of interest is limited by boundary values \( u(x,y) \). Press et al. (2007).

A number of PDE solver methods exist. These include finite element methods (FEM). This approach is used in solid mechanics, structural engineering and fluid mechanics because it can deal with complex geometries, Press et al. (2007). Whereas finite difference methods (FDM) (e.g. Crank Nicholson) deal best with rectangular geometries, (Crank 1976). Hybrid methods containing finite elements and orthogonal collocation (Alpay 1992 citing Carey and Finlayson 1975, Paterson and Cresswell 1971) also exist. Orthogonal collocation (OC) assumes the solution can be expressed as a system of orthogonal polynomials and reduces the problem to one of determining the coefficients of these polynomials such that the solution is accurate at a finite number of nodes in the solution space.

2.9.2 Statistical Mechanics

Statistical Mechanics (SM) is the science which studies the macroscopic behaviour of a system and uses statistics to predict the behaviour of its individual constituents including atoms, molecules and phonons (Glazer and Wark 2001). The latter authors
consider this science to constitute a link between classical thermodynamics which deals with large-scale continua and particle statistical mechanics that describes the behaviour of atomic and sub-atomic entities through probabilities.

Monte Carlo (MC) simulation is a solution technique for models based on probabilities whereby a stochastic repetition for the evaluation of a solution to a problem yields an average value. Its application to the glass area was pioneered by Aertsens and Ghaleb (2001) citing Aertsens and Isenghem (1996), Aertsens (1998), (1999a, b), in its application to the dissolution of borosilicate glass used for nuclear waste storage. For this Aertsens and Ghaleb (2001) assumed glass to be essentially made of sodium and silica; in other words easily dissolving components and slowly dissolving components.

Molecular Dynamics (MD) studies the motion of atoms and the forces between atoms or molecules. These forces are known as interaction potentials and determine whether a system has enough energy for motion and reaction to occur (Billing and Milkkensen 1996). Molecular dynamics has been used to describe the silica structure e.g. Bakaev et al. (2001), hydroxylation of a glass surface Du and Cormack (2005), simulation of diffusion in the glass e.g. Soules (1979) and hydration of silica glasses Garofalini (1990a, 1990b).

Due to the use of atomic systems in MD, structural changes can be modelled in the order of picoseconds only, whereas MC can be used to model the kinetics in a more realistic and relevant time scale compared to actual experimental data. On the other hand the modelling of a system structure such as glass is too simplistic in MC compared to the detailed atomic structure used by MD, Aertsens and Ghaleb (2001). Together these constitute the main advantages and disadvantages of these techniques. Molecular dynamics would seem a good candidate to apply to this present study. However, MD simulations are very computationally intensive and the time scale used tends to be in the order of 100 ps (Aertsens and Ghaleb 2001), making the comparison with the experimental time scale unrealistic.


2.9.3 Cellular Automaton

Cellular automaton (CA) is a solution technique which studies the behaviour of a system that tends to be a mathematical idealisation of a physical system where space and time are discrete and physical quantities take on a finite number of discrete values (Wolfram 1983). The continuous system is translated into a number of nodes arranged in a grid. The nodes behave according to a set of rules, which are applied iteratively over a number of time steps, (Wolfram 2002). The most famous and original CA is the 2-dimensional rectangular automaton ‘Game of life’ developed by John Conway, where each node can either have a value of 1 (alive) or 0 (dead) (Wolfram 1983 citing Conway 1970). The state of a node is dependent on the eight immediate neighbouring nodes positioned in vertical, horizontal and diagonal directions which behave according to the following rules (Wolfram 1983):

- Any live node with fewer than two neighbours alive dies of loneliness.
- Any live node with more than three neighbours alive dies of crowding.
- Any dead node with exactly three neighbours alive comes to life.
- Any live node with two or three neighbours alive, lives, unchanged, to the next generation.

A schematic representation of the CA ‘Game of life’ is shown in Figure 2-18, below.

![Figure 2-18; Schematic representation of CA, ‘Game of Life’. Five subsequent steps are shown. Gray filled squares represent ‘living’ nodes, while empty squares are ‘dead’ nodes. In each time step, the following rule is applied to each square simultaneously: A ‘living’ node surrounded by less than three or more than three ‘living’ nodes amongst its eight neighbours dies of isolation or overcrowdedness. On the other hand, a ‘dead’ cell will come to ‘life’ if there are exactly three ‘living’ cells amongst its eight nearest neighbours, (Deutsch and Dormann 2005)](image)

CA techniques have been applied in many areas including physics, biology, traffic flow and even tapestry design. Wolfram (1983) lists a number of references which applies CA in these systems. CA techniques can also accommodate phenomena that act simultaneously, over very different timescales. Furthermore, the individual processes can be turned off without preventing a solution from being obtained. In this thesis three 1-dimensional CA were used to calculate four different processes.
including diffusion-reaction because it can calculate the solution quickly and more components can be added easily if needed.

**2.10 Concluding Comments**

The literature survey has provided an insight into the current understanding of glass corrosion. It is clear that whilst the basic mechanisms of glass corrosion are established, the mechanisms by which stain inhibitors operate are still not adequately understood. Also no mention of the effect of the adsorbed layer on the corrosion rate was found, therefore this is the main theme of this current work. Quantification of the effectiveness of zinc for corrosion inhibition in terms of adsorbed water was also not found in literature hence this will also be addressed. From the experimental techniques reviewed gravimetric analysis will be used because it appears this will provide in situ measurement of the corrosion kinetics. Gravimetric analysis will not provide information on the glass elemental composition therefore ion beam analysis i.e. PIXE/RBS, SIMS and XPS will also be used. The glass surfaces will be imaged using AFM.

The application of a cellular automaton procedure to model glass corrosion appears to be unique. The ambiguity of the zinc treatment effect on glass made the choice of this solution technique even more relevant. The further suitability of this model can then be tested by comparison with the gravimetric experiments.
3 Theory

3.1 Introduction

During exposure of glass to humid air we assume that four processes occur: mass transfer of water vapour from bulk gas to the glass surface, adsorption of water at the glass surface, diffusion of water from the glass surface to the glass bulk and reaction of water within the bulk. These processes constitute the foundations of the model developed in this thesis. The objective is to compare the amount of water uptake in the simulation results in the early stages with the experimental results from gravimetric analysis shown in Chapter 5. In the current chapter, a detailed account of the assumptions made in the model will be shown, followed by the model theory which includes the equations, the numerical method used and a summary of the parameters used in the simulation and their respective units.

3.2 System description and assumptions

The system used to model the water mass uptake by glass is shown in Figure 3-1. The symbols shown in this figure will be defined in Section 3.4.4.
In this figure three main phases are described; a gas phase (comprising a gas bulk and a gas film), an adsorbed phase and a solid phase (glass bulk). A number of assumptions were made regarding the properties of this system and these will be described below.

1. The system is isothermal.
2. The bulk gas is assumed to be well-mixed hence the %RH is not a function of position but may vary with time.
3. Mass transfer from the gas phase to the glass surface is expressed by an external mass transfer coefficient following the Whitman film theory (Coulson et al. 1998 referring to Whitman 1923). The external mass transfer coefficient is assumed to be based on a single system with a specific surface area that is based on the gross dimensions of the sample holder.
4. Adsorption at the glass surface follows the BET adsorption theory for water adsorbing on to glass hence this process is temperature and pressure dependent only.
5. Equilibrium between the gas and the adsorbed water layer occurs at the glass surface instantaneously.
6. The glass is assumed to be a homogeneous solid and the detailed elemental structure and the formation of a gel layer are not considered.
7. Water in the glass bulk diffuses undissociated.
8. Water diffusion in the glass is Fickian with an exponential temperature dependency.
9. A 1st order irreversible reaction of the form $A + H_2O \rightarrow P$ is assumed where $A$ represents the glass and $P$.
10. The solid reactant component A and component P are assumed to be incapable of diffusion.

Overall the devised model is simplistic because the ion-exchange mechanism discussed in Chapter 2 is not directly accounted for and this constitutes the main reaction in the initial stages of corrosion. The possible variation of diffusivity with time is also not considered.
If this theory does not match experimental results at the time scales considered then the sodium ion-exchange, its counter-diffusion with water, and structural changes to the glass may be the cause and will have to be added.

3.3 Theory

This section describes the equations used in the developed model, which represent the four processes that occur in the glass when exposed to humid conditions.

In the gas phase the transport of water vapour to the glass surface at pseudo-steady state can be expressed by the general mass transfer equation as shown below (Coulson et al. 1998):

\[ N = k_e (p_\infty - p_s) \]  

(3.1)

Here \( N \) is the water flux (mol s\(^{-1}\)m\(^{-2}\)), \( k_e \) is the mass transfer coefficient in the gas film (mol s\(^{-1}\)m\(^{-2}\) Pa\(^{-1}\)), \( p_\infty \) is the partial pressure in the gas bulk (Pa) and \( p_s \) is the partial pressure at the glass surface (Pa). Note that \( N \), \( p_\infty \) and \( p_s \) are time dependent. Equation (3.1) is based on Whitman’s film theory. This assumes that the gas is a quiescent film, i.e. no convection, so the transport of water vapour to the glass surface occurs by molecular diffusion only.

To calculate the saturated vapour pressure of water (\( p_0 \)) the Antoine equation was used, (Reid et al. 1987), see Equation 3.2 below (this is Equation 2.28 reproduced).

\[ \log p_0 = A' - \frac{B'}{T + C'} \]  

(3.2)

Here \( T \) is the temperature (K), \( A' \), \( B' \) and \( C' \) are the Antoine constants. \( A' \) and \( B' \) are dimensionless, and \( C' \) has units of K, \( p_0 \) is the saturated vapour pressure (kPa).

For the determination of the partial pressure (\( p_\infty \)) in the gas, Equation (3.3) is used, (Equation 2.27 reproduced).
\[ %RH = \frac{p_w}{p_0} \times 100 \]  \tag{3.3}

Note \( p_w \) and \( p_0 \) are defined in the nomenclature on page xv.

The external mass transfer coefficient for particles is calculated from the Ranz-Marshall Equation, see Equation (3.4) below. The latter is usually applied for particles in an infinite expanse of fluid, Coulson et al. (1998).

\[ Sh = 2 + 0.6 Sc^{1/3} Re^{1/2} \]  \tag{3.4}

Here \( Sh \) is the Sherwood number, \( Sc \) is the Schmidt number and \( Re \) is the Reynolds number. Note that all of these parameters are dimensionless. \( Sh \) corresponds to the ratio of the mass transfer coefficient and a characteristic length to the diffusion coefficient (see Equation 3.5). In this thesis the Sherwood number is assumed to be 2 because the Reynolds number is small (see details in Section 3.4.5). \( Sc \) corresponds to the ratio of the kinematic viscosity to the mass diffusivity (see Equation 3.6), the Reynolds number (see Equation 3.7) determines the type of flow regime i.e. laminar, transient or turbulent.

\[ Sh = \frac{k_g d_{pan}}{D_{AB}} \]  \tag{3.5}

Here \( k_g \) is the mass transfer coefficient (m s\(^{-1}\)), \( D_{AB} \) is the molecular diffusivity of water in air (m\(^2\) s\(^{-1}\)), and \( d_{pan} \) is the diameter (m) of the conical pan in which the particles are loaded for the gravimetric experiments (0.009 m).

\[ Sc = \frac{\mu}{\rho_{flow} D_{AB}} \]  \tag{3.6}

\[ Re = \frac{\rho_{flow} ud_{tube}}{\mu} \]  \tag{3.7}
Here $\mu$ (N m$^{-1}$) is the flow viscosity, $\rho_{\text{flow}}$ (kg m$^{-3}$) is the density of the flow, $d_{\text{tube}}$ is the tube diameter (m), $u$ is the flow velocity (m s$^{-1}$).

The mass transfer coefficient needed for Equation (3.1) $k_g$ has units of (mol s$^{-1}$ m$^{-2}$ Pa$^{-1}$), hence the units of $k'_g$ (m s$^{-1}$) need to be converted.

Considering Equation (3.1) and multiplying top and bottom by $RT$ converts the partial pressure value into molar concentration values hence Equation (3.8) is obtained.

$$N = k_g RT (C_\infty - C_s) \quad (3.8)$$

Here $k_g$ is the mass transfer coefficient (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$), $C$ is the concentration (mol m$^{-3}$), and $R$ is the universal gas constant (m$^3$ Pa K$^{-1}$ mol$^{-1}$). The subscripts $\infty$ and $s$ denote gas bulk and glass surface respectively. The water flux $N$ can be expressed similarly in terms of $k'_g$ (m s$^{-1}$) using Equation (3.9).

$$N = k'_g (C_\infty - C_s) \quad (3.9)$$

Equating (3.8) and (3.9) results in Equation (3.10).

$$k_g = \frac{k'_g}{RT} \quad (3.10)$$

The molecular diffusion coefficient in a binary mixture of gases is known to be proportional to $T^{3/2}$. This is based on the Chapman-Enskog equation which will be discussed further below, (see Equation 3.46), Reid et al. (1987). The effective diffusion coefficient $D$ (m$^2$s$^{-1}$) in molecular diffusion is expressed by Equation (3.11) below:

$$D = D_0 T^{3/2} \quad (3.11)$$

Here $D_0$ (m$^2$ s$^{-1}$ K$^{-3/2}$) is the diffusion constant.
The BET theory is used in this simulation to predict the amount adsorbed at equilibrium. The BET equation is frequently used to estimate the monolayer capacity of a surface and hence estimate the specific surface area of a sample. The standard form of the BET equation is shown below (Gregg and Sing 1967):

\[
\frac{q}{q_m} = \frac{c(p_s/p_0)}{(1 - p_s/p_0)(1 + (c-1)p_s/p_0)}
\]

(3.12)

Here \(p_s\) is the partial pressure in the gas phase (Pa), \(p_0\) is the saturated vapour pressure (Pa), \(c\) is the BET constant (-), \(q\) (mol kg\(^{-1}\)) is the amount adsorbed and \(q_m\) (mol kg\(^{-1}\)) is the monolayer capacity at the equilibrium relative pressure \(p_s/p_0\).

At the glass surface the quantity of water vapour adsorbed is expressed in terms of an amount \(q_1\) (mol kg\(^{-1}\)), whereas just inside the glass the amount of water is expressed by a concentration value \(C_1\) (mol m\(^{-3}\)). The following equation can be used to relate the two.

\[
C_1 = K_p q_1
\]

(3.13)

Here \(K_p\) is the partition coefficient (kg m\(^{-3}\)). This assumed equation ressembles Henry’s law and may be approximately valid for \(q < q_m\).

It is assumed that the water adsorbed layer at the glass surface is stationary and the water transport to the glass bulk occurs by diffusion only.

For the diffusion of water in the glass, \(D\) (m\(^2\)s\(^{-1}\)) is the effective diffusion coefficient with an Arrhenius-type dependence typical of solid diffusion, as given by Equation (3.14), Doremus (1975), Holland (1964).

\[
D = D_0 \exp\left(-\frac{E_a}{RT}\right)
\]

(3.14)
Here $E_a$ is the activation energy ($J \text{ mol}^{-1}$), $R$ is the universal gas constant ($J \text{ K}^{-1} \text{ mol}^{-1}$), and $D_0$ is a diffusion constant ($m^2 \text{ s}^{-1}$).

To model diffusion and reaction for a system with plane geometry, a material balance on an infinitesimal slice of solid yields Equation (3.15):

$$D \frac{\partial^2 C_w}{\partial z^2} = \frac{\partial C_w}{\partial t} + r$$  \hspace{1cm} (3.15)

Here $r$ is the reaction rate ($\text{mol m}^{-3} \text{ s}^{-1}$), $z$ is the position (m), $C_w$ is the concentration of water ($\text{mol m}^{-3}$), and $D$ is the diffusion coefficient ($m^2 \text{ s}^{-1}$).

The boundary conditions of Equation (3.15) are shown below. It is assumed that diffusion is only occurring in the $z$ direction.

$$C_w = 0, \quad z > 0, \quad t = 0$$  \hspace{1cm} (3.16)

$$C_w = 0, \quad z = \infty, \quad t > 0$$  \hspace{1cm} (3.17)

$$C_w = C_0, \quad z = 0, \quad t > 0$$  \hspace{1cm} (3.18)

The reaction rate in this model has been assumed to be expressed by Equation (3.19):

$$r = k C_w C_A$$  \hspace{1cm} (3.19)

In the equation above, $r$ is the reaction rate ($\text{mol m}^{-3} \text{ s}^{-1}$), $k$ is the rate constant ($m^3 \text{ mol}^{-1} \text{ s}^{-1}$), $C_w$ is the water concentration ($\text{mol m}^{-3}$) and $C_A$ is the concentration of the solid reactant $A$ ($\text{mol m}^{-3}$).

This section introduced the main equations used for the development of the simulation model, including the BET theory. Mass transfer of water vapour from bulk gas to the glass surface, adsorption of water at the glass surface, diffusion of water from the glass surface to the glass bulk and reaction of water within the bulk were all translated.
into equations. In the following section an automaton representation of the current model will be shown, and the diffusion mechanism in a cellular automaton will also be presented. The equilibration equations at the glass surface will also be shown and a section on parameter estimation is also included.

3.4 Cellular Automaton

A cellular automaton (CA) was used in this thesis as a solution technique for the presented equations. This technique was introduced in the literature survey in Section 2.9.3. To the author's knowledge this solution technique has not been applied to adsorption, diffusion and reaction in glass, hence making its current application unique.

3.4.1 Automaton Representation of Current Problem

The diagram shown in Figure 3-1 is translated into three different automata i.e. one automaton for the gas phase, one for the glass surface and one automaton for the glass bulk as shown in Figure 3-2 below.
Figure 3-2: Automaton diagram for the glass-water-air system shown in Figure 3-1.

The gas and glass automata comprise a minimum of two nodes each whereas the surface automaton requires exactly one node because only the equilibration between the adsorbed layer at the glass surface and the amount of water just inside the glass is being calculated. The equations for adsorption applied in the surface automaton will be presented in Section 3.4.3.

In the gas automaton, Equations (3.1) up to Equation (3.5) and Equation (3.8) and Equation (3.10) are solved. The glass automaton represents the glass bulk. Node 1 in this automaton represents the first node inside the glass. This is the automaton in which the diffusion and reaction Equations (3.14), (3.15) and Equation (3.19) are solved. In the first node inside the glass different parameter values can be entered from Node 2 and beyond. Figure 3-3 below, is a flow chart of the steps to be followed. In Appendix C the preceding calculation steps involving setting the parameter values are described in further detail.
Allocate memory and initialise nodes in Automaton

Calculate all gas nodes

Calculate surface node (adsorption equilibrium)

Calculate all solid nodes

Integrate profile

Store what's needed for plotting

Plot $q$ vs. $t$

Do results match with gravimetric data?

Yes → STOP

No → Go back and change %RH

Figure 3-3: Flow chart for CA calculation steps involved in generating mass uptake profiles
3.4.2 Diffusion in a cellular automaton

Diffusion problems have been solved previously using a cellular automaton e.g. Dab and Boon (1999) and Garofalini (1990a, b), Richard et al. (2009). To simulate diffusion using the CA solution technique the position axis is created from a number of nodes arranged side by side in a row. In a 1-D cellular automaton each node is cubic with a side $\delta z$ (m) and is divided into a left ($l$) and right ($r$) compartment. At each time step $t$ (s) two main operations occur: exchange between adjacent nodes and complete mixing within nodes. Typically it is assumed that conditions at the start of the simulation are such that all the nodes are empty.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{cellular_automaton.png}
\caption{Representation of a 1-D cellular automaton. Each node has a thickness $\delta z$ and is composed of a left and right compartment. They are positioned in a horizontal line and range from node 1 to the $i^{th}$ node. At the start of the simulation some amount of compound A is present in the right hand-side compartment of the first node.}
\end{figure}

Each node and compartment can contain compound $A$, and the amount of $A$ in each node represents the concentration at the location of the node. The amount of $A$ in node $i$ before mixing is

\[ n_A = (\delta z)^3 C_{Ai} \]  

(3.20)

Here $n_A$ is the amount of material in the node (mol), $C_{Ai}$ is the concentration of compound A in the $i^{th}$ cell (mol m$^{-3}$) and $\delta z$ is the thickness of a node (m).

During the first operation, the compound $A$ in the right hand side of the $i^{th}$ node exchanges with the left hand side compartment of node $i+1$. When the exchange step is complete, the concentration of $A$ is the same in both compartments. The first operation can be represented by Equation (3.21) below.
For the second operation involving complete mixing within nodes, the two compartments within each node exchange $A$ until the compartments contain the same amount of $A$. The amount in the right hand-side compartment of the $i^{th}$ node is represented by the equation below:

$$n_A = \frac{\frac{1}{2} \left( \frac{\delta z}{2} C_{Ai} - \frac{\delta z}{2} C_{A{i+1}} \right)}{C_{A{i+1}} - C_{A{i+1}}}$$

For the calculation of the flux of compound $A$, at each iteration step Equation (3.23) is used as follows:

$$N_A = \frac{1}{\Delta t(\delta z^2)} \left( \frac{\delta z}{4} \right) \left( C_{A{i+1}} - C_{A{i+1}} \right) = \frac{\delta z}{4\Delta t} \left( C_{A{i+1}} - C_{A{i+1}} \right)$$

Here $N_A$ is the flux (mol m$^{-2}$ s$^{-1}$), and $\Delta t$ is the time for one complete iteration of the cellular automaton.

The concentration gradient in Fick’s first law can be approximated by the equation below:

$$\frac{\partial C_{A{i+1}}}{\partial z} \approx \frac{C_{A{i+1}} - C_{A{i+1}}}{\delta z}$$

To represent absolute maximum diffusion, Equation (3.25) is used.

$$D_a \approx \frac{\delta z^2}{4\Delta t}$$

Here $D_a$ is the absolute maximum diffusion coefficient (m$^2$s$^{-1}$) and $t$ is time (s).
The relative diffusion coefficient $D_R$ (-), can be obtained by the ratio of the effective diffusion coefficient of water in the glass ($D_{gi}$) to the absolute maximum diffusion coefficient ($D_a$), i.e:

$$D_R = \frac{D_{gi}}{D_a} \quad (3.26)$$

It is clear that $D_R$ has to be less than one. This condition is checked in the numerical procedure for initialising the diffusion parameters, as shown in Appendix C.

### 3.4.3 Equilibration at the Glass Surface

At each time step, the function of the surface automaton is to allow the simulation of an equilibration process at the surface. The preceding mass transfer step in the gas and the proceeding steps after adsorption, i.e. diffusion and reaction in the solid, results in a situation in which the concentration in the gas at the surface, the amount adsorbed, and the amount of water just inside the glass, are not in equilibrium. The objective here is to bring these three to equilibrium without violating the law of conservation of mass.

Consider a material balance on a unit mass of clean solid. The interfacial area per unit mass of solid is $a_i$ ($m^2 \text{ kg}^{-1}$), the temperature is $T$ (K), the partial pressure in the gas node adjacent to the surface is $p$ (Pa) and the thickness of that node is $\delta z_g$ (m). The amount adsorbed on the surface is $q$ (mol kg$^{-1}$) and the concentration of water in the first node inside the solid is $C_w$ (mol m$^{-3}$) where that node has thickness $\delta z_s$ (m). The equation below represents the conservation of mass. This brings the amount adsorbed per unit mass of solid at the glass to equilibrium.

$$p_i \delta z_g \frac{a_i}{RT} + q_1 + C_i a_i \delta z_s = p_2 \delta z_g \frac{a_i}{RT} + q_2 + C_e a_i \delta z_s \quad (3.27)$$

Here $R$ is the universal gas constant 8.314 m$^3$ Pa K$^{-1}$ mol$^{-1}$. 
Subscript 1 denotes the initial condition and subscript 2 the condition at equilibrium. Note that in Figure 3.1 the equilibrium condition was represented by the symbol *.

At equilibrium, two additional conditions are assumed. First it is assumed that the partial pressure in the BET equation is in equilibrium with the amount adsorbed (see Equation 3.28). The second condition assumes that the amount adsorbed at the glass surface is in equilibrium with the concentration just inside the glass (see Equation 3.27). Furthermore the amount of water present can be expressed as a concentration by the use of a partition coefficient, $K_p$ (m$^3$ kg$^{-1}$). These conditions can be expressed as follows:

Condition 1: \[ \text{BET} \, p_2 = m \, q_2 \quad (3.28) \]

Condition 2: \[ C_2 = K_p q_2 \text{ where } q_2 = m C_2 \quad (3.29) \]

Equation (3.27) and Equation (3.29) constitute two equations and three unknowns ($p_2$, $q_2$ and $C_2$). These equations were solved by substituting for $C_2$ in the right hand side of Equation (3.27) giving Equation (3.30), as shown below. Note that the parameters in the equation below are in the same units as shown in Equation (3.27).

\[ \tau = \frac{p_1 a_i}{RT} + q_1 + C_1 a_i \delta z_s = \frac{p_2 a_i}{RT} + q_2 + K_p q_2 a_i \delta z_s = p_2 \delta z_s \frac{a_i}{RT} + q_2 \left( 1 + K_p a_i \delta z_s \right) \quad (3.30) \]

Here $\tau$ is the total amount of water (mol kg$^{-1}$) at equilibrium.

The BET isotherm equation used is as follows:

\[ q_2 = \frac{q_m c X}{(1 - X)(1 + (c - 1)X)} \quad (3.31) \]

Here $X = \frac{p_2}{p_0} \Leftrightarrow p_2 = Xp_0$ \quad (3.32)
Substituting Equation (3.31) into Equation (3.30) and replacing $p_2$ by Equation (3.32) gives Equation (3.33).

$$\tau = \delta z_s \frac{a_1 P_0}{RT} X + \frac{q_m c X (1 + K a_1 \delta z)}{(1 - X)(1 + (c - 1)X)} \quad (3.33)$$

Here

$$k_1 = \delta z_s \frac{a_1 P_0}{RT} \quad (3.34)$$

and

$$k_2 = q_m c (1 + K a_1 \delta z_s) \quad (3.35)$$

After substitution of Equations (3.34) and Equation (3.35) in Equation (3.33), Equation (3.36) is obtained.

$$\tau = k_1 X + \frac{k_2 X}{(1 - X)(1 + (c - 1)X)} \quad (3.36)$$

Multiplying through and expanding the terms gives Equation (3.37).

$$\tau \{1 - X + (c - 1)X - (c - 1)X^2\} = k_1 \{X - X^2 + (c - 1)X^2 - (c - 1)X^3\} + k_2 X \quad (3.37)$$

Writing Equation (3.37) in a cubic form in $X$ gives:

$$a_3 X^3 + a_2 X^2 + a_1 X + a_0 = 0 \quad (3.38)$$

Applying this notation to the equation above gives:

$$a_3 \equiv (c - 1)k_1 \quad (3.39)$$

$$a_2 \equiv \tau (1 - c) + k_1 (2 - c) \quad (3.40)$$

$$a_1 \equiv \tau (c - 2) - k_1 - k_2 \quad (3.41)$$

$$a_0 \equiv \tau \quad (3.42)$$
Equation (3.37) (with restrictions $0 \leq X \leq 1$) was solved by Laguerre’s method (Press et al. 2007) giving back the solution for $X$ hence $p_2$ is obtained from Equation (3.30). Applying this value to Equation (3.31) gives the value for $q_2$, and finally using this value in Equation (3.29) gives the value for $C_2$.

The main numerical methods used to solve this model have been introduced. Next it will be shown how the parameters used in these equations were obtained.

### 3.4.4 Reaction in the Solid

During the reaction step in the CA, each node is regarded as a batch reactor. Equation 3.19 is solved by ordinary Euler integration. The initial value of $C_A$ is called the reaction capacity because once $C_A$ has dropped to zero no further reaction is possible. The calculation of the reaction step in each node is as follows.

\[
C_{wi}(t + \delta t) = C_{wi}(t) - kC_{wi}(t)C_{ai}(t)\delta t
\]  
(3.43)

\[
C_{ai}(t + \delta t) = C_{ai}(t) - kC_{wi}(t)C_{ai}(t)\delta t
\]  
(3.44)

Where $C_{wi}$ is the concentration of water in the $i$th node (mol m$^{-3}$).

### 3.4.5 Parameter Estimation

It is important to remember at this stage that the simulation was developed with the purpose of comparing theoretical results with the experimental results measured by a gravimetric analysis technique. An IGAsorp instrument was used to this end (see Section 4.2 in Chapter 4 for more details). The parameters described below were already introduced in Section 3.4.1.

In Equation 3.4 the Sherwood number ($Sh$) is assumed to be equal to 2 because the Reynolds number ($Re$) is 0.132 and the Schmidt number ($Sc$) is 0.059. Therefore if these values are replaced in Equation 3.4, this will give $Sh = 2.18$. Hence to a first approximation it is reasonable to assume that $Sh = 2$. 
Two humidity steps were used in the simulation. The first %RH (%RH₁) was considered to be the humidity conditions in the laboratory to which the sample was briefly exposed prior to its loading in the IGAsorp chamber. The second %RH (%RH₂) corresponds to the conditions set in the gravimetric instrument i.e. 70% RH at a given temperature. The choice of value for %RH₂ will be explained in Chapter 5.

It took approximately 10 minutes in between removing the sample from storage at dry conditions and loading it in the instrument. This brief exposure of the sample to the laboratory environment possibly resulted in the sorption of some moisture (qₐ). Figure 3.5 below illustrates the humidification history of the sample, which consists of the amount adsorbed as a function of time.

Figure 3-5; Schematic diagram of humidification history for crushed float glass during loading, and during exposure to 70% RH inside the IGAsorp chamber (shown in figure as gravimetric experiment). During sample loading, the sample is exposed to ambient relative humidity (%RH) and absorbs an amount of water qₐ in an estimated loading time of 10 minutes. Once the sample is loaded in the IGAsorp chamber the balance is tared, therefore the initial amount adsorbed q is set to zero. Note that the two stages have been separated on the q-axis for clarity.

In Figure 3-5, t = 0 corresponds to the start of the gravimetric experiment; the sample has already adsorbed qₐ at an unknown humidity (%RHᵢ). At the different
temperatures used and for both untreated and zinc-treated samples, Equation (3.45) shown below was used for the calculation of the mass adsorbed ($q_a$) prior to sample loading, (mol kg$^{-1}$).

$$q_a = q_{70\%} - \zeta$$  \hspace{1cm} (3.45)

Here $q_{70\%}$ (mol kg$^{-1}$) is the equilibrium amount of moisture adsorbed at 70% RH, given by the adsorption isotherm measured gravimetrically for a given temperature, (not shown in Figure 3-5), and $\zeta$ (mol kg$^{-1}$) is the intercept value after a straight line is fitted to the mass uptake region corresponding to long time scales in the gravimetric experiments. The %RH$_f$ value can therefore be determined from the water sorption isotherm using the value of $q_a$ obtained with Equation (3.45).

The BET monolayer capacity value ($q_m$) and the BET constant ($c$) values used in this model were measured experimentally in this project using a gravimetric technique (see Section 4.2). The monolayer value obtained in g g$^{-1}$ was converted to mol kg$^{-1}$ using the molecular weight of water.

The interfacial area of the sample exposed to water vapour i.e $a_i$ (see Section 3.4.3) was calculated from the surface area of a cone, given the dimensions of the conical sample pan, resulting in a value of $191 \times 10^{-6}$ m$^2$. Given a typical sample mass of 100 mg, the interfacial area per unit mass of sample $a_i$ is $1.91$ m$^2$ kg$^{-1}$.

The mass transfer coefficient was initially calculated using the Chapman-Enskog equation (see Equation 3.46) Reid et al. (1987), and converting the diffusion coefficient value ($D_{AB}$) to the correct units using Equation (3.5) and Equation (3.10) assuming a Sherwood number of 2.0. Table 3-1 below summarises the diffusivity of water in air ($D_{AB}$) and the respective mass transfer coefficient values at 15°C, 20°C and 30°C.

$$D_{AB} = \frac{0.002667^{3/2}}{pM_{AB}^{1/2} \sigma_{AB}^{2} \Omega_{D}}$$  \hspace{1cm} (3.46)
Here $D_{AB}$ is the diffusion coefficient (cm$^2$ s$^{-1}$), $M_A$ and $M_B$ are the molecular weights of A and B (g mol$^{-1}$), $p$ is the pressure (bar), $\sigma_{AB}$ is the characteristic length (Å), and $\Omega_D$ is the diffusion collision integral (-). Details of the method used for the calculation of the diffusion values can be found in Reid et al. (1987).

The diffusion constant and the activation energy values used at the surface and in the glass bulk were taken from Helmich and Rauch (1993), who measured the diffusion value for water using a NRA (nuclear reaction analysis) technique after pre-treatment of silica at 100°C and 200°C. The diffusion constant was estimated from an Arrhenius plot for the samples exposed at these temperatures.

The value for the partition coefficient ($K_p$), see Equation (3.29), was assumed to be 0.1 m$^3$ kg$^{-1}$. This parameter appears to only have <5 % effect on the amount adsorbed according to the sensitivity analysis see Section 5.3.3 and Table 5-20 therefore the actual value used does not seem to be of great importance.

For the kinetics at the glass surface and in the glass bulk the reaction parameters such as reaction capacity ($R_c$) and rate constant ($k$) were used. The reaction capacity value represents the sodium concentration available in the glass for reaction with a water molecule. This value was calculated from the glass concentration of Na$_2$O in float glass i.e. 13.2 wt%, (Staunton 2007). The rate constant value was estimated by curve fitting to the experimental data of mass adsorbed as a function of time, at 70% RH for a given temperature.

The number of integration time steps is calculated from Equation (3.47), below.

\[
t_s = \delta t \times t_i
\]  

(3.47)
Here $t_s$ is the maximum number of time steps (-), $\delta t$ is the time step length (s), and $t_l$ (s) is the time length required for the experiment.

Table 3-2 below is a summary of the simulation parameters used.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value/Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>%RH</td>
<td>Gravimetric experimental %RH.</td>
<td>70 (%)</td>
<td>User parameter, chosen to match gravimetric experiments</td>
</tr>
<tr>
<td>$\rho_{\text{sample}}$</td>
<td>Sample density</td>
<td>2530 kg m$^{-3}$</td>
<td>Pilkington (2008), fact sheet</td>
</tr>
<tr>
<td>$a_i$</td>
<td>Interfacial area</td>
<td>1.91 m$^2$ kg$^{-1}$</td>
<td>Area of pan exposed to moisture</td>
</tr>
<tr>
<td>$D_{\text{bg}}$</td>
<td>Relative diffusion in bulk glass ($D_{\text{bg}}$) and glass surface ($D_{\text{gsl}}$)</td>
<td>$7.52 \times 10^{-11}$ m$^2$ s$^{-1}$</td>
<td>Value from Helmich and Rauch (1993) based on hydrogen profiles at 100 and 200°C on silica glass</td>
</tr>
<tr>
<td>$D_{\text{gsl}}$</td>
<td></td>
<td>$7.52 \times 10^{-11}$ m$^2$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$\delta t$</td>
<td>Time step length</td>
<td>$1 \times 10^{-3}$ s</td>
<td>User Parameter</td>
</tr>
<tr>
<td>$\delta z$</td>
<td>Distance step length in solid, width of node</td>
<td>$5 \times 10^{-5}$ m</td>
<td></td>
</tr>
<tr>
<td>$E_a_{\text{bg}}$</td>
<td>Activation energy in bulk glass ($E_a_{\text{bg}}$) and glass surface ($E_a_{\text{gsl}}$)</td>
<td>57702 kJ kmol$^{-1}$</td>
<td>Helmich and Rauch (1993), from hydrogen profiles at 100 and 200°C on silica</td>
</tr>
<tr>
<td>$E_a_{\text{gsl}}$</td>
<td></td>
<td>57702 kJ kmol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$\delta g$</td>
<td>Gas film thickness</td>
<td>$5 \times 10^{-5}$ m</td>
<td>User parameter</td>
</tr>
<tr>
<td>gas_dz</td>
<td>Distance step length in gas</td>
<td>$1.67 \times 10^{-5}$ m</td>
<td>Notional parameter</td>
</tr>
<tr>
<td>Integration step number</td>
<td>Time steps at initial %RH</td>
<td>700000 (-)</td>
<td>User parameter</td>
</tr>
<tr>
<td>$K_p$</td>
<td>Partition coefficient</td>
<td>0.1 m$^2$ kg$^{-1}$</td>
<td>User parameter</td>
</tr>
<tr>
<td>$k_g$</td>
<td>Mass transfer coefficient</td>
<td>$1.73 \times 10^{-7}$ mol s$^{-1}$ kPa$^{-1}$ m$^{-2}$</td>
<td>User parameter</td>
</tr>
<tr>
<td>$N_{\text{gas}}$</td>
<td>Nodes in gas</td>
<td>4 (-)</td>
<td>User parameter</td>
</tr>
<tr>
<td>$N_{\text{g}}$</td>
<td>Nodes in solid</td>
<td>10 (-)</td>
<td>User parameter</td>
</tr>
<tr>
<td>$R_{\text{c, bg}}$</td>
<td>Reaction capacity in bulk glass ($R_{\text{c, bg}}$) and glass surface ($R_{\text{c, gsl}}$)</td>
<td>10780 mol m$^{-2}$</td>
<td>Sodium concentration in bulk glass from Staunton (2007) analysis</td>
</tr>
<tr>
<td>$R_{\text{c, gsl}}$</td>
<td></td>
<td>10780 mol m$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>$t_s$</td>
<td>Number of time steps</td>
<td>(-)</td>
<td>User parameter</td>
</tr>
</tbody>
</table>
Table 3-3 below is a summary of the unknown parameters in the simulation.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value/Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>%RH&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Exposure %RH prior to loading</td>
<td>(-)</td>
<td>Estimated parameter by curve fitting to gravimetric data</td>
</tr>
<tr>
<td>c</td>
<td>BET constant</td>
<td>(-)</td>
<td>Value from experimental data</td>
</tr>
<tr>
<td>q&lt;sub&gt;m&lt;/sub&gt;</td>
<td>BET statistical monolayer</td>
<td>mol kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Value from experimental data</td>
</tr>
<tr>
<td>k&lt;sub&gt;bg&lt;/sub&gt;</td>
<td>Rate constant in bulk glass (kg)</td>
<td>m&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Estimated parameter by curve fitting to linear region of mass uptake as a function of time</td>
</tr>
<tr>
<td>k&lt;sub&gt;gsl&lt;/sub&gt;</td>
<td>and glass surface (gsl)</td>
<td>m&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Estimated parameter by curve fitting to linear region of mass uptake as a function of time</td>
</tr>
</tbody>
</table>

### 3.5 Concluding Comments

In this chapter a model was developed to describe glass corrosion using a 1-D cellular automaton. It is believed this is a unique application of the CA approach. The simulation model will be compared with the gravimetric experimental results in this dissertation in order to validate the model outputs in Chapter 5. In the next chapter the experimental methods used for the study of float glass corrosion in this current work will be shown. These include a gravimetric technique for the measurement of the mass uptake as a function of time, and surface analysis techniques for the study of the elemental composition of glass.
4 Experimental Methods

4.1 Introduction

Different experimental techniques were used during this work to study the corrosion of float glass. The techniques included gravimetric analysis (IGAsorp) using water vapour to determine the glass corrosion flux. Atomic Force Microscopy (AFM) was used to study the glass surface topography under dry conditions and after exposure to high humidity. Surface analysis techniques were used, including ion beam analysis i.e. Particle Induced X-ray Emission (PIXE) combined with Rutherford Backscattering Spectroscopy (RBS), Secondary Ion Mass Spectroscopy (SIMS) and X-Ray Photoelectron Spectroscopy (XPS). These surface analysis techniques gave data for the glass elemental composition, and the elemental depth profiling. The various techniques will be described below.

4.2 IGAsorp (Intelligent Gravimetric Analyser)

The IGAsorp enables the study of the response of materials to changes in relative humidity (%RH) and temperature, and is therefore useful when considering the storage stability of materials such as pharmaceuticals and foods. Figure 4-1 shows the IGAsorp used in this study.

![IGAsorp gravimetric water sorption analyser](Image)

The air is supplied to the IGAsorp through an air drier mounted on the wall, (see Figure 4-1). The %RH is regulated by controlling the flow rates of both wet and dry air, which are mixed before being introduced to the sample. The sample temperature
Experimental Methods

is controlled by a circulating water bath which is external to the chamber. Full
operation and control of the IGAsorp is effected through an interfaced PC. Figure 4-2
below shows a schematic of the IGAsorp including the microbalance, gas flow,
sample chamber and control system.

![Schematic of the IGAsorp](image)

Figure 4-2; Schematic of the inside of the IGAsorp (Hiden Isochema 2003).

The experimental conditions were set in the IGAsorp chamber prior to sample
loading. An empty pan was loaded (see Figure 4-3) and its mass trace was monitored
for several hours to test that the balance was operating within its limits of stability.

![Picture of the IGAsorp pan](image)

Figure 4-3; Picture of the IGAsorp pan in which samples are loaded
Figure 4-4 below illustrates the mass response of an empty pan at 25°C and 70% RH over a 4 day period. Note that the balance response over this time only varies within 2 μg which is within acceptable limits of stability for the instrument.

Before the start of an IGAsorp experiment (run) an empty pan mass reading is taken and the balance is tared. The sample is then loaded on to the pan and a reading of the sample mass is taken. This can be monitored over time using the chart mode allowing user-specified variations in temperature and %RH. Alternatively an isotherm can be measured where the %RH has a progressive and automatic increment of usually 5 or 10% intervals. In this mode the software continually monitors the mass and attempts to predict the asymptote for equilibrium assuming first order kinetics. This in principle reduces the operating time and provides a consistent method of assessing equilibrium. In some cases equilibrium can not be predicted satisfactorily and the machine defaults to a pre-specified “time-out” value.

4.2.1 Preparation of Materials

Table 4-1 below summarises the composition of float glass in units of wt% as measured by Staunton (2007) using XRF (X-ray fluorescence).
Experimental Methods

Table 4-1: Composition of float glass used in this dissertation, Staunton (2007)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>71.8</td>
</tr>
<tr>
<td>Na₂O</td>
<td>13.5</td>
</tr>
<tr>
<td>CaO</td>
<td>8.59</td>
</tr>
<tr>
<td>MgO</td>
<td>3.99</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.10</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.65</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.186</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.131</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.03</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.01</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>122 ppm</td>
</tr>
</tbody>
</table>

For the gravimetric method a batch of clear float glass of 4 mm thickness produced by Pilkington on 09/11/06 was ground down to a particle size of less than 90 μm, using a pestle and mortar. Particles < 90 μm were obtained using a standard sieve. Crushed glass was used in this dissertation to get sufficient surface area to detect the mass uptake of water due to corrosion. Two batches of crushed glass were prepared; one was left untreated, and the other was treated with a corrosion inhibitor in the form of Zn(NO₃)₂ solution to a concentration of 100 ppm of zinc. These were denoted Batch 1 and Batch 2 respectively. Both batches were stored in sealed polythene bags inside a desiccator. For each experiment a ‘fresh’ sample was taken from the sealed bags. Table 4-2 summarises the batches used, their preparation dates and periods of analysis. The details of the zinc treatment are specified further below.

Table 4-2: Summary of ground float glass samples used in this study

<table>
<thead>
<tr>
<th>Batch name</th>
<th>Preparation Month</th>
<th>Description</th>
<th>Period of analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 1</td>
<td>April 2008</td>
<td>Untreated</td>
<td>April- October 2008</td>
</tr>
<tr>
<td>Batch 2</td>
<td>April 2008</td>
<td>Treated with Zn(NO₃)₂</td>
<td>April- October 2008</td>
</tr>
</tbody>
</table>

When sheet float glass samples were used in surface analysis techniques *i.e.* AFM, ion beam, XPS and SIMS the air side had to be distinguished from the tin side. In order to do this an UV lamp was shined on each side of the float glass samples’ surface. The side which fluoresced was considered to be the tin side, due to the adsorption of the UV rays, (Tiwari *et al.* 2005).
Method for treating glass with zinc nitrate:

The following procedure was recommended by Holmes (2007). A solution containing 100 ppm of zinc ions was prepared by dissolving zinc nitrate in powder form in 100 ml of de-ionised water at room temperature (20°C). The solution pH was monitored using a pH meter to ensure that it stayed close to 5.5. The zinc solution was then heated to 60°C and the crushed float glass was immersed in the solution. The glass particles were filtered off using a Buchner funnel. Filtering was repeated until the decanted liquid was clear of particles after visual evaluation. Then the filtered glass particles which had been collected by deposition on a filter paper were rinsed with a pipette containing DI water and were dried in an oven at 80°C. After this the particles were stored in a desiccator inside a plastic bag. A similar method was used to treat sheet float glass samples. These were immersed for approximately 15 seconds in a zinc nitrate solution and were then immediately washed off by immersion in DI water. The amount of zinc deposited for both forms of glass was measured by XPS, see the results in Chapter 5.

4.2.2 Data Analysis

A method for the direct measurement of the corrosion flux for crushed float glass was developed based on gravimetric water sorption and BET analysis of the sorption isotherms, (see Appendix A for more details on the BET theory). The primary assumption for the calculation of the corrosion flux for crushed glass is that the flux of water uptake by the sample is purely a result of water adsorption to the surface, where the water adsorbed is replacing the water that has diffused into the bulk glass. This leads to the assumption that the quantity of water on the surface remains constant, for any given %RH and temperature, once the initial adsorption transient is complete.

The calculation steps for the measurement of the corrosion flux are as follows. The mass adsorbed at each exposure condition \( (w_a) \) is calculated using the difference between the total sample weight \( (w_T) \) and the dry weight of the sample \( (w_{dry}) \) which is taken to be the first data point registered by the IGAsorp software at the start of the experimental run, see Equation (4.1).
\[ w_a = w_T - w_{dry} \]  
\hspace{10cm} (4.1)

Note that all the parameters in Equation (4.1) have units of grams. The amount adsorbed was then converted into a fractional mass uptake \( x \) which represents the mass adsorbed at each point divided by the dry weight of the sample, as shown by Equation (4.2).

\[ x = \frac{w_a}{w_{dry}} \]  
\hspace{10cm} (4.2)

Note that units of \( \mu g \ g^{-1} \) were used to express the fractional mass uptake in the results graphs of the gravimetric experiments, in order to reduce the number of decimal points.

The fractional mass uptake values were divided by the mean BET specific surface area \( S \) in order to express the water uptake in terms of mass per unit area of sample surface, \( i.e. \) g m\(^{-2} \). The determination of \( S \) is presented in section 5.2.5. To obtain the corrosion flux the mass uptake curves as a function of time were fitted with polynomials. These equations were differentiated, resulting in an expression for corrosion flux in units of mass uptake per unit surface area per unit time \( i.e. \) g m\(^{-2} \) min\(^{-1} \). See Section 5.2.9 for the results obtained.

### 4.3 Surface Analysis Techniques

A range of surface analysis techniques was also used. These included AFM, ion beam analysis \( i.e. \) PIXE/RBS, XPS and SIMS. For these techniques a sample size of 1cm\( \times \)1cm square with a thickness of 4 mm was used. Note that the XPS analysis also included samples in crushed form. The results for the techniques described below can be found in Chapter 5 and include results for both untreated and zinc-treated float glass samples.
4.3.1 AFM (Atomic Force microscopy)

The AFM (Atomic Force Microscope) is ideal for providing quantitative data on surface topography and roughness, as well as enabling adhesion and nanoindentation studies to be performed. Numerous papers have been published giving general reviews of uses of the AFM and its principles (Radlein and Frischat 1997, Zarzycki 1996). Papers have also been published in more specific areas like the investigation of cracks on glass surfaces (Guin and Wiedehorn 2003, Célarié et al. 2003), changes in glass surfaces over time at different exposure conditions (Sharma et al. 2002, Schmitz et al. 1997, Garcia-Heras et al. 2005) and even measurement of inter-atomic distances between groupings of atoms and network holes in a glass surface (Frischat et al. 2004).

The AFM is simple to use, requiring no conductive preparation, so it allows the observation of pristine glass. Its method of operation is based on the scanning tunnelling microscope principle, but uses a sharp probe tip to scan the sample. It has a piezo drive for high precision positioning of the tip, signal amplifier, feedback loop and image processing, Radlein and Frischat (1997).

Figure 4-5 below illustrates the AFM used in this study. The surface of the sample is mapped by profiling it with a very fine tip of radius between 20-50 nm which is mounted on a cantilever that is 100 to 200 µm long. The movement of the tip is sensed by the reflection of the laser beam which forms an optical lever (see Figure 4-6). The cantilever position is held constant by feedback control on the vertical piezo element. The current required to maintain constant cantilever height provides the topography data. The disadvantage of the AFM is its inability to characterise the chemical composition of the corrosion products on the surface. Also the images can contain artefacts which can induce error. For example, glass corrosion product debris can adhere to the tip and be dragged on the surface leading to streaks on the image.

In this project a Thermomicroscopes Explorer AFM was used to image a float glass sheet which had previously been exposed to 30% and 90% RH for 12 hours at 20°C. It was also used to measure the depth of the etched crater resulting from the ToF-SIMS analysis.
4.3.2 Ion Beam Analysis (IBA)

PIXE (Particle Induced X-ray Emission) is a non-destructive quantitative analytical technique which detects trace elements down to 10’s of ppm. A beam of high energy particles (typically protons) is directed at the sample which can cause electrons to be excited and atoms to become ionised (see step 1 in Figure 4-7 below). The available sites are then filled with outer electrons and subsequently an X-ray of characteristic energy is emitted, (see step 2 in Figure 4-7 below), Johansson and Campbell (1988). The X-ray energy is then used for the identification of the elements present in the sample, and in addition, the intensity gives their concentration. When carried out simultaneously with RBS (Rutherford Backscattering Spectroscopy see Figure 4-7 below), PIXE is a quantitative technique with absolute accuracy. The height of the peaks in the PIXE spectrum depends on a number of parameters, including the charge delivered to the sample during the measurement. The RBS technique allows the charge delivered to the sample to be accurately determined (because the charge determines the height of the RBS spectrum). This allows quantification of the PIXE data. PIXE and RBS are often referred to generally as ion beam analysis techniques.
Figure 4-7; Physical principle of IBA (Ion Beam Analysis) techniques. Particle Induced X-ray Emission (PIXE) is a two step process: an inner shell electron of the target atom is expelled by the impinging ion, then follows an electronic rearrangement accompanied by X-ray emission. Rutherford Backscattering Spectroscopy (RBS) relies on a purely elastic process based upon the electrostatic repulsion between positively charged projectiles and nuclei, Calligaro et al. (2004)

The ion beam analysis was carried out at the University of Surrey in the Ion Beam Centre, using a hydrogen beam with an energy of 2.5 MeV. A 2MV Tandetron accelerator (see Figure 4-8) from High Voltage Engineering Europe was used. Two detectors were used with the following scattering angles 148.2° (IBM geometry), 172.8° (Cornell geometry), and solid angles of 1.24 and 6.9 msr respectively. Two different detectors were used for the analysis to avoid the problem of mass ambiguity which is inherent in RBS data. The ion beam current was ~20 nA with a nominal beam size (normal incidence) of 1 mm. The X-ray intensity is measured by an SiLi detector* with a Beryllium window to prevent the backscattered particles from reaching the detector. The absorption of the X-rays by the Beryllium results in no elements below the atomic number 14 in the periodic table being detected. More details of the instrument used can be found in Simon et al. (2004).

* SiLi or lithium drifted silicon detector is a type of detector which operates at low temperatures and liquid nitrogen is used to this end.
4.3.3 XPS (X-ray Photoelectron Spectroscopy)

XPS (X-ray Photoelectron Spectroscopy) is a quantitative surface chemical analysis technique which identifies the chemical elements present at a given sample surface as well as the chemical state of the elements (binding energy, peak shape, Auger parameter) and the concentration of the elements present (atom%).

At the time of the analysis the sample surface is illuminated with X-rays. Core level electrons within the atoms present in the top atomic layers of the sample absorb the energy from incoming X-ray photons resulting in the photo-emission of an electron, see Figure 4-9. An analyser measures the kinetic energy and the number of electrons which are photo-emitted from the sample surface. This technique does not need preconditioning of the sample and is essentially non-destructive; however, some materials will react and possibly degrade due to the presence of the X-ray beam (e.g. PVC).
Five float glass samples were analysed using XPS including untreated and zinc-treated float glass samples in both crushed and sheet forms. The samples analysed also included a float glass sample which had been treated by Pilkington with 130 ppm of zinc from a zinc nitrate solution.

XPS analyses were performed on a Thermo VG Scientific Sigma Probe spectrometer (East Grinstead, UK); see Figure 4-10 below. The instrument is equipped with both a microfocus monochromated AlKα source and a standard twin anode source (AlKα/MgKα). In this work the twin anode AlKα X-ray source (hv = 1486.6 eV) was used at 300 W (15 kV x 20 mA). For all survey spectra the pass energy was set at 150 eV. The pass energy was set at 20 eV for C1s, Ca2p, Na1s, O1s, Si2p and Sn3d5/2 high resolution, core level spectra. For elements present in very low concentration the pass energy was set at 50 eV. These elements included Cu2p3/2 and Mg1s high resolution, core level spectra. The samples were held in place on the instrument sample stage by sprung Cu/Be clips. The crushed glass samples were fixed to a sample holder by means of a double-sided tape and were mounted on a sample stage together with the continuous samples.
4.3.4 SIMS (Secondary Ion Mass Spectrometry)

The SIMS (Secondary Ion Mass Spectrometry) technique consists of sputtering the surface of materials with a primary beam, which results in positively and negatively charged secondary ions as well as neutral ions being ejected from the sample surface, see Figure 4-11. The secondary ions are then analysed by mass spectrometry that enables the identification of elements, isotopes, molecules and molecular fragments from materials present at the sample surface, Robinnet (2006).
Currently two different SIMS techniques exist; Static and Dynamic SIMS. According to Vickerman and Swift (1997) static SIMS maintains the integrity of the surface layer within the time scale of the analytical experiment by using a low primary beam dose. Because low sputtering rates are used, a low yield of secondary particles is emitted hence a high sensitivity detector is used. Dynamic SIMS on the other hand uses high primary beam energy. The use of a high energy beam technique will not analyse the top surface layers of the sample as static SIMS does, Vickerman and Swift (1997). In this dissertation Static SIMS was chosen over Dynamic SIMS therefore the latter will not be further discussed and the reader is referred to Vickerman (1997) for more information.

Static SIMS using a Time-of-Flight-SIMS (ToF-SIMS) instrument was used in this study, due to its availability and because it is the best system for depth profile analysis (Watts 2009). For this current study ideally a technique which would have provided information on the elemental concentration within the top surface layers would have been beneficial.

ToF-SIMS (see Figure 4-12) uses a pulsed primary beam which is directed at the sample surface. The sputtered secondary ions are extracted and their masses determined. An electron flood gun is used to compensate the ion charges after each analysis when insulating samples are studied such as glass.

![Diagram illustrating the operation steps inside a ToF-SIMS instrument](Carleton 2009)
Using this technique for depth profiling involves recording mass spectra as the sample material is eroded away, and then plotting the intensity of a mass signal versus time. The sputtering rate $S_R$ (nm s$^{-1}$) can be calculated by dividing the etch crater depth $c_d$ (nm), by the total etch time $t_t$ in (s); see equation below, Robinnet (2006).

$$S_R = \frac{c_d}{t_t} \quad (4.3)$$

Note that the size of the etched crater was measured using an AFM after the ToF-SIMS analysis.

The depth of etching ($d_e$) at each time unit is calculated by multiplying the sputtering rate ($S_R$) by the time step ($t$) as shown in the equation below.

$$d_e = S_R \times t \quad (4.4)$$

The sputtering rate is assumed to be linear with time as long as the energy and current of the etching beam is stable and the size of the etched area is not changed. Therefore, if different regions of the same sample are to be analysed they should give roughly the same values. The calculation of the sputtering rate can be affected by errors in the measurement of the crater depth. The sample roughness can introduce a component of error in the measurement of the etched crater size. This can be minimised by taking different depth measurements with the AFM and taking an average value from the readings.

ToF-SIMS analysis was carried out on an ION-ToF GmbH (Münster, Germany) ToF.SIMS 5 system, see Figure 4-13 below. The instrument is equipped with a bismuth liquid metal ion source. Mass data were acquired using Bi$_3^+$ (bismuth) cluster at 25 keV delivering 0.35 pA of ion current by raster scanning over a $100 \times 100$ μm$^2$ area. A 3 kV caesium ion source was also used as the sputter/etch tool. The Cs$^+$ (caesium) sputter/etch area was $400 \times 400$ μm$^2$. The depth profiling analyses were performed in the ‘non-interlaced’ mode, i.e. repeat cycles of mass data acquisition,
followed by charge compensation using a low energy electron flood gun. A sputter/etch interval of 1 s was used for all of the depth profile studies described here.

Figure 4-13; ToF.SIMS 5 system from ION-ToF GmbH (Münster, Germany), (Watts 2009)

ToF-SIMS was used in this study to depth profile the air side of both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples exposed to dry and saturated conditions.

4.4 Concluding Comments

In this section the preparation of the crushed float glass samples was described. The application of the zinc-treatment at the glass surface was also portrayed. A range of experimental techniques were also described this included a gravimetric analysis technique (IGAsorp) and four surface analysis techniques. These included: AFM, ion beam analysis i.e. PIXE/RBS, XPS and SIMS.

In the next chapter the results obtained with these various techniques will be shown, and the main trends and features will be identified. A more complete discussion of the results in the context of previously published work and the theoretical simulation is reserved for Chapter 6.
5 RESULTS

5.1 Introduction

The current chapter presents results from various experiments aimed at investigating the corrosion of untreated and zinc-treated float glass. The techniques used include gravimetric analysis (IGAsorp), imaging (AFM) as well as surface analysis techniques (PIXE/RBS, SIMS, XPS). These were described in Chapter 4. In Chapter 3, a mathematical model was developed to simulate the initial mass uptake of water at the same exposure conditions used for the gravimetric experiments. The results of the simulations are also included in this chapter. Detailed discussion of the results is reserved for the following chapter.

5.2 Gravimetric Analysis

In this section the results from a gravimetric water sorption technique will be presented. Gravimetric measurements of glass corrosion were made using the IGAsorp instrument. For more details of the instrument see Section 4.1. Crushed float glass samples with a particle size less than 90 \( \mu \)m were used, for both untreated and zinc treated material. The experimental conditions for the IGAsorp experiments are summarised in Table 5-1 below. Key experimental parameters are exposure temperature, relative humidity and the desiccator storage time prior to the experimental run.
Table 5-1; Summary of exposure conditions and sample description for the IGAsorp gravimetric experiments, see Table 4-2 in Chapter 4 for the description of the individual batches including their production and preparation date. The letter R denotes repeated experiments

<table>
<thead>
<tr>
<th>Batch 1 (untreated)</th>
<th>Exposure temperature (°C)</th>
<th>Exposure relative humidity (%RH)</th>
<th>Desiccator storage time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>70</td>
<td>137</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>50</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>70</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>30 R</td>
<td>70</td>
<td>102</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Batch 2 (treated with Zn(NO₃)₂)</th>
<th>Exposure temperature (°C)</th>
<th>Exposure relative humidity (%RH)</th>
<th>Desiccator storage time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>70</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>50</td>
<td>154</td>
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</tr>
<tr>
<td>20 R</td>
<td>70</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

5.2.1 Mass Uptake as a Function of Relative Humidity

Samples from Batch 1 (untreated) and Batch 2 (zinc-treated) crushed float glass of a particle size less than 90 µm were submitted to 20°C and to three different humidities (30%, 50% and 70% RH) for up to 6000 minutes in the IGAsorp. The results of fractional mass uptake are shown in Figure 5-1 and Figure 5-2 respectively, see below.
Figure 5-1; Fractional mass uptake at 20°C for Batch 1 (untreated) float glass samples with a particle size < 90 µm, exposed to 30%, 50% and 70% RH

Comparing Figure 5-1 and Figure 5-2 it is immediately apparent that the untreated float glass samples take up considerably more water over time. For example at 70% RH, the untreated sample (Figure 5-1) has taken up more than twice the amount compared to the zinc-treated float glass sample (Figure 5-2), after 4000 minutes of
Results

exposure. Note that for 30% RH the zinc-treated sample (Figure 5-2) shows an initial mass decrease followed by an essentially constant mass, indicating the potential effectiveness of the zinc treatment, when compared to the same conditions for untreated glass, (Figure 5-1). The initial decrease in mass over the first 1000 minutes for the zinc treated sample cannot readily be explained. A similar phenomenon is observed when measuring water adsorption isotherms for this sample, as reported in section 5.2.4 and so it is considered to be a real effect. This phenomenon is recommended for further research.

Both untreated and zinc-treated float glass samples (see Figure 5-1 and Figure 5-2 respectively) gained more mass at 70% RH, in comparison to lower %RH values. Therefore, this was the humidity value selected for the next experiments to compare the effect of temperature on corrosion.

5.2.2 Mass Uptake as a Function of Temperature

Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples were submitted to three different temperatures (15°C, 20°C and 30°C) at 70% RH, and the fractional mass uptake was measured for up to 9000 minutes, see Figure 5-3 and Figure 5-4 below.

![Figure 5-3; Fractional mass uptake over time for Batch 1 (untreated) float glass samples with a particle size < 90 μm, exposed to 15°C, 20°C and 30°C at 70% RH](image-url)
It is apparent from Figure 5-3 and Figure 5-4 that both the untreated and zinc-treated float glass samples show a higher water uptake with increasing temperature. Further analysis of the uptake kinetics will be presented in section 5.2.3. It is also clear that the zinc-treated samples take up less water, indicating the apparent effectiveness of the zinc treatment.

An initial mass decrease was measured for the float glass samples exposed to 30°C for both untreated and zinc-treated samples. This is characteristic of all samples exposed to 30°C in this current work, and most likely reflects the removal of physisorbed water that occurs on suddenly increasing the sample temperature from ambient to 30°C when introducing the sample to the instrument.

The mass uptake for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples is shown individually at the same temperature in Figure 5-5, 5-6 and Figure 5-7 for clarity.
Figure 5-5: Fractional mass uptake over time for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 µm, exposed to 15°C and 70% RH.

Figure 5-6: Fractional mass uptake over time for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 µm, exposed to 20°C and 70% RH.
Figure 5-7: Fractional mass uptake over time for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 30°C and 70% RH.

Figure 5-5, Figure 5-6 and Figure 5-7 shown above confirm that the zinc-treated float glass samples adsorb less moisture in comparison with the untreated samples exposed at the same conditions. For instance at 15°C (t = 4218 minutes) the zinc-treated sample sorbs 5 times less, at 20°C 2.64 times less and at 30°C 1.54 times less, compared to the Batch 1 (untreated) sample. Note that the difference in amount adsorbed between batches decreases with increasing temperature of exposure.

5.2.3 Corrosion Kinetics

It was seen in the literature review (Section 2.6.1) that at short time-scales and low temperatures the rate of alkali extraction was reported to be proportional to the square root of time whereas at long times of exposure and high temperatures a linear time dependency prevailed, (Douglas and El-Shamy 1967). This can be expressed by Equation (5.1) which is adapted from Equations (2.11) and (2.12) shown in Chapter 2.

\[ x = k_r t^a \]  

(5.1)

Here \( x \) (μg g\(^{-1}\)) is the fractional mass uptake, \( k_r \) is the corrosion constant (μg g\(^{-1}\) min\(^{-a}\)), \( a \) (-) is the time index and \( t \) (min) is the experimental time of exposure.
The gravimetric experimental results shown in Figure 5-3 and Figure 5-4 were used to quantify the corrosion constant \( k_r \) and the time index \( \alpha \) by plotting the logarithm of the fractional mass uptake as a function of the logarithm of time. This was performed for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples exposed to 15°C, 20°C and 30°C at 70% RH. Sections of linearity were identified by eye. Values of \( k_r \) and \( \alpha \) were obtained from the equations of the fitted lines as shown in Figure 5-8 and Figure 5-9. The time index value \( \alpha \) was obtained from the slope of the fitted equations (see equations in the individual figures), and the corrosion constant \( k_r \) was obtained by taking the anti-logarithm of the intercept values. For the data at 30°C the initial mass decrease value (see Figure 5-7) were added to all the data points for the time intervals shown in Figure 5-8 and Figure 5-9 below. This is justified because the initial mass decrease occurs as part of the transient response to the step change in humidity and temperature. The main concern here is the diffusion controlled uptake that is established at longer time-scales once the sample has adjusted to these step changes.

In order to study the extent of the linearity for the time intervals chosen in Figure 5-8 and Figure 5-9 below, the residuals were plotted and are shown in Appendix B.
Figure 5-8: Log of fractional mass uptake as a function of the log of time, for samples from Batch 1 (untreated) float glass samples with particle size < 90 µm, exposed to 15°C, 20°C and 30°C. Regions of linearity are shown for determination of the time index (α) and the corrosion constant (kₐ) as depicted in Equation (5.1)
Figure 5-9: Log of fractional mass uptake as a function of the log of time for samples from Batch 2 (zinc-treated) float glass samples with particle size < 90 μm, exposed to 15°C, 20°C and 30°C. Regions of linearity are shown for determination of the time index (α) and the corrosion constant (κ) as depicted in Equation (5.1).
Table 5-2 below summarises the time index (α) and the corrosion constant (k_r) values for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples. Values in this table also include error values; the method used to generate these is described in Appendix B. The errors for the corrosion constant are expressed as a percentage.

Table 5-2: Summary of time index (α) and corrosion constant (k_r) in Equation 5.1 obtained from Figure 5-8 and Figure 5-9.

![Table 5-2](image-url)
index value ($\alpha$) and the corrosion constant ($k_r$), for both untreated and zinc-treated samples were considered.

Mean values of the time index parameter ($\alpha$) from Table 5-2 are plotted as a function of temperature in Figure 5-10 and straight lines are fitted. Note that $\alpha$ increases with temperature for both untreated and zinc-treated float glass samples. The figure appears to show that $\alpha$ increases more sharply with temperature for the zinc-treated float glass samples. However there is so much uncertainty in the data that further work is recommended to confirm this observation.

![Figure 5-10: Values for the time index parameters ($\alpha$) at 15°C, 20°C and 30°C for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 µm](image)

Figure 5-11 below shows the temperature dependence of the corrosion constant ($k_r$) for both untreated and zinc-treated float glass samples. A clear trend of $k_r$ decreasing with temperature is apparent in both cases. However this result is not conclusive because only three temperatures were considered and there is significant error, at least in the data for the untreated sample. Further work is recommended in this area. Note that mean values of $k_r$ have been used for clarity.
Results

Figure 5-11; Mean values for the corrosion constant \((k_r)\) at 15°C, 20°C and 30°C for both Batch 1 (untreated) and Batch 2 (zinc treated) float glass samples with a particle size < 90 μm

5.2.4 Isotherms

Water sorption isotherms for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples were generated at three temperatures \(i.e.\ 15^\circ C, 20^\circ C\ and 30^\circ C\) over a range of 0 - 70% RH; at intervals of 5% RH. The maximum value of 70% RH, was chosen to correspond with the mass uptake experiments shown previously in Section 5.2.2. The method for producing the isotherms using the IGAsorp is described fully in Chapter 4. Note that the fractional mass uptake is based on the dry mass of the sample which was taken to be the first registered mass value at the beginning of the experiment, because the material had been stored in a desiccator prior to the test. The isotherms corresponding to the three temperatures are shown in Figure 5-12, 5-13 and Figure 5-14 below.
Results

Figure 5-12; Fractional mass adsorbed and desorbed as a function of percent relative humidity for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 µm, exposed to 15°C.

Figure 5-13; Fractional mass adsorbed and desorbed as a function of percent relative humidity for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 µm, exposed to 20°C.
The results of the water sorption experiments for the Batch 1 (untreated) float glass samples presented in Figure 5-12, 5-13 and Figure 5-14, show a gradual mass increase with increasing %RH. These isotherms show upon desorption that some moisture is retained causing hysteresis.

It is clear from Figure 5-12, 5-13 Figure 5-14 that the Batch 2 (zinc-treated) float glass samples uptake around half the amount of moisture compared to Batch 1 (untreated) samples exposed to the same conditions. This is clear evidence of the effect of zinc treatment. The mass uptake curves for the isotherm data points for zinc-treated float glass samples show a slow but steady increase in mass even when decreasing the RH to 50%. This behaviour suggests that above this RH value equilibrium is not attained within the four hour time limit allowed for each isotherm data point. Consequently water is still adsorbing during the desorption steps (see Figure D-2 in Appendix D). Furthermore, a decrease in mass was measured for the zinc-treated samples during adsorption at 20°C, 40% RH see Figure 5-13 and at 30°C, 35% RH and 40% RH see Figure 5-14. The mass uptake curves for these isotherm data points show an initial short term increase in mass presumably due to physisorption, followed by a sudden and systematic mass decrease to a lower equilibrium value, (see Figure D-1 in Appendix D). A similar reduction in mass was
seen in Figure 5-2 for a zinc treated float glass sample held at 20°C and 30% RH. No explanation can be offered on this phenomenon without further investigation.

5.2.5 BET Analysis

The BET model equations are described in Appendix A; therefore this section will be a presentation of the results obtained. BET analysis is performed on both adsorption and desorption stages of the isotherm. The desorption isotherm is likely to represent physisorption only, because there is strong evidence to suggest that it occurs at a much faster rate than the chemisorption (dehydroxylation). It should therefore be better suited to BET analysis giving a more reliable estimate of specific surface area. However, in the following sections both the adsorption and desorption data are analysed to determine the specific surface area (S) of the sample, the monolayer value (x_m) and the value of the BET constant (c). The latter two parameters are key input parameters in the CA model described in Chapter 3.

5.2.5.1 Adsorption Data

Figure 5-15, 5-16 and Figure 5-17 are an evaluation of the suitability of the BET model using the water sorption experiments corresponding to the adsorption branch of the isotherms presented in Figure 5-12, 5-13 and Figure 5-14. The straight lines in these figures are lines of linear best fit. The data have been plotted on axes corresponding to the linearised form of the BET equation, see Equation (A-1) in Appendix A. For the calculation of the saturated vapour pressure and corresponding values see Section 5.2.7.
Figure 5-15; BET plots of \( \frac{p}{x(p_0-p)} \) vs. \( \frac{p}{p_0} \) for the data from the water adsorption isotherms for float glass samples with particle size < 90 μm, exposed to 15°C for fractional pressures between 0.1-0.3

Figure 5-16; BET plots of \( \frac{p}{x(p_0-p)} \) vs. \( \frac{p}{p_0} \) for the data from the water adsorption isotherms for float glass samples with < 90 μm, exposed to 20°C for fractional pressures between 0.1-0.3
Results

Figure 5-17: BET plots of $p/x(p_o-p)$ vs. $p/p_0$ for the data from the water adsorption isotherms for float glass samples with a particle size $< 90 \mu m$, exposed to 30°C for fractional pressures between 0.1-0.3.

The BET method seems to fit reasonably well for water adsorption on zinc-treated float glass samples as shown by the linearity over the $p/p_0$ range 0.10 - 0.30 in Figure 5-15, 5-16 and Figure 5-17. Table 5-3 below, shows the intercept ($\frac{1}{x_m c}$), slope ($\frac{c-1}{x_m c}$), and the regression coefficient ($R^2$) of the straight line fitted to the data for the adsorption stage of the isotherms. The BET constant ($c$) and the monolayer value ($x_m$) are also shown. These values were calculated using the BET theory and the corresponding BET equations, see Equation A-4 and Equation A-5 respectively in Appendix A. Values in Table 5-3 also include error values. The method used to generate these are described in Appendix B. Note that for the BET analysis, the fractional mass uptake was expressed in g g$^{-1}$. 

\begin{align*}
p/x(p_o-p) &= 7037(p/p_0) + 833 \\
R^2 &= 0.99 \\
p/x(p_o-p) &= 4290(p/p_0) + 939 \\
R^2 &= 0.97
\end{align*}
Table 5-3; Data from the BET analysis for water adsorption on ground float glass samples relating to Figure 5-15, 5-16 and Figure 5-17

<table>
<thead>
<tr>
<th>Batch 1 (untreated)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( T(°C) )</td>
<td>( \frac{1}{x_m c} )</td>
<td>( \frac{c-1}{x_m c} )</td>
<td>( c )</td>
<td>( x_m \times 10^{-4} )</td>
</tr>
<tr>
<td>15</td>
<td>897 ± 120</td>
<td>4231 ± 562</td>
<td>5.72 ± 1.52</td>
<td>1.95 ± 0.78</td>
</tr>
<tr>
<td>20</td>
<td>1215 ± 178</td>
<td>3528 ± 839</td>
<td>3.9 ± 1.50</td>
<td>2.11 ± 0.11</td>
</tr>
<tr>
<td>30</td>
<td>939 ± 94</td>
<td>4290 ± 444</td>
<td>5.57 ± 1.14</td>
<td>1.91 ± 0.58</td>
</tr>
<tr>
<td>Mean value</td>
<td>5.06 ± 1.39</td>
<td>1.99 ± 0.49</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Batch 2 (zinc-treated)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( T(°C) )</td>
<td>( \frac{1}{x_m c} )</td>
<td>( \frac{c-1}{x_m c} )</td>
<td>( c )</td>
<td>( x_m \times 10^{-4} )</td>
</tr>
<tr>
<td>15</td>
<td>1362 ± 36</td>
<td>5654 ± 171</td>
<td>5.15 ± 0.29</td>
<td>1.43 ± 0.12</td>
</tr>
<tr>
<td>20</td>
<td>1900 ± 57</td>
<td>4987 ± 271</td>
<td>3.62 ± 0.31</td>
<td>1.45 ± 0.17</td>
</tr>
<tr>
<td>30</td>
<td>833 ± 98</td>
<td>7037 ± 460</td>
<td>9.45 ± 1.73</td>
<td>1.27 ± 0.38</td>
</tr>
<tr>
<td>Mean value</td>
<td>6.07 ± 0.78</td>
<td>1.38 ± 0.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5-3 shows an apparent minimum in the BET constant value \( c \) at 20°C for both batches. No explanation can currently be offered for this. For convenience of further analysis a mean value of the BET constant has been taken.

The mean BET constant value \( c \) for the zinc-treated float glass sample was 20% higher compared to the untreated sample. As a result, the mean monolayer fractional mass uptake \( x_m \) was 44% higher for the untreated samples compared to the zinc-treated samples.

Once the BET parameter values \( c \) and \( x_m \) were determined for both batches at all three temperatures, the specific surface area \( S \) could be estimated using Equation (5.2) below, (Gregg and Sing 1967). Table 5-4 summarises the BET specific surface area values \( S \) obtained.

\[
S = \frac{x_m \times N \times A_m \times 10^{-20}}{M}
\]

(5.2)

Here \( S \) is the specific surface area \( (\text{m}^2 \text{g}^{-1}) \), \( N' \) is Avogadro’s constant \( (6.02 \times 10^{23} \text{ mol}^{-1} \text{ in Atkins and Jones 1999}) \), \( A_m \) is the cross-sectional area of the adsorbed water molecule \( (10.6 \text{ Å}^2) \), \( M \) is the molecular weight of water \( (18 \text{ g mol}^{-1}) \) and \( x_m \) is the monolayer capacity \( (\text{g} \text{ g}^{-1}) \).
Results

Table 5-4: BET Specific surface area ($S$) from adsorption isotherm for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm

<table>
<thead>
<tr>
<th>Batch 1 (untreated)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (°C)</td>
<td>$S$ (m$^2$ g$^{-1}$)</td>
</tr>
<tr>
<td>15</td>
<td>0.69 ± 0.28</td>
</tr>
<tr>
<td>20</td>
<td>0.74 ± 0.05</td>
</tr>
<tr>
<td>30</td>
<td>0.67 ± 0.21</td>
</tr>
<tr>
<td><strong>Mean value</strong></td>
<td><strong>0.70 ± 0.18</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Batch 2 (zinc-treated)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (°C)</td>
<td>$S$ (m$^2$ g$^{-1}$)</td>
</tr>
<tr>
<td>15</td>
<td>0.50 ± 0.05</td>
</tr>
<tr>
<td>20</td>
<td>0.51 ± 0.06</td>
</tr>
<tr>
<td>30</td>
<td>0.45 ± 0.14</td>
</tr>
<tr>
<td><strong>Mean value</strong></td>
<td><strong>0.49 ± 0.08</strong></td>
</tr>
</tbody>
</table>

The specific surface area values in Table 5-4 appear to vary with temperature, however this is not conclusive and for convenience the mean values are calculated. The mean value of the specific surface area for Batch 1 (untreated) samples is 0.7 m$^2$ g$^{-1}$ and for Batch 2 (zinc-treated) samples is 0.49 m$^2$ g$^{-1}$. The mean value of $S$ obtained for Batch 1 samples is 43% higher compared to the measured value for Batch 2 samples. This difference is not considered to be due to a change in the actual sample surface area. It is associated with the different water sorption behaviour of the two samples due to the zinc treatment.

Using Equation 5.3 below (Gregg and Sing 1967), an effective Sauter\(^\dagger\) mean particle diameter (Seville et al. 1997) was calculated as a matter of interest. The results are shown in Table 5-5, below.

\[
S = \frac{6}{\rho D_p} \tag{5.3}
\]

Here $\rho$ is the glass density (kg m$^{-3}$) with a value of 2530 kg m$^{-3}$ for float glass (Pilkington 2008), and $d_{\text{particle}}$ is the Sauter mean equivalent sphere diameter.

\(^\dagger\) Note Sauter mean equivalent sphere diameter is the diameter of the sphere that has the same surface area to volume ratio of the entire sample.
The values of $d_{\text{particle}}$ shown in Table 5-5 appear to be consistent with the sieve size of $< 90 \mu m$ used for the tests.

Table 5-5: Summary of particle size diameter for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size $< 90 \mu m$ particle size calculated from data at different temperatures

<table>
<thead>
<tr>
<th>Batch 1 (untreated)</th>
<th>$T (^{\circ}C)$</th>
<th>$d_{\text{particle}}$ (um) ± mean error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
<td>3.44 ± 1.65</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3.20 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3.54 ± 1.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Batch 2 (zinc-treated)</th>
<th>$T (^{\circ}C)$</th>
<th>$d_{\text{particle}}$ (um) ± mean error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
<td>4.74 ± 0.47</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>4.65 ± 0.59</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>5.27 ± 1.80</td>
</tr>
</tbody>
</table>

5.2.5.2 Desorption Data

It was proposed in Section 5.2.5 that the desorption stage of the isotherms would relate primarily to the removal of physisorbed water, and that the BET analysis of this stage would give a more reliable measurement of specific surface area. In order to conduct this analysis, the dry mass value used as a reference for the fractional mass uptake was obtained from the final registered mass value at dry conditions once desorption was complete. The BET plots for the desorption data are shown in Figure 5-18, 5-19 and Figure 5-20. Table 5-6 below summarises the BET parameters including the BET constant ($c$), the statistical monolayer values ($x_m$) and the BET specific surface ($S$) values.
Figure 5-18; BET plots of p/x(p₀-p) vs. p/p₀ for the data from the water desorption isotherms for float glass samples with a particle size < 90 μm, exposed to 15°C for fractional pressures between 0.1-0.3

Figure 5-19; BET plots of p/x(p₀-p) vs. p/p₀ for the data from the water desorption isotherms for float glass samples with a particle size < 90 μm, exposed to 20°C for fractional pressures between 0.1-0.3
Figure 5-20; BET plots of $p/(p_0-p)$ vs. $p/p_0$ for the data from the water desorption isotherms for float glass samples with a particle size < 90 μm, exposed to 30°C for fractional pressures between 0.1-0.3.

Table 5-6: BET parameters from desorption data for the isotherms shown in Figure 5-12 to Figure 5-14 at 15°C, 20°C and 30°C for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples.

<table>
<thead>
<tr>
<th>$T$(°C)</th>
<th>$\frac{1}{x_mC}$</th>
<th>$\frac{c-1}{x_mC}$</th>
<th>$c$ (-)</th>
<th>$x_m*10^{-4}$ (g g$^{-1}$)</th>
<th>$S$ (m$^2$ g$^{-1}$)</th>
<th>$R^2$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>897 ± 71.5</td>
<td>3630 ± 337</td>
<td>5.05±0.87</td>
<td>2.21 ± 0.56</td>
<td>0.78 ± 0.20</td>
<td>0.97</td>
</tr>
<tr>
<td>20</td>
<td>675 ± 53.7</td>
<td>4271 ± 253</td>
<td>7.33±1.02</td>
<td>2.02 ± 0.44</td>
<td>0.71 ± 0.16</td>
<td>0.99</td>
</tr>
<tr>
<td>30</td>
<td>659 ±59.6</td>
<td>5241 ± 281</td>
<td>8.96±1.29</td>
<td>1.70 ± 0.40</td>
<td>0.60 ± 0.14</td>
<td>0.99</td>
</tr>
<tr>
<td>Mean value</td>
<td></td>
<td></td>
<td>7.11±0.16</td>
<td>1.98 ± 0.46</td>
<td>0.69 ± 0.16</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T$(°C)</th>
<th>$\frac{1}{x_mC}$</th>
<th>$\frac{c-1}{x_mC}$</th>
<th>$c$ (-)</th>
<th>$x_m*10^{-4}$ (g g$^{-1}$)</th>
<th>$S$ (m$^2$ g$^{-1}$)</th>
<th>$R^2$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1391±106.7</td>
<td>7089 ± 503</td>
<td>6.09±0.90</td>
<td>1.18 ± 0.26</td>
<td>0.41 ± 0.10</td>
<td>0.99</td>
</tr>
<tr>
<td>20</td>
<td>1031±107.8</td>
<td>5214 ± 508</td>
<td>6.06±1.22</td>
<td>1.60 ± 0.49</td>
<td>0.56 ± 0.18</td>
<td>0.97</td>
</tr>
<tr>
<td>30</td>
<td>840 ± 67.4</td>
<td>7276 ± 318</td>
<td>9.67±1.20</td>
<td>1.23 ± 0.25</td>
<td>0.43 ± 0.10</td>
<td>0.99</td>
</tr>
<tr>
<td>Mean value</td>
<td></td>
<td></td>
<td>7.27±1.11</td>
<td>1.33 ± 0.34</td>
<td>0.46 ± 0.13</td>
<td></td>
</tr>
</tbody>
</table>

A clear dependency of the BET constant ($c$) on temperature is measured for the untreated float glass samples. A temperature dependency for the zinc-treated samples is less clear. For the purpose of comparing data between both batches, mean values have been calculated.
It is interesting to compare the mean specific surface area values obtained from the desorption stage of the isotherms with those obtained from the adsorption stage. For the untreated samples there is no detectable difference in specific surface area between the two measurements; both are around 0.7 m$^2$.g$^{-1}$. For the zinc-treated samples the adsorption isotherm analysis yields a marginally higher value of 0.49 m$^2$.g$^{-1}$ compared to the desorption isotherm analysis (0.46 m$^2$.g$^{-1}$).

For the calculation of the corrosion constant ($k_r$), corrosion flux ($J$) and adsorbed layer thickness ($l$), the mean specific surface area value for the untreated samples based on the desorption isotherms was used, i.e. 0.7 m$^2$.g$^{-1}$ because it was felt to be more representative of the true surface area. The BET constant ($c$) and the monolayer ($x_m$) values measured for the adsorption stage at each temperature are input parameters in the CA simulation.

### 5.2.6 Layer Thickness

Another relevant value which can be estimated from the isotherm data is the adsorbed layer thickness ($l$). To calculate this value, the mass adsorbed is firstly converted to a volume using the density of the adsorbate (998 kg m$^{-3}$ at 21°C, Coulson and Richardson 1999). The volume is then converted to a layer thickness using the mean BET specific surface area ($S$) obtained from the desorption water isotherms i.e. 0.7 m$^2$.g$^{-1}$ for the Batch 1 (untreated) float glass samples, see Equation A-10. The number of molecular layers ($n'$) (see Equation A-11), can also be obtained assuming a molecular diameter of 0.3 nm for water as quoted by Kalra et al. (2003). The monolayer thickness $l_t$ (nm) and the number of molecular layers $n'$ (-) are shown in Figure 5-21 below for Batch 1 (untreated) and Batch 2 (zinc-treated) samples exposed to 30°C. Note that the same specific surface area value ($S$) of 0.7 m$^2$.g$^{-1}$ was used for both untreated and zinc-treated float glass samples.
Figure 5-21: Layer thickness ($l$) and number of molecular layers ($n'$) plotted as a function of %RH for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 µm, exposed to 30°C during adsorption. The dashed horizontal lines correspond to monolayers.

Figure 5-21 shows that monolayer coverage is predicted at approximately 30% RH for Batch 1 (untreated), and at 60% RH for Batch 2 (zinc-treated) float glass samples. A second monolayer was also predicted to occur for the untreated sample at approximately 60% RH.

5.2.7 Thermodynamics

The saturated vapour pressure ($p_0$) values of water at 15°C, 20°C and 30°C were calculated from the Antoine equation (see Equation 3.2, in Chapter 3). The values obtained are shown in Table 5-7. These were used in the BET equation (see Equation A.1) in Appendix A to generate the BET plots such as Figure 5-17.

Table 5-7: Summary of saturated vapour pressure ($p_0$) values obtained using the Antoine equation (see Equation 3.2 in Chapter 3) at 288.15, 293.15 and 303.15 K

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$p_0$ (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.15</td>
<td>12.61</td>
</tr>
<tr>
<td>293.15</td>
<td>17.35</td>
</tr>
<tr>
<td>303.15</td>
<td>31.65</td>
</tr>
</tbody>
</table>
The latent heat of vaporisation ($L_v$) values at 15°C, 20°C and 30°C were calculated using the Watson equation; see Equation 5.4 (Reid et al. 1987). The results are summarised in Table 5-8, below.

\[
L_v = L_{v,b} \left[ \frac{T_c - T}{T_c - T_b} \right]^{0.38}
\]

(5.4)

Here $L_{v,b}$ is the latent heat at normal boiling point i.e. 40626 J mol$^{-1}$ (Coulson and Richardson 1998), $L_v$ is the latent heat of vaporisation at the experimental temperature, $T_c$ is the critical temperature i.e. 647.3 K, $T_b$ is the boiling temperature i.e. 373.2 K and $T$ is the experimental temperature (K).

As a matter of interest the energy of adsorption in the first layer ($E_1$) was also calculated for both untreated and zinc-treated float glass samples from the desorption isotherms. Equation 5.5 (Gregg and Sing 1967) below was used to this end. The results are summarised in Table 5-8 below.

\[
c = \exp \left( \frac{E_1 - L_v}{RT} \right) \Leftrightarrow E_1 = \ln cRT + L_v
\]

(5.5)

Here $c$ is the BET constant (-), $R$ is the universal gas constant which is taken to be 8.314 (J K$^{-1}$ mol$^{-1}$) and $T$ is the temperature (K), $E_1$ is the energy of adsorption in the first layer (J mol$^{-1}$).
The $E_l$ values are strongly dependent on temperature for the untreated float glass samples as seen in Table 5-8. The higher $E_l$ values compared with the $L_v$ indicate some interaction between the sample and the water vapour, Gregg and Sing (1967).

### 5.2.8 Correlating Mass uptake per Unit Surface Area

The reaction parameters were determined in Section 5.3.2 by plotting the logarithm of the fractional mass uptake as a function of the logarithm of time. This was performed for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples. Sections of linearity were identified by eye. Values of $k_r$ and $\alpha$ were obtained from the equations of the fitted lines as shown in Figure 5-8 and Figure 5-9.

In order to convert the corrosion constant ($k_r$) previously given in units of $\mu$g g$^{-1}$ min$^{-\alpha}$ (see Equation 5.1), into units of $\mu$g m$^{-2}$ min$^{-\alpha}$ a mean value of the BET specific surface area from the desorption isotherms i.e. 0.7 m$^2$ g$^{-1}$ was used (see Table 5-6). The same BET specific surface area value was used for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples.

The log of the mass uptake per unit surface area was plotted as a function of the log of time in minutes. These graphs are identical in form to Figure 5-8 and Figure 5-9 and
are therefore not shown. The data are summarised in Table 5-9, below. Note that the same regions of linearity as the ones shown in Figure 5-8 and Figure 5-9 were used. Converting the corrosion constant into µg m⁻² min⁻¹ avoids the issue of particle size, and gives a value that can be related directly to the corrosion of flat glass sheet on a unit area basis.

Table 5-9; Summary of corrosion constant \( (k_r') \) values for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples with a particle size < 90 µm, exposed to 15°C, 20°C and 30°C

<table>
<thead>
<tr>
<th>Batch 1 (untreated)</th>
<th>T(°C)</th>
<th>( \alpha ) ( - ) ( \pm ) standard error</th>
<th>( k_r' ) (µg m⁻² min⁻¹) ( \pm ) estimated uncertainty (%)</th>
<th>( R^2 ) ( - )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.06 ( \pm ) 9.28( \times )10⁻⁴</td>
<td>469 ( \pm ) 0.81</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.13 ( \pm ) 1.03( \times )10⁻³</td>
<td>307 ( \pm ) 1.03</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.21 ( \pm ) 7.54( \times )10⁻⁴</td>
<td>167 ( \pm ) 0.87</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.32 ( \pm ) 8( \times )10⁻³</td>
<td>23 ( \pm ) 4.28</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.45 ( \pm ) 6.02( \times )10⁻⁴</td>
<td>16 ( \pm ) 0.65</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.77 ( \pm ) 1.27( \times )10⁻²</td>
<td>3 ( \pm ) 12.85</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.45 ( \pm ) 9.15( \times )10⁻³</td>
<td>24 ( \pm ) 10</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.58 ( \pm ) 3.75( \times )10⁻³</td>
<td>10 ( \pm ) 4.28</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.46 ( \pm ) 4.21( \times )10⁻³</td>
<td>26 ( \pm ) 5.71</td>
<td>0.98</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Batch 2 (zinc-treated)</th>
<th>T(°C)</th>
<th>( \alpha ) ( - ) ( \pm ) standard error</th>
<th>( k_r' ) (µg m⁻² min⁻¹) ( \pm ) estimated uncertainty (%)</th>
<th>( R^2 ) ( - )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.06 ( \pm ) 4.76( \times )10⁻⁴</td>
<td>117 ( \pm ) 0.53</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.17 ( \pm ) 3.85( \times )10⁻³</td>
<td>94 ( \pm ) 0.38</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.26 ( \pm ) 3.53( \times )10⁻³</td>
<td>44 ( \pm ) 4.2</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.40 ( \pm ) 3.55( \times )10⁻²</td>
<td>0.015 ( \pm ) 35.7</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.08 ( \pm ) 1.53( \times )10⁻²</td>
<td>0.124 ( \pm ) 15.71</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.68 ( \pm ) 3.25( \times )10⁻³</td>
<td>2 ( \pm ) 4.28</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.22 ( \pm ) 3.87( \times )10⁻³</td>
<td>96 ( \pm ) 4.28</td>
<td>0.86</td>
<td></td>
</tr>
</tbody>
</table>

Decreasing \( k_r' \) values were measured for the Batch 1 (untreated) float glass samples with time at 15°C and 20°C (see Table 5-9). At 30°C, varying \( k_r' \) values were measured with time. The Batch 2 (zinc-treated) samples showed increasing \( k_r' \) values at 30°C and increasing values at 20°C. Whereas at 15°C, only one region of linearity was identified.
5.2.9 Determination of Corrosion Flux

In this section polynomials were fitted to the mass uptake per unit area (J) curves as a function of exposure time. Using this method, irregularities in the mass uptake curves were smoothed out. Figure 5-22 and Figure 5-23 below show these results for the Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples respectively. The initial 1000 minutes of the mass uptake curves were ignored in order to avoid contributions to the flux from chemisorption and physisorption processes. This should ensure that the uptake studied is entirely the result of physisorption to replace the water that penetrates the sample by diffusion.

![Graph showing mass uptake per unit area as a function of time for different temperatures](image)

Figure 5-22; Polynomial fit to data of mass uptake per unit surface area as a function of time for Batch 1 (untreated) float glass samples with a particle size < 90 µm, exposed to 15°C, 20°C and 30°C at 70% RH
Figure 5-23; Polynomial fit to data of mass uptake per unit surface area as a function of time for Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 15°C, 20°C and 30°C at 70% RH

The polynomial equations shown in Figure 5-22 and Figure 5-23 were differentiated so that an equation for the corrosion flux \((J')\) could be obtained. These are shown in Table 5-10 below.

Table 5-10; Summary of corrosion flux equations for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples exposed to 15°C, 20°C and 30°C

<table>
<thead>
<tr>
<th>Batch 1 (untreated)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T (°C)</strong></td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Batch 2 (zinc-treated)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T (°C)</strong></td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>30</td>
</tr>
</tbody>
</table>

The corrosion flux values \((J')\) were obtained using the corresponding equation from Table 5-10 for a specific value of time. Table 5-11 below compares the corrosion flux values at 3000 minutes for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass
samples exposed to 15°C, 20°C and 30°C. Overall the corrosion flux values ($J'$) for the Batch 2 (zinc-treated) float glass samples are lower compared to the results for the Batch 1 (untreated) samples. The corrosion flux for an untreated sample was 11.8 times higher that of a zinc treated sample exposed to 15°C, 9.25 times higher at 20°C and 2.85 times higher at 30°C. These results are direct evidence that zinc is effectively reducing the corrosion flux.

The effect of temperature on corrosion flux can also be obtained. Results for the untreated samples show the flux values increase by a factor of 2.1 for a temperature increase between 15°C and 20°C, and by a factor of 1.5 for a temperature increase from 20°C to 30°C. The results for the zinc-treated float glass samples showed a more significant increase in corrosion flux values with temperature compared to the untreated samples. The same increase in temperature resulted in an increase in corrosion flux of 2.7 times and 4.7 times, respectively.

### Table 5-11: Summary of corrosion flux ($J'$) values at $t = 3000$ minutes for Batch 1 (untreated) and Batch 2 (zinc treated) float glass samples exposed to 15°C, 20°C and 30°C

<table>
<thead>
<tr>
<th>Batch 1 (untreated) at $t = 3000$ minutes</th>
<th>$T$ (°C)</th>
<th>$J'$ (μg m$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.0628 ± 5.45 × 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.1314 ± 1.46 × 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.1926 ± 1.67 × 10^{-3}</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Batch 2 (zinc-treated) at $t = 3000$ minutes</th>
<th>$T$ (°C)</th>
<th>$J'$ (μg m$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.0053 ± 2.86 × 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.0142 ± 8.78 × 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.0675 ± 1.95 × 10^{-3}</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5-24 and Figure 5-25 below show the corrosion flux values every 100 minutes for untreated and zinc-treated float glass samples exposed to 15°C, 20°C and 30°C. For the untreated samples exposed to 20°C and 30°C the corrosion flux values ($J'$) decrease with time. By extrapolating the data it appears that the corrosion flux values at 15°C will surpass the values at 20°C and 30°C, for both untreated and zinc-treated float glass samples.
Results

Figure 5-24; Corrosion flux values for every 100 minutes up to 6000 minutes for Batch 1 (untreated) float glass samples with a particle size < 90 µm

Figure 5-25; Corrosion flux values for every 100 minutes up to 6000 minutes for Batch 2 (zinc-treated) float glass samples with a particle size < 90 µm

As a matter of interest the corrosion flux data were plotted in an Arrhenius plot (see Figure 5-26, below) to measure the activation energy ($E_a$) values for the Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples. Note that the results in Figure 5-26 are based on the data shown previously in Table 5-11. There is reasonable linearity of the data for both types of sample, confirming the suitability of an
Arrhenius dependency of $J'$ on temperature. This type of dependency on temperature is expected for diffusion through solids, as discussed in section 2.6.2 and 2.6.5.

Figure 5-26; Arrhenius plot for Batch 1 (untreated) and Batch 2 (zinc treated) float glass samples with a particle size < 90 µm, showing the logarithm of the flux values as a function of the inverse of temperature for a time $t = 3000$ minutes

Figure 5-26 suggests an activation energy value of the corrosion flux ($J'$) to be $50885 \pm 19143 \text{ J mol}^{-1}$ and $122289 \pm 6008 \text{ J mol}^{-1}$ for the Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples respectively.

### 5.2.10 Data Reproducibility and Ageing

In this section the data reproducibility will be shown. A possible ageing effect will also be identified.

**Data reproducibility**

In order to study the data reproducibility for the Batch 2 (zinc-treated) float glass samples the isotherm at 30°C (shown in Figure 5-14) was repeated. The original experiment and the repeated experiment are shown in the same graph, see Figure 5-27, below.
Figure 5-27; Fractional mass adsorbed and desorbed as a function of relative humidity for Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 30°C.

The isotherms in Figure 5-27 show the same pattern for desorption only; see the %RH interval of 40% until 5%. The minor deviations during adsorption were discussed in Section 5.2.4. Figure 5-28 below show the BET plots for the %RH interval 10-30% RH based on the data shown in Figure 5-27.

Figure 5-28; BET plots of \( p/x(p/p_0) \) vs. \( p/p_0 \) for the data from the water desorption isotherms for Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 30°C.
Results

From Figure 5-28 the BET constant (c) and the monolayer (x_m) values were calculated using the method described in Section 5.2.5. The results are summarised in Table 5-12, below. In order to distinguish the two experiments the letter R is used denoting repeat.

Table 5-12: BET parameters from desorption data for the isotherms at 30°C shown in Figure 5-27 for two Batch 2 (zinc-treated) float glass samples with a particle size < 90µm

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>c (-)</th>
<th>x_m*10^-4 (g g^-1)</th>
<th>R² (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>9.67 ± 0.42</td>
<td>1.23 ± 5.38*10^-6</td>
<td>0.99</td>
</tr>
<tr>
<td>30 R</td>
<td>11.77 ± 0.30</td>
<td>1.22 ± 3.15*10^-6</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The BET monolayer values (x_m) in Table 5-12 show for the repeated experiment (30 R) a 0.81% lower value compared to the original experiment. This value lies within the range of experimental error and therefore these results appear to have a good reproducibility.

Ageing Effect

The data reproducibility in terms of a possible ageing effect is shown for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples in Figure 5-29 and Figure 5-30. The samples from each batch were stored for different lengths of time under dry conditions inside a desiccator. The storage times are shown for each sample in the figures below.
Results

Figure 5-29; Fractional mass uptake vs. time for two samples from Batch 1 (untreated) float glass samples with a particle size < 90 μm, exposed to 30°C and 70% RH. These samples were stored in a desiccator for 63 and 103 days at dry conditions prior to sample analysis.

Figure 5-30; Fractional mass uptake vs. time for two samples from Batch 2 (zinc-treated) float glass samples with a particle size < 90 μm, exposed to 20°C. These samples were stored in a desiccator for 12 and 150 days at dry conditions prior to sample analysis.

Figure 5-29 shows very little difference between the mass uptake of Batch 1 (untreated) samples stored for different time periods, confirming the reproducibility of the procedure. However, the Batch 2 (zinc-treated) float glass sample stored for 150 days at dry conditions adsorbs significantly more water compared to the sample stored...
for a 12 day period, (see Figure 5-30). This high increase in mass suggests an ageing effect during storage for the zinc-treated float glass samples. To quantify this effect the log of the fractional mass uptake as a function of the log of time was plotted, see Figure 5-31 below, for the zinc-treated samples.

![Figure 5-31: Log of fractional mass uptake as a function of the log of time for Batch 2 (zinc-treated) samples with a particle size < 90 μm, exposed to 20°C. Regions of linearity are shown for determination of the time index and the corrosion constant as depicted in Equation (5.1)](image)

Table 5-13 summarises the time index \( (a) \), the corrosion constant \( (k_r) \) as well as \( (k_r') \) values suggested from Figure 5-31. The regression coefficient \( (R^2) \) values are also included.

<table>
<thead>
<tr>
<th>Storage time at dry conditions (days)</th>
<th>( a ) ((-)) ± absolute error</th>
<th>( k_r ) (μg g(^{-1}) min(^{-4})) ± estimated uncertainty (%)</th>
<th>( k_r' ) (μg m(^{-2}) min(^{-4})) ± estimated uncertainty (%)</th>
<th>( R^2 ) (-)</th>
<th>Time interval (log min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 days</td>
<td>0.24 ± 5.22 \times 10^{-3}</td>
<td>14 ± 4 %</td>
<td>20 ± 5.7 %</td>
<td>0.78</td>
<td>2.69 – 3.15</td>
</tr>
<tr>
<td>150 days</td>
<td>0.17 ± 3.85 \times 10^{-4}</td>
<td>66 ± 0.3 %</td>
<td>94 ± 0.4 %</td>
<td>1.00</td>
<td>1.64 – 3.41</td>
</tr>
<tr>
<td></td>
<td>0.26 ± 3.53 \times 10^{-3}</td>
<td>31 ± 3 %</td>
<td>44 ± 10 %</td>
<td>0.93</td>
<td>3.49 – 3.63</td>
</tr>
</tbody>
</table>

The table above shows that the time index parameter \( (a) \) is similar for both storage times. However a greater influence of the storage time is measured in the equation
constant values \( (k_r) \). This value is lower for the zinc-treated float glass sample that had been stored for the shortest amount of time. This will be discussed in the next chapter.

**Summary**

In this section the gravimetric corrosion measurements of float glass were presented. The kinetics of corrosion for untreated and zinc-treated float glass samples were included at various environmental conditions. Water sorption measurements according to the BET theory were shown. The calculated BET parameters included the specific surface area \( (S) \), monolayer uptake \( (x_m) \) and the BET constant \( (c) \) values for both adsorption and desorption isotherms. The float glass nominal particle diameter \( (d_{\text{particle}}) \) was also calculated from the adsorption isotherm and the energy of adsorption in the first layer \( (E_i) \) was also calculated, based on the desorption isotherms.

Finally, the reproducibility of the gravimetric experiments was examined. A sample ageing effect has been illustrated for samples that have undergone zinc treatment.

Next, the results of the numerical simulation developed in Chapter 3 will be presented and compared to results from the gravimetric experiments at different temperatures presented in this current section.

### 5.3 Cellular Automaton Simulation Results

In Chapter 3, a model was developed with the objective of establishing whether the initial mass uptake of the gravimetric experimental results could be modelled on the basis of mass transfer, adsorption, diffusion and reaction processes. In the current chapter a comparison between the simulation results and the gravimetric experimental results for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples will be shown. A summary of the simulation parameters used is also shown here. This section will conclude with a sensitivity analysis.
### 5.3.1 Simulation Parameters

Table 5-14 (Table 3-2 reproduced) below, summarises the simulation input parameters as well as their value and units, and Table 5-15 (Table 3-3 reproduced) below summarises the parameter values which were unknown in Chapter 3.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value/Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>%RH$_2$</td>
<td>Gravimetric experimental %RH</td>
<td>70 (%)</td>
<td>User parameter, chosen to match gravimetric experiments</td>
</tr>
<tr>
<td>$\rho_{sample}$</td>
<td>Sample density</td>
<td>2530 kg m$^{-3}$</td>
<td>Pilkington (2008), fact sheet</td>
</tr>
<tr>
<td>$a_i$</td>
<td>Interfacial area</td>
<td>1.91 m$^2$ kg$^{-1}$</td>
<td>Area of pan exposed to moisture</td>
</tr>
<tr>
<td>$D_{0,bg}$</td>
<td>Relative diffusion in bulk glass ($bg$) and glass surface ($gsl$)</td>
<td>$7.52 \times 10^{-11}$ m$^2$ s$^{-1}$</td>
<td>Value from Helmich and Rauch (1993) based on hydrogen profiles at 100 and 200°C on silica glass.</td>
</tr>
<tr>
<td>$D_{0,sl}$</td>
<td></td>
<td>$7.52 \times 10^{-11}$ m$^2$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$\delta t$</td>
<td>Time step length</td>
<td>$1 \times 10^{-3}$ s</td>
<td>User Parameter</td>
</tr>
<tr>
<td>$\delta z$</td>
<td>Distance step length in solid, width of node</td>
<td>$5 \times 10^{-3}$ m</td>
<td></td>
</tr>
<tr>
<td>$E_{a,bg}$</td>
<td>Activation energy in bulk glass ($bg$) and glass surface ($gsl$)</td>
<td>57702 kJ kmol$^{-1}$</td>
<td>Helmich and Rauch (1993), from hydrogen profiles at 100 and 200°C on silica.</td>
</tr>
<tr>
<td>$E_{a,sl}$</td>
<td></td>
<td>57702 kJ kmol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$\delta g$</td>
<td>Gas film thickness</td>
<td>$5 \times 10^{-5}$ m</td>
<td>User parameter</td>
</tr>
<tr>
<td>gas$_dz$</td>
<td>Distance step length in gas</td>
<td>$1.67 \times 10^{-3}$ m</td>
<td>Notional parameter</td>
</tr>
<tr>
<td>Integration step number</td>
<td>Time steps at initial %RH</td>
<td>700000 (-)</td>
<td>User parameter</td>
</tr>
<tr>
<td>$K_p$</td>
<td>Partition coefficient</td>
<td>0.1 m$^3$ kg$^{-1}$</td>
<td>User parameter</td>
</tr>
<tr>
<td>$k_g$</td>
<td>Mass transfer coefficient</td>
<td>$1.73 \times 10^{-7}$ mol s$^{-1}$ kPa$^{-1}$ m$^{-2}$</td>
<td>User parameter</td>
</tr>
<tr>
<td>$N_{n,gas}$</td>
<td>Nodes in gas.</td>
<td>4 (-)</td>
<td>User parameter</td>
</tr>
<tr>
<td>$N_{n,glass}$</td>
<td>Nodes in solid</td>
<td>10 (-)</td>
<td>User parameter</td>
</tr>
<tr>
<td>$R_{c,bg}$</td>
<td>Reaction capacity in bulk glass ($bg$) and glass surface ($gsl$)</td>
<td>10780 mol m$^{-3}$</td>
<td>Sodium concentration in bulk glass from Staunton (2007) analysis</td>
</tr>
<tr>
<td>$R_{c,sl}$</td>
<td></td>
<td>10780 mol m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$t_s$</td>
<td>Number of time steps</td>
<td>(-)</td>
<td>User parameter</td>
</tr>
</tbody>
</table>
### Table 5-15; Summary of unknown parameters, Table 3-3 reproduced from Chapter 3

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value/Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>%RH&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Exposure %RH prior to loading.</td>
<td>(-) (see Table 5-17)</td>
<td>Estimated parameter by curve fitting to gravimetric data</td>
</tr>
<tr>
<td>c</td>
<td>BET constant</td>
<td>(-) (see Table 5-18)</td>
<td>Value from experimental data</td>
</tr>
<tr>
<td>q&lt;sub&gt;lm&lt;/sub&gt;</td>
<td>BET statistical monolayer</td>
<td>mol kg&lt;sup&gt;-1&lt;/sup&gt; (see Table 5-18)</td>
<td>Value from experimental data</td>
</tr>
<tr>
<td>k&lt;sub&gt;bg&lt;/sub&gt;</td>
<td>Rate constant in bulk glass (bg) and glass surface (gsl)</td>
<td>m&lt;sup&gt;2&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt; (see Table 5-19)</td>
<td>Estimated parameter by curve fitting to linear region of mass uptake as a function of time.</td>
</tr>
</tbody>
</table>

#### Mass Transfer

The diffusivity of water in air (\(D_{ab}\)) was, as a first approach, calculated from the Chapman-Enskog equation (see Equation 3.42 in Chapter 3). This value was then converted to the mass transfer coefficient (\(k'_g\)) value (see Equation 3.5) using the definition of the Sherwood number. Equation 3.8 was then used to convert \(k'_g\) into units of \(k_g\). The results were shown in Table 3-1 of Chapter 3. The calculated \(k_g\) values proved to be too high. This issue is discussed in the following chapter. Therefore the mass transfer coefficient value was estimated using a trial-and-error method by curve fitting the predicted initial water uptake to the uptake measured by gravimetric analysis. A value for \(k_g\) of \(1.73 \times 10^{-7}\) mol s<sup>-1</sup> kPa<sup>-1</sup> m<sup>-2</sup> was used for both untreated and zinc-treated glass exposed to 15°C, 20°C and 30°C.

A two step %RH method as described in Section 3.4.4 was used to account for the environmental conditions in the laboratory prior to sample loading and the conditions inside the IGAsorp chamber, see Figure 3-5, in Chapter 3. Two different %RH values were used i.e. \(%RH_1\) and \(%RH_2\). The \(%RH_1\) is unknown and the \(%RH_2\) is 70% corresponding to the conditions chosen for the gravimetric experiments. To determine the initial %RH value (i.e. \(%RH_1\)) the mass adsorbed by the sample prior to its loading i.e. \(q_a\) (mol kg<sup>-1</sup>) was calculated using Equation (5.2) below, (this is Equation 3.41 reproduced).
\[ q_a = q_{70\%} - \zeta \quad (5.2) \]

Here \( q_{70\%} \) (mol kg\(^{-1}\)) is the amount adsorbed according to the isotherm at 70\% RH for a given temperature (see Figure 5-33), and \( \zeta \) (mol kg\(^{-1}\)) is the intercept of the mass uptake slope when a straight line is fitted through the final mass region, (see Figure 5-32). Hence by cross-referencing the now known \( q_a \) value to the adsorption isotherm at the same experimental temperature used for the gravimetric experiment, the initial humidity value (\%RH\(_i\)) was determined, see Figure 5-33 further below. These values are summarised in Table 5-16.

![Figure 5-32; Mass uptake as a function of time at 15\(^\circ\)C and 70\% RH from gravimetric experiments. Here \( \zeta \) is the intercept of the final mass uptake region](image)

**Table 5-16; Summary of parameters from Equation 5.2 for both untreated and zinc-treated glass exposed to 15\(^\circ\)C, 20\(^\circ\)C and 30\(^\circ\)C**

<table>
<thead>
<tr>
<th></th>
<th>Untreated</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( T ) ((^\circ)C)</td>
<td>( q_{70%} ) (mol kg(^{-1}))</td>
<td>( \zeta ) (mol kg(^{-1}))</td>
<td>( q_a ) (mol kg(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.036</td>
<td>0.022</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.033</td>
<td>0.008</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.032</td>
<td>-0.014</td>
<td>0.046</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Zinc-treated</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( T ) ((^\circ)C)</td>
<td>( q_{70%} ) (mol kg(^{-1}))</td>
<td>( \zeta ) (mol kg(^{-1}))</td>
<td>( q_a ) (mol kg(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.017</td>
<td>0.006</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.015</td>
<td>0.003</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.014</td>
<td>-0.002</td>
<td>0.016</td>
<td></td>
</tr>
</tbody>
</table>
If the mass uptake curve after running the simulation did not match the gravimetric experimental results, the initial %RH ($%RH_i$) value was adjusted by eye to match the theoretical and experimental mass uptakes. Table 5-17 below, shows the predicted %RH$_i$ value based on the calculated $q_a$ value (see Table 5-16 for these values), and the adjusted %RH$_i$ value used in the simulations for both untreated and zinc-treated glass exposed to 15°C, 20°C and 30°C. This table shows that for the samples exposed to 15°C and 20°C, all %RH$_i$ values are below 70% RH, whereas at 30°C values above 70% RH were better suited. This is associated with the initial mass decrease observed in the experiments conducted at 30°C (Figure 5-7). Note that the mass decrease at 30°C makes Figure 3.5 misleading.

### Table 5-17: Summary of predicted %RH$_i$ and adjusted %RH$_i$ values based on $q_a$ from Equation 5.2 at 15°C, 20°C and 30°C for untreated and zinc-treated glass

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Predicted %RH$_i$ value from $q_a$ and adsorption isotherm</th>
<th>Adjusted %RH$_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>38</td>
<td>32</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>65</td>
</tr>
<tr>
<td>30</td>
<td>$&gt;$70</td>
<td>80</td>
</tr>
</tbody>
</table>

### Zinc-treated

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Predicted %RH range from $q_a$ and adsorption isotherm</th>
<th>Adjusted %RH$_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>45</td>
<td>63</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>69</td>
</tr>
<tr>
<td>30</td>
<td>$&gt;$70</td>
<td>75</td>
</tr>
</tbody>
</table>
Adsorption

The BET values used in the simulation included the adsorption BET constant value \( c \) and the monolayer uptake value \( q_m \). These were based on the experimental adsorption isotherms and corresponding BET plots shown in Figure 5-15, 5-16 and Figure 5-17 for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples exposed to 15°C, 20°C and 30°C. These results are summarised in Table 5-18 below.

| Batch 1 (untreated) |  |
|---------------------|--|------------------|
| \( T \) (°C) | \( c \) (-) | \( q_m \) (mol kg\(^{-1}\)) |
| 15 | 5.72 | 10.8\( \times 10^{-3} \) |
| 20 | 3.9 | 11.7\( \times 10^{-3} \) |
| 30 | 5.57 | 10.6\( \times 10^{-3} \) |

| Batch 2 (zinc treated) |  |
|------------------------|--|------------------|
| \( T \) (°C) | \( c \) (-) | \( q_m \) (mol kg\(^{-1}\)) |
| 15 | 5.15 | 7.49\( \times 10^{-3} \) |
| 20 | 3.62 | 8.06\( \times 10^{-3} \) |
| 30 | 9.45 | 7.06\( \times 10^{-3} \) |

Diffusion/Diffusion with Reaction

The mass uptake for the untreated samples was modelled using mass transfer, adsorption, diffusion and reaction processes. This gave reasonable agreement with experimental data for mass uptake. For the zinc-treated samples the experimental mass uptake curves are flatter, and therefore the reaction mechanism in the simulation was not activated in order to give reasonable agreement. The difference in mass uptake behaviour predicted with diffusion and reaction, and with diffusion only is shown in Figure 5-34 below.
The gravimetric results suggest a steeper mass increase for the untreated samples compared to the zinc-treated float glass samples at 15°C (see Figure 5-5). This trend is also confirmed by comparison of the flux values presented in Table 5-11. Hence the steeper mass increase of the untreated samples was modelled by trial and error of the reaction rate constant value by curve fitting to the gravimetric mass uptake results. For Batch 2 (zinc-treated) float glass samples the mass uptake measured gravimetrically is comparatively constant with time after the initial transient (see Section 5.3.2 below). Therefore the reaction rate constant \( k \), as defined in Equation (3.17) was assumed to be zero at the glass surface for these samples. Table 5-19 below, summarises the reaction rate constant values obtained for the untreated glass samples exposed to 15°C, 20°C and 30°C. Note that no apparent trend is observed for these values in spite of the experimental evidence of increasing flux with temperature in Table 5-11. This may be due to inaccuracies in the fitting procedure.

Table 5-19 Summary of estimated reaction rate constant values for untreated glass samples for the temperatures used in the gravimetric experiments

<table>
<thead>
<tr>
<th>Untreated</th>
<th>$T$ (°C)</th>
<th>$k$ (m$^3$ mol$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>$6 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Figure 5-34; Mass uptake curve from simulation for glass exposed to 15°C when diffusion and reaction occurs in the glass. Diffusion only is also shown in the same graph.
5.3.2 Simulation and gravimetric mass uptake results

In this section a comparison is made between the simulation results and the gravimetric results for Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples exposed to 15°C, 20°C and 30°C. To this end both data sets are plotted on the same graph. Figures 5-35, 5-36 and 5-37 show the results for the untreated glass and Figures 5-38, 5-39 and 5-40 for the zinc-treated glass at the various temperatures studied.

*Batch 1 (Untreated)*

![Graph showing mass uptake comparison](image-url)

*Figure 5-35: Comparison of mass uptake on untreated float glass at 15°C for simulation and gravimetric experimental data reproduced from Figure 5-3*
Figure 5-36; Comparison of mass uptake on untreated float glass at 20°C for simulation and gravimetric experimental data reproduced from Figure 5-3.

Figure 5-37; Comparison of mass uptake on untreated float glass at 30°C for simulation and gravimetric experimental data reproduced from Figure 5-29, for the sample stored at dry conditions for 63 days prior to sample analysis.
Results

Batch 2 (Zinc-Treated)

Figure 5-38; Comparison of mass uptake on zinc treated float glass at 15°C for simulation and gravimetric experimental data reproduced from Figure 5-4

Figure 5-39; Comparison of mass uptake on zinc treated float glass at 20°C for simulation and gravimetric experimental data reproduced from Figure 5-30, for the sample stored at dry conditions for a 12 day period prior to the sample analysis
Good agreement is found between the simulation results and the experimental gravimetric results for both untreated and zinc-treated float glass samples. In order to check the suitability of the model for longer time scales, the simulations for the samples exposed to 15°C were run up to 500 minutes. Figure 5-41 and Figure 5-42 below show these results for untreated and zinc-treated glass respectively.
Figure 5-42; Comparison of mass uptake on zinc treated float glass at 15°C for simulation and gravimetric experimental data reproduced from Figure 5-4.

Figure 5-41 and Figure 5-42 show that the devised model 'breaks down' at around 200 minutes for both untreated and zinc treated samples. This will be discussed in the following chapter. A check was made to see if the original parameters used in the simulation for an untreated and a zinc-treated sample would apply when these were stored for longer at dry conditions. The results are shown in Figure 5-43 and Figure 5-44 below.
Figure 5-43; Comparison of mass uptake on untreated float glass at 20°C for simulation and gravimetric experimental data for a sample stored for 103 days as shown in Figure 5-29

Figure 5-44; Comparison of mass uptake on zinc treated float glass at 20°C for simulation and gravimetric experimental data for sample stored for 150 days as shown in Figure 5-30

Figure 5-44 suggests that the parameters and assumptions made for the zinc-treated sample stored for 150 days at dry conditions no longer holds. Further discussion is reserved for the next chapter.
5.3.3 Sensitivity analysis for simulation

In this section a sensitivity analysis is shown for the simulation model running for a nominal 10,000 s for an untreated sample and zinc-treated sample exposed to 15°C. A 5% perturbation of twenty parameters included in the simulation was studied. These results were based on the relative difference of the absolute measured total mass uptake value to the base case result. This is the final mass uptake measured in the original simulation at 15°C for the untreated and zinc-treated samples shown in Figure 5-35 and Figure 5-38 respectively. Table 5-20 and Table 5-21 below show in the left column the parameters which were varied by ± 5%, and on the right hand side the corresponding relative results are shown. Note that the relative results are presented in descending order of importance. The results for the untreated glass are shown in Table 5-20, and for the zinc-treated glass in Table 5-21.

From Table 5-20 it appears that the parameter which has the largest influence on the final mass adsorbed by the untreated sample is the partial pressure value ($p_0$). A significant number of parameters are seen to have little or no effect. For example in terms of number of nodes used, the total number of nodes in the glass does not appear to be of influence. No effect is measured either when the number of nodes in the gas phase is increased. Also, in this case, the parameters used for the glass bulk do not have any effect on the final amount adsorbed. This was because the simulation was not run for long enough in order for these to have any effect. Therefore it appears that only parameters related to the gas phase and surface layer are of significance.
Table 5-20: Relative results of sensitivity analysis for a 5% perturbation in the simulation parameters for untreated glass exposed to 15°C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Relative change from base case</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base case</strong></td>
<td>0</td>
</tr>
<tr>
<td>( p_0 ) (kPa) + 5.00 %</td>
<td>1.443E-01</td>
</tr>
<tr>
<td>( p_0 ) (kPa) - 5.00 %</td>
<td>1.150E-01</td>
</tr>
<tr>
<td>( q_m ) (mol/kg) - 5.00 %</td>
<td>4.999E-02</td>
</tr>
<tr>
<td>( q_m ) (mol/kg) + 5.00 %</td>
<td>4.999E-02</td>
</tr>
<tr>
<td>( t_s ) (-) - 5.00 %</td>
<td>4.686E-03</td>
</tr>
<tr>
<td>( t_s ) (+) + 5.00 %</td>
<td>4.685E-03</td>
</tr>
<tr>
<td>( \delta t ) (s) - 5.00 %</td>
<td>4.474E-03</td>
</tr>
<tr>
<td>( \delta t ) (s) + 5.00 %</td>
<td>4.473E-03</td>
</tr>
<tr>
<td>( \delta z ) (m) + 5.00 %</td>
<td>4.343E-03</td>
</tr>
<tr>
<td>( \delta z ) (m) - 5.00 %</td>
<td>4.343E-03</td>
</tr>
<tr>
<td>( R_{C _gel} ) (mol/m3) - 5.00 %</td>
<td>4.343E-03</td>
</tr>
<tr>
<td>( R_{C _gel} ) (mol/m3) + 5.00 %</td>
<td>4.343E-03</td>
</tr>
<tr>
<td>( K_p ) (kg/m3) - 5.00 %</td>
<td>4.337E-03</td>
</tr>
<tr>
<td>( K_p ) (kg/m3) + 5.00 %</td>
<td>4.336E-03</td>
</tr>
<tr>
<td>( k _gsl ) (m3/s/mol) - 5.00 %</td>
<td>4.336E-03</td>
</tr>
<tr>
<td>( k _gsl ) (m3/s/mol) + 5.00 %</td>
<td>4.336E-03</td>
</tr>
<tr>
<td>( c ) (-) - 5.00 %</td>
<td>3.688E-03</td>
</tr>
<tr>
<td>( c ) (+) + 5.00 %</td>
<td>3.362E-03</td>
</tr>
<tr>
<td>( n _gas _max ) (-) - 5.00 %</td>
<td>1.350E-03</td>
</tr>
<tr>
<td>( k _g ) (mol/s/kPa/m2) - 5.00 %</td>
<td>1.451E-04</td>
</tr>
<tr>
<td>( k _g ) (mol/s/kPa/m2) + 5.00 %</td>
<td>1.379E-04</td>
</tr>
<tr>
<td>( T ) (K) - 5.00 %</td>
<td>2.728E-11</td>
</tr>
<tr>
<td>( T ) (K) + 5.00 %</td>
<td>8.303E-12</td>
</tr>
<tr>
<td>( Nn _glass ) (-) - 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( Nn _glass ) (+) + 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( Nn _gas ) (-) + 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( k _be ) (m3/s/mol) - 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( k _be ) (m3/s/mol) + 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( R_{C _be} ) (mol/m3) - 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( R_{C _be} ) (mol/m3) + 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( D_o _gel ) (m2/s) - 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( D_o _gel ) (m2/s) + 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( E_a _gel ) (J/mol) - 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( E_a _gel ) (J/mol) + 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( D_o _be ) (m2/s) - 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( D_o _be ) (m2/s) + 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( E_a _be ) (J/mol) - 5.00 %</td>
<td>0</td>
</tr>
<tr>
<td>( E_a _be ) (J/mol) + 5.00 %</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 5-21: Relative results of sensitivity analysis for a 5% perturbation in the simulation parameters for zinc-treated glass exposed to 15°C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Relative change from base case</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_0$ (kPa) + 5.00%</td>
<td>1.461E-01</td>
</tr>
<tr>
<td>$p_0$ (kPa) - 5.00%</td>
<td>1.164E-01</td>
</tr>
<tr>
<td>$q_m$ (mol/kg) + 5.00%</td>
<td>5.000E-02</td>
</tr>
<tr>
<td>$q_m$ (mol/kg) - 5.00%</td>
<td>5.000E-02</td>
</tr>
<tr>
<td>$c$ (-) - 5.00%</td>
<td>4.027E-03</td>
</tr>
<tr>
<td>$\delta z$ (m) + 5.00%</td>
<td>3.672E-03</td>
</tr>
<tr>
<td>$K_p$ (kg/m3) + 5.00%</td>
<td>4.775E-07</td>
</tr>
<tr>
<td>$\delta z$ (m) - 5.00%</td>
<td>4.775E-07</td>
</tr>
<tr>
<td>$K_e$ (kg/m3) - 5.00%</td>
<td>4.775E-07</td>
</tr>
<tr>
<td>gas $\delta z$ (m) - 5.00%</td>
<td>4.980E-11</td>
</tr>
<tr>
<td>$N_n$ gas (-) - 5.00%</td>
<td>3.826E-11</td>
</tr>
<tr>
<td>$T$ (K) + 5.00%</td>
<td>2.510E-11</td>
</tr>
<tr>
<td>$k_e$ (mol/s/kPa/m²) - 5.00%</td>
<td>7.022E-12</td>
</tr>
<tr>
<td>$\delta t$ (s) - 5.00%</td>
<td>7.022E-12</td>
</tr>
<tr>
<td>$k_e$ (mol/s/kPa/m²) + 5.00%</td>
<td>6.637E-12</td>
</tr>
<tr>
<td>$\delta t$ (s) + 5.00%</td>
<td>6.385E-12</td>
</tr>
<tr>
<td>$T$ (K) - 5.00%</td>
<td>2.635E-12</td>
</tr>
<tr>
<td>$E_a_{gel}$ (J/mol) - 5.00%</td>
<td>2.220E-16</td>
</tr>
<tr>
<td>$N_n$ glass (-) - 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$N_n$ glass (-) + 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$N_n$ gas (-) + 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$k_{gel}$ (m³/s/mol) - 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$k_{gel}$ (m³/s/mol) + 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$k_{bg}$ (m³/s/mol) - 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$k_{bg}$ (m³/s/mol) + 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$R_{c_{gel}}$ (mol/m³) - 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$R_{c_{gel}}$ (mol/m³) + 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$R_{c_{bg}}$ (mol/m³) - 5.00%</td>
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</tr>
<tr>
<td>$R_{c_{bg}}$ (mol/m³) + 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$t_e$ (-) - 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$t_e$ (-) + 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$D_{o_{gel}}$ (m²/s) - 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$D_{o_{gel}}$ (m²/s) + 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$E_{a_{gel}}$ (J/mol) + 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$D_{o_{bg}}$ (m²/s) - 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$D_{o_{bg}}$ (m²/s) + 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$E_{a_{bg}}$ (J/mol) - 5.00%</td>
<td>0</td>
</tr>
<tr>
<td>$E_{a_{bg}}$ (J/mol) + 5.00%</td>
<td>0</td>
</tr>
</tbody>
</table>

For the zinc-treated glass the parameter of most influence relative to the base case is the partial pressure ($p_0$). Again parameters relating to the glass bulk have no effect on the mass uptake.
5.4 Surface Analysis Techniques

In this section results from a range of surface analysis techniques are shown. The aims were to characterise the air side surface of float glass for samples exposed to dry and humid conditions, and to characterise the elemental composition of zinc-treated and untreated float glass using qualitative (PIXE and SIMS) and quantitative techniques (XPS). Only the air side was analysed with these techniques as this is believed to be the side which corrodes the most, Feldmann and Weibmann (1997).

5.4.1 AFM

Figure 5-45 below, shows the surfaces of two float glass sheet samples imaged using the AFM, after exposure to 30% RH and to 90% RH for 12 hours at 20°C in the IGAsorp.

![AFM images after exposure of two float glass sheet samples to 30% and 90% RH at 20°C for 12 hour period in the IGAsorp](image)

Figure 5-45: AFM images after exposure of two float glass sheet samples to 30% and 90% RH at 20°C for a 12 hour period in the IGAsorp

Figure 5-45 shows for the sample exposed to 30% RH the existence of pores with diameters in the range of 4 nm (see pore circled in figure). For the sample previously exposed to 90% RH the sample surface appears to have a more irregular structure compared to the sample previously exposed to 30% RH. This is suspected to be due to the presence of corrosion products.

The AFM was also used to measure the depth of the etched crater after the SIMS analysis. This was carried out by taking a 100 µm×100 µm square image across one of the crater edges. The line analysis tool of the AFM was used to obtain a depth profile across the edge of the crater at various positions to estimate the etched crater
depth \(c_d\). This was done for three different locations represented by individual lines as shown in Figure 5-46. Individual line scans were analysed and their profiles plotted as a function of depth (nm) vs. position (μm), see Figure 5-47, further below.

Figure 5-46; Edge of crater formed by SIMS etching. The spotted SIMS etching region on the right hand side of the image represents the sample with gold coating on the surface. Note the faint vertical line in the middle of the image indicates the edge of the etched crater. The horizontal lines represent the positions taken for the line scan analysis.

Figure 5-47; Line profile for the individual lines corresponding to Figure 5-46. The figure labels a, b and c correspond to the respective labels in Figure 5-46.
An average reading of the data at either side of the edge of the etched crater was calculated as summarised in Table 5-22 below. The large errors in crater depth arise from the surface roughness, and imply significant uncertainty in the speed of etching, see (Equation 4.3) and erosion per unit time (see Equation 4.4, Section 4.3.4). The values of absolute depth in the SIMS depth profile results must therefore be considered as approximate, especially when considering the assumption that the depth is a linear function of etching time. Based on the results in Table 5-22 an etched crater depth of 11 nm was assumed for both batches. Using this value and subtracting the thickness of the gold layer which is estimated to be 5 nm, it is estimated that the glass was etched down to a depth of 6 nm.

Table 5-22: Summary of etched crater depth ($c_d$) measurements

<table>
<thead>
<tr>
<th>Line</th>
<th>Unetched surface</th>
<th>Gold surface</th>
<th>$c_d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Height (nm)</td>
<td>Standard deviation (nm)</td>
<td>Height (nm)</td>
</tr>
<tr>
<td>a</td>
<td>53.78</td>
<td>4.25</td>
<td>42.91</td>
</tr>
<tr>
<td>b</td>
<td>40.38</td>
<td>5.22</td>
<td>29.83</td>
</tr>
<tr>
<td>c</td>
<td>4.45</td>
<td>4.45</td>
<td>5.76</td>
</tr>
</tbody>
</table>

| Batch 1 (untreated) | Batch 2 (zinc-treated) |

<table>
<thead>
<tr>
<th>Line</th>
<th>Unetched surface</th>
<th>Gold surface</th>
<th>$c_d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Height (nm)</td>
<td>Standard deviation (nm)</td>
<td>Height (nm)</td>
</tr>
<tr>
<td>a</td>
<td>41.15</td>
<td>5.24</td>
<td>27.98</td>
</tr>
<tr>
<td>b</td>
<td>47.38</td>
<td>3.72</td>
<td>36.28</td>
</tr>
<tr>
<td>c</td>
<td>33.2</td>
<td>4.23</td>
<td>20.2</td>
</tr>
</tbody>
</table>

Figure 5-48, below, shows a gold (Au) and a silicon (Si) depth profile measured by ToF-SIMS for an untreated float glass sample etched for a total time of 500 s. Two regions are identified in this figure corresponding to the gold layer and the glass sample. The point at which these two profiles cross (88 s), is considered to be the end of the gold layer etching. Therefore, it is now known that the total etching time ($t_i$) of the glass took 412 s. Using this value in Equation (4.3) and a value of 6 nm
corresponding to the etched crater depth \( (c_d) \) for the glass, the sputtering rate \( (S_R) \) was calculated to be \( 0.015 \text{ nm s}^{-1} \).

Figure 5-48; Depth profile of gold (Au) and silicon (Si) for an untreated sample etched for 500 s. It can be seen that both depth profiles cross each other at around 88 time units, this value was taken to be the point at which the glass starts being etched

5.4.2 Ion Beam Analysis

Three samples were used for the ion beam analysis; one untreated and two treated with 100 ppm and 130 ppm of zinc nitrate. The latter sample was treated by Pilkington. PIXE together with RBS (see Chapter 4, Section 4.3.2) was used to investigate the elements present in the float glass composition and furthermore to verify that zinc had effectively deposited on the sample which was treated in the laboratory. Figure 5-49 below shows the spectra for the air side of a float glass sample; the elements detected are included. No concentrations are given because of a fault with the software.
The results of surface elemental composition are shown in Figure 5-50 for the untreated float glass, for the glass treated with 100 ppm of zinc in solution (in the laboratory), and for the sample treated by Pilkington with 130 ppm of zinc in solution.

The ion beam analysis results show that traces of zinc are present in the industrially treated sample but not in the sample treated in the laboratory. The apparent absence of zinc in the laboratory-treated sample will be discussed in Chapter 6. The elements detected in the order shown in the Figure 5-50, above are: aluminium, calcium,
Results

chlorine, copper, iron, potassium, manganese, phosphorous, sulphur, silicon, tin, titanium and zinc. The detection of tin on the air side of float glass is in accordance with what is found in literature, see Sieger (1975). It is believed that the presence of some elements arises from impurities because these are not present in the nominal float glass composition. These include elements such as copper, manganese and phosphorous.

Because zinc was not detected on the sample treated in the laboratory using the ion beam analysis this experiment was not repeated. Therefore other surface analysis techniques such as XPS and SIMS were used. These results are described next.

5.4.3 XPS

Five float glass samples including zinc-treated and untreated samples in both powder and sheet form were analysed with XPS, in order to measure the concentration of zinc deposited from solution at the glass surface. The zinc-treated samples included one treated in the laboratory with 100 ppm zinc and one treated by Pilkington with 130 ppm of zinc. The XPS technique was described in detail in Section 4.3.3 and the experimental procedure for zinc treating the samples was presented in Section 4.2.1 in Chapter 4. Figure 5-51 below represents an XPS survey spectrum of the air side of float glass for an untreated sheet sample.

![Graph of XPS survey spectrum](image)

Figure 5-51; XPS survey spectrum of the air side of an untreated float glass sheet sample
The concentration of the elements shown in Figure 5-51 are summarised in Table 5-23, below. For the zinc-treated float glass samples, the concentration of this element is also shown.

Table 5-23; XPS results for zinc-treated and untreated float glass sheet and crushed float glass samples with a particle size < 90 μm.

<table>
<thead>
<tr>
<th>Name</th>
<th>Untreated sheet sample</th>
<th>Zinc-treated sheet sample</th>
<th>Industrially zinc-treated sample</th>
<th>Batch 1 (untreated) crushed glass</th>
<th>Batch 2 (zinc-treated) crushed glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cls</td>
<td>36.1</td>
<td>20.95</td>
<td>28.44</td>
<td>9.32</td>
<td>8.38</td>
</tr>
<tr>
<td>Ca2p</td>
<td>1.54</td>
<td>1.27</td>
<td>1.01</td>
<td>2.16</td>
<td>1.81</td>
</tr>
<tr>
<td>Cu2p3</td>
<td>0.09</td>
<td>0.03</td>
<td>0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mgls</td>
<td>0.43</td>
<td>0.74</td>
<td>0.35</td>
<td>2.14</td>
<td>2.25</td>
</tr>
<tr>
<td>Nals</td>
<td>4.49</td>
<td>5.48</td>
<td>6</td>
<td>12.27</td>
<td>8.88</td>
</tr>
<tr>
<td>Ols</td>
<td>41.94</td>
<td>50.22</td>
<td>46.54</td>
<td>57.89</td>
<td>56.17</td>
</tr>
<tr>
<td>Si2p</td>
<td>15.02</td>
<td>16.87</td>
<td>12.79</td>
<td>16.22</td>
<td>15.49</td>
</tr>
<tr>
<td>Sn3d5</td>
<td>0.38</td>
<td>0.65</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn2p3</td>
<td>3.78</td>
<td>3.39</td>
<td>7.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1s</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr2p3</td>
<td>0.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that 0.1 atom % = 1000 ppm.

XPS results are influenced by carbon impurities at the surface and this affects the values of the atom% measured (Holmes 2009, Castle 2008). For the crushed float glass, the sodium amount present is almost 3 times higher than the value measured on the glass sheet for the same element. This may be because crushing the glass exposes fresh surface which is likely to have higher sodium content than an older surface due to ion-exchange at the glass surface.

Tin and copper were not detected in the crushed glass samples and nitrogen and chromium were only detected in the sample which had been treated in industry. These elements can be considered as impurities.
5.4.4 SIMS

The samples used for the SIMS analysis are summarised in Table 5-24 below. Note that only the air side of sheet float glass samples was analysed, because this is believed to be the side which corrodes the most, Feldmann and Weibmann (2007).

Table 5-24: Summary of sheet float glass samples, used in the SIMS analysis.

<table>
<thead>
<tr>
<th>Description</th>
<th>Analysis date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated float glass sample stored at dry conditions</td>
<td>April 2008</td>
</tr>
<tr>
<td>Zinc-treated float glass sample stored at dry conditions</td>
<td>April 2008</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Description</th>
<th>Analysis date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated float glass sample stored at dry conditions</td>
<td>December 2008</td>
</tr>
<tr>
<td>Zinc-treated float glass stored at dry conditions.</td>
<td>December 2008</td>
</tr>
<tr>
<td>Untreated float glass sample stored at saturated conditions.</td>
<td>December 2008</td>
</tr>
<tr>
<td>Zinc-treated float glass samples stored at saturated conditions.</td>
<td>December 2008</td>
</tr>
</tbody>
</table>

The samples from Set 1 were coated with a gold layer of 5 nm thickness with a quartz oscillator, in an attempt to assist the location of the etched region after analysis. This was considered unnecessary in subsequent tests. The samples that are described as ‘untreated’, are samples which were analysed as-received, whereas ‘zinc-treated’ refer to samples to which zinc was applied. Saturated conditions refer to samples that were placed in an open Petri dish, inside a desiccator filled with de-ionised water for a two week period in order to replicate a corrosive environment.

Figure 5-52 below shows a SIMS surface scan for an untreated float glass sample from Set 2 stored at dry conditions. Note that only sodium, silicon and calcium are shown because these are the most abundant elements in the float glass composition as shown in Chapter 4, Table 4-1. A similar scan could not be obtained for the Set 1 samples due to the gold coating on the glass surface.
Figure 5-52; ToF-SIMS surface scan for an untreated sample from Set 2 stored at dry conditions

**Depth Profiling**

ToF-SIMS was used to determine the depth-concentration profiles of the main three elements in the float glass composition. The concentration scale, formerly shown in Figure 5-48 as number of counts was quantified to give atom%. These values were obtained by setting the bulk glass signals to the bulk concentration values which were measured by XRF (Staunton 2007), see Table 4-1 in Chapter 4. The conversion of number of counts to atom% was also performed by Fearn et al. (2004), see Figure 2-10 in Chapter 2. Table 5-23 (reproduction of Table 4-1) is a summary of the wt% and atom% concentrations for silicon, sodium and calcium. Elements with a lower bulk concentration in float glass than calcium are not included in Table 5-23. For the zinc-treated float glass samples, the zinc concentration measured by XPS (see Table 5-21) was used, i.e. the zinc signal was normalised to a value of 3.78 atom%.

To convert wt% into atom% a conversion factor \( f_{Si} \) was first obtained for the silicon, using Equation (5.7) below.

\[
 f_{Si} = \frac{m_{wSi}}{m_{wSi} + 2m_{wO}} \tag{5.7}
\]
Here $f_{Si}$ is the correction factor for silicon (-), $mw$ is the molecular weight in (g mol$^{-1}$) and the subscript $Si$ and $O$ correspond to silicon and oxygen respectively.

The concentration of silicon in atom% ($atom\%_{Si}$) is obtained by multiplying $f_{Si}$ by the wt% concentration of SiO$_2$ ($wt\%_{SiO_2}$) as shown in Equation (5.8) below. Equation (5.7) and Equation (5.8) were repeated for the sodium and calcium cations. The atom% results are summarised in Table 5-25 below.

$$atom\%_{Si} = wt\%_{SiO_2} f_{Si}$$ \hspace{1cm} (5.8)

<table>
<thead>
<tr>
<th>Compound</th>
<th>wt%</th>
<th>Cation atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>71.8</td>
<td>33.51</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>13.5</td>
<td>10.02</td>
</tr>
<tr>
<td>CaO</td>
<td>8.59</td>
<td>6.14</td>
</tr>
</tbody>
</table>

The atom% values listed in Table 5-25 were then used in Equation (5.9) to express the atom% value with erosion depth ($atom\%_{depth}$).

$$atom\%_{depth} = atom\%_{Si} \frac{counts}{bulksignal}$$ \hspace{1cm} (5.9)

The time scale originally shown in Figure 5-48 has been converted to erosion depth ($d_e$), calculated at each time step with Equation 4.6 (see Chapter 4) using a sputtering rate ($S_A$) for the glass of 0.015 nm s$^{-1}$. See Section 5.4.1 for more details on this calculation.

The data corresponding to the Set 1 samples will be presented first followed by the data for the Set 2 samples.

**Set I**

Samples from Set 1 had a 2 nm gold layer applied to the glass surface; hence for the depth profile analysis the data in this range were ignored. This approach was also
Results

adopted by Lombardo et al. (2005). The SIMS intensity signal is shown on a log scale of atom% as a function of erosion depth \(d_e\) in Figure 5-53 and Figure 5-54 below, for the untreated and zinc-treated float glass samples respectively.

Figure 5-53 below, shows the concentration depth profiles of silicon (Si), sodium (Na) and calcium (Ca) as a function of erosion depth for an untreated float glass sample. No zinc was detected by XPS or SIMS for this sample. Note that in this figure the silicon concentration is higher than 100%; this line was produced by normalising the SIMS data using Equation (5.9). The abnormal increase in this value should be interpreted as an experimental artefact and the data before a 4 nm depth should therefore be ignored. An initial surface depletion of sodium and calcium was also measured. The sodium depletion has been explained in literature to be due to the removal of corrosion products from the glass surface, (Fearn et al. 2004), or due to surface artefacts (Lacharme and Léhuéde 1985).

---

Figure 5-53; ToF-SIMS concentration depth profile for an untreated float glass sample, for the silicon, sodium and calcium elements. The sample was analysed after storage for a 6 month period at dry conditions

Two individual regions are identified in Figure 5-53 below. In Region 1 a depletion of the silicon and sodium elements was measured near the surface. Region 2 in the same figure shows flat constant concentration values, meaning that the bulk glass
composition has been reached. This figure shows the silicon concentration to decrease rapidly down to an approximate depth of 10 nm. Fearn et al. (2004) observed a similar phenomenon which they describe as a ‘concentration effect’. This relates to the systematic increase in silicon concentration as a consequence of sodium leaching from the surface. Note that the calcium concentration appears to reach its bulk concentration value at approximately 4 nm.

Figure 5-54 below, shows the concentration depth profiles for a zinc-treated float glass sample. A similar concentration effect is measured for this sample. The zinc profile in this figure is higher near the surface and decreases steadily until a constant concentration value is measured. This may suggest that zinc has diffused inside the glass however the fluctuations in the signal suggest that the trace is background noise that has been amplified by the normalisation.

Figure 5-54: ToF-SIMS concentration depth profile for a zinc-treated float glass sample, for silicon, sodium and calcium. The zinc depth profile is also shown, the concentration value of zinc was based on the XPS data, shown in Table 5-23. The sample was analysed after storage for a 6 month period at dry conditions.
Set 2
Next the results from Set 2 samples are shown. These differ from samples in Set 1 because no gold layer was applied to their surfaces thereby enabling a full characterisation of the glass surface.

The initial sodium depletion has been considered to be a measure of how much the glass has corroded, (Fearn et al. 2004). Therefore in Figure 5-55 and Figure 5-56 only the sodium concentration depth profiles are shown. Two untreated, and two zinc-treated samples were used, one of each had been stored under dry conditions, and the remaining two samples stored at saturated conditions for a two week period. Figure 5-55 and Figure 5-56 show the sodium concentration depth profiles for untreated and zinc-treated float glass samples respectively.

Figure 5-55 below, shows a sodium depletion extending down to 5 nm for the sample exposed to dry conditions. Whereas, for the sample exposed to saturated conditions a sodium depletion is measured down to approximately 8 nm. This higher value could be due to an increase in water availability to the sample surface, resulting in more sodium leaching out from the glass.

Figure 5-55; Sodium concentration depth profile for untreated float glass samples stored at dry and saturated conditions for a two week period

Figure 5-56 below, shows a similar shape of the depth profiles for the zinc-treated samples exposed to dry and saturated conditions for a two week period. Note that for
the sample exposed to saturated conditions the surface sodium concentration is higher. Presumably this represents a surface accumulation of the sodium that has diffused from the bulk. The similarity of the two profiles in Figure 5-56 compared to those in Figure 5-55 is further evidence of the corrosion protection effect of zinc treatment.

Figure 5-56; Sodium concentration depth profile for zinc-treated float glass samples stored at dry and saturated conditions for a two week period

Figure 5-57 below, shows the zinc depth profile for the same samples shown in Figure 5-56. It can be seen from this figure, that the zinc is present in a very thin surface layer. The difference between the two samples is attributed to sample and treatment variation and is not thought to be a consequence of the different storage conditions.
The use of a CA numerical procedure for simulating glass corrosion was also demonstrated.

In this chapter the extent of corrosion for untreated and zinc-treated float glass samples was measured by a number of techniques. These included: gravimetric analysis and surface analysis techniques, i.e. ion beam analysis, XPS, and SIMS. The use of a CA numerical procedure for simulating glass corrosion was also demonstrated.

In Section 5.2 the gravimetric corrosion measurements of float glass were presented. The kinetics of corrosion for untreated and zinc-treated float glass samples were quantified at various environmental conditions. It is clear from the gravimetric data that zinc treatment results in a profound reduction in the extent of water adsorption and also reduces the rate of corrosion as indicated by the reduction in corrosion flux. Temperature was shown to increase the rate of corrosion for both untreated and zinc-treated samples.

Water sorption isotherms were analysed using the BET theory. The calculated BET parameters included the specific surface area ($S$), monolayer uptake ($x_m$) and the BET
constant ($c$) for both adsorption and desorption isotherms. The float glass nominal particle diameter ($d_{\text{particle}}$) was also calculated from the adsorption isotherm and the energy of adsorption in the first layer ($E_1$) was also calculated, based on the desorption isotherms.

An anomalous behaviour was observed specifically for zinc-treated samples, in that a systematic decrease in mass occurred during adsorption for a relative humidity of between 30% and 40% RH.

The reproducibility of the gravimetric experiments was examined and found to be acceptable. However, an ageing effect has been identified for samples that have undergone zinc treatment. It appears that the effect of the zinc treatment wears off with storage time.

The results for the model solved by CA agree well with the gravimetric analysis data of water uptake, confirming that this solution technique has great potential for modelling glass corrosion. A sensitivity analysis revealed that the CA model was mostly influenced by parameters relating to the gas phase and surface reaction. The model was insensitive to parameters relating to the bulk glass phase, including diffusivity.

SIMS analysis showed sodium concentration depth profiles on float glass to be dependent on the exposure conditions of the samples. Furthermore, the application of zinc-treatment to the float glass surface proved to have a strong effect on the depth profile of sodium. The untreated sample showed a significantly larger depletion of sodium compared to the zinc-treated sample.

Ion beam analysis only detected zinc traces in the industrially treated sample but not in the sample treated in the laboratory. XPS measurements on glass demonstrated the concentration of zinc deposited at the glass surface.

In the next chapter the results presented here will be discussed in terms of the Batch 1 (untreated) samples and the Batch 2 (zinc-treated) samples. This will be followed by a discussion of the simulation model.
6 DISCUSSION

In this chapter the results shown in the previous chapter will be discussed in the context of the reported findings from the published literature. Gravimetric results for Batch 1 (untreated) will be discussed first, followed by the discussion for Batch 2 (zinc-treated) float glass samples. This chapter will conclude with a discussion on the simulation of glass corrosion.

6.1 Water Adsorption Experiments

6.1.1 Effect of Relative Humidity

The experimental gravimetric results for Batch 1 (untreated) samples showed a mass increase with time and %RH. The fractional mass uptake proved to be more significant at 70% RH, see Figure 5-1. The value of the fractional mass uptake accounts for adsorbed water only; no corrosion products are expected to have formed on the glass during the experiments as the dry air supplied to the IGAsorp contains no detectable CO₂ or SO₂, therefore these will not contribute to the mass uptake. A %RH dependency on the amount adsorbed was also measured by Collins et al. (2005) after silica exposure to humidities ranging from 11% to 85% RH at 22°C. Figure 6-1 below illustrates the work of Collins et al. simultaneously with the superimposed mass uptake for a Batch 1 sample exposed to 20°C and RH values of 30%, 50% and 70%. This is Figure 5-1 reproduced, using units of μmol m⁻² for the water uptake as a function of time in hours. The present data have been converted to a flux using the mean specific surface area of 0.7 m² g⁻¹ to enable a direct comparison with the data of Collins et al. (2005). The dotted lines in the figure correspond to the number of adsorbed molecular layers of water on silica, according to Collins et al. Note that in general the present work shows significantly higher water uptake per unit area compared to the published data. This will be discussed further below.
Figure 6-1 Adsorption curves for crushed float glass (current work) of particle size < 90 µm at 20°C and 30%, 50% and 70% RH (these data were previously shown in Figure 5-1) and silica at 11% (a), 33% (b), 43% (c), 51% (d), 75% (e) and 85% (f) RH, all at a temperature of 22°C. The dashed horizontal lines correspond to one, two and three times, etc. the monolayer concentration of 7.68 µmol m⁻² as estimated by Collins et al. (2005) from the stable region of (c) and (d).

Collins et al. (2005) used a porous sample (mean pore size of 10 nm) with a very high specific surface area (313-324 m² g⁻¹). The porosity may well cause additional complexity to the adsorption and diffusion behaviour and therefore large discrepancies with the present work are not surprising. Furthermore, no sodium is present in the silica samples used by Collins et al. (2005) therefore no ion-exchange is thought to have occurred in the sample, only adsorption and diffusion.

From the isotherm for a float glass sample exposed to 20°C, (see Figure 5-13) the monolayer uptake value was calculated for the %RH range from 10% until 30% using the BET model. Cross-referencing the monolayer value i.e. 16 µmol m⁻² (see Table 5-6) to the desorption isotherm shows monolayer coverage is achieved at approximately 25% RH. The reason for choosing the desorption isotherm will be discussed later in Section 6.1.3. Collins et al. (2005) suggest from their adsorption
results on silica (see Figure 6-1) that monolayer formation occurs at 43% RH and 51% RH with a value of 7.68 μmol m$^{-2}$.

Apart from the lack of sodium in the samples used by Collins et al. (2005) another difference between the gravimetric data in this dissertation and their data is the experimental method. Collins et al. stored silica samples in a polymethylmethacrylate box with an appropriate salt solution to establish the required %RH conditions of the air inside the box. The samples were then weighed periodically over approximately a 3 month period. In the current dissertation a gravimetric technique was also used. However, this allowed measurement of the mass adsorbed on average for every 3 minutes over the duration of the experiment, providing many more data points for the mass uptake compared to the data of Collins et al. For example Figure 6-1 shows over 100 minutes Collins et al. only collected 5 data points. The fact that Collins et al. (2005) had to remove their samples from the environment for weighing will also have introduced errors. Furthermore Collins et al. submitted the silica samples to 140°C for 12 to 24 hours before the start of the experiment and left the samples to cool down prior to analysis. The use of a high temperature is known to cause the sample surface to dehydroxylate, making the surface more hydrophobic and therefore inhibiting water adsorption, Naono et al. (1980). Given the differences between the present work and that of Collins et al. (2005) it is hardly surprising that they observe lower amounts of adsorbed water.

The %RH dependency on the mass adsorbed in the current dissertation has also been studied by the use of isotherms. These were shown in Figure 5-12, 5-13 and Figure 5-14 in Section 5.2.4. In these figures the hysteresis observed indicates that at each point equilibrium is not achieved. When considering the adsorption isotherms, physisorption, chemisorption (hydroxylation) and corrosion on the sample are believed to be occurring simultaneously, because the glass samples do not have previous treatment to ensure that chemisorption is complete prior to the start of the experiment. This will be further discussed in Section 6.1.3.
Furthermore the BET analysis on isotherms will be significantly in error. However the method is applicable in this instance for the purpose of comparison between the various experimental conditions.

The effect of %RH was also studied in this work using SIMS, after exposing untreated samples to dry and saturated conditions for a two week period, see (Figure 5-55). For the sample exposed to saturated conditions the concentration of sodium leached extends down to an approximate depth of 8 nm. This is 1.6 times deeper than the sodium depletion depth for the sample stored at dry conditions (i.e. 5 nm), suggesting an increase in sodium depletion with increasing %RH. Fearn et al. (2004) also studied the extent of Na depletion in antique museum glass. The authors aged the samples by placing these in environmental chambers at known humidities and room temperature for a 91 hour period. The exposure conditions chosen by Fearn et al. were: dry conditions (analysed 1 day after it was produced), 37% RH and, 55% RH (see Figure 2-10 in Chapter 2). The sodium concentration depth profile reported in the work of Fearn et al. also showed an increase in sodium depletion with increasing %RH down to a greater depth than the values measured in this dissertation for float glass. For instance, for a sample at dry conditions, Fearn et al. measured the sodium concentration to be depleted down to a depth of 22 nm, and for a sample exposed to 55% RH down to 85 nm. These values are significantly larger than the measured depleted depth for the untreated float glass samples exposed to dry and saturated conditions (see Figure 5-55). This is believed to be due to a difference in glass sample composition as shown in Table 6-1 below.
Table 6-1 shows the sodium oxide concentration in the replica glass to be 1.33 times the amount measured in float glass. According to Davison (2003) the higher the amount of alkali in glass, the more prone it is to diffusion from the glass. Therefore, it would be expected that the antique glass would exhibit a greater extent of sodium depletion.

The mass proportion of calcium to sodium oxide for float glass is 0.636 (see Table 6-1). This is 5.3 times lower the proportion for the replica antique glass used by Fearn et al. (2004). According to Davison (2003) this implies that float glass is more stable. The addition of sodium and calcium oxides to the basic glass structure makes the glass network less interconnected, and non-bridging oxygen ions (oxygen atoms bound to only one silicon atom, Jiang 2002) are created resulting in regions of unbalanced negativity. The presence of unbalanced regions in the glass provides paths or percolation channels for ionic diffusion as shown in Figure 2-3 see Chapter 2 (Greaves 1985). Furthermore, experimental results on soda-lime-silica glasses in literature have shown the addition of calcium oxide (lime) in concentrations of up to 10 mol% enhances the glass durability. However, the addition of lime to a
concentration higher than 15 mol% is considered to have a damaging effect (Paul 1982). The float glass used in this work had a lime concentration of 9.1 mol% which is close to the reported value for optimum durability.

### 6.1.2 Corrosion Kinetics

An increase in the fractional mass uptake at 70% RH was measured with increasing temperature for Batch 1 (untreated) samples, see Figure 5-3. For the sample loaded into the IGAsorp chamber at 30°C, an initial mass decrease was measured, see Figure 5-7. This is believed to be caused by an increase in the sample temperature from ambient to 30°C which promoted desorption of loosely bound water. The opposite effect seems to have occurred for the sample exposed to 15°C; placing the sample into a temperature lower than the ambient storage temperature of 20°C is expected to promote adsorption on the sample. Once the initial temperature transient has passed, a clear trend of corrosion rate increase with temperature is apparent from Figure 5-3.

The effect of temperature on float glass corrosion was determined from the gravimetric experimental data using reaction parameters. These were determined by plotting the logarithm of the fractional mass uptake as a function of the logarithm of time, for Batch 1 samples. Sections of linearity were identified by eye. Values of corrosion constant ($k_c$) and time index parameter ($\alpha$) (see Equation 5.1) were obtained from the equations of the fitted lines as shown in Figure 5-8. The reaction parameters were then summarised in Table 5-2.

The time index value was reported in literature to be proportional to the square root of time at short time-scales (up to 100 minutes) and low temperatures. At long times of exposure ($t > 2000$ min) and high temperatures a linear time dependency prevailed, (Douglas and El-Shamy 1967). These observations related to aqueous corrosion. However because weathering and aqueous corrosion share the same corrosion mechanism (Schmitz et al. 1995), it is interesting to compare the values obtained in the present work with those previously published.
The time index parameter ($\alpha$) was measured, for untreated float glass samples exposed to 15°C, 20°C and 30°C (see Figure 5-8 and Table 5-2). The mean $\alpha$ value increased with temperature (see Figure 5-10). It appears from the variation in the time index parameter values that the corrosion mechanisms occurring in float glass are not constant with time. This could mean that structural changes are occurring over time, as also suggested by Douglas and El-Shamy (1967). Time indices of 0.5 within 11% were measured at 20°C for the time interval 2.70 until 3.63 log minute, and at 30°C for the time interval 3.05 until 3.20 log minute for the Batch 1 (untreated) float glass samples. A time index value approaching unity, within 29.8%, was measured for the untreated sample exposed to 30°C for the time interval 2.92 - 3.03 log minute, see Table 5-2. The square root of time dependency has been suggested in literature to be caused by a diffusion barrier at the glass surface increasing in depth with time, (Douglas and El-Shamy 1967). For linear time dependency this was suggested to be due to diffusion occurring through a layer of constant thickness, (Douglas and El-Shamy 1967).

The corrosion constant ($k_r$) was also measured for untreated float glass samples exposed to 15°C, 20°C and 30°C, (see Figure 5-8 and Table 5-2). A clear trend of the mean $k_r$ value decreasing with temperature is apparent from Figure 5-11. The corrosion constant values for these samples varied as a function of time and temperature as shown in Table 5-2. For float glass samples exposed to 15°C and 20°C, the $k_r$ values appear to decrease with time and with increasing temperature. The apparent decrease of the reaction constant values with time e.g. for a sample exposed to 15°C could be due to the development of protective silica-rich layer in accordance with the behaviour of a Type 2 surface as classified by Hench et al. (1980), Section 2.5.2.

The corrosion constant value ($k_r$) obtained at 70% RH and 30°C was 24 ± 10 µg m⁻² min⁻¹ (for $\alpha = 0.45 ± 9.15 \times 10^{-3}$, see Table 5-9). The $k_r$ value was converted to units of mol Na m⁻² min⁻¹ so that a comparison could be made with the work of Douglas and El-Shamy (1967). The reaction constant in these units is given the notation $k_{Na}$, see Table 6-2 below. Douglas and El-Shamy (1967) measured the corrosion constant for sodium released in solution to be 0.064 mg Na₂O g⁻¹ glass min⁻¹ for $\alpha = 0.513$. This value was also converted to units of mol Na m⁻² min⁻¹ by assuming a specific surface
area of $1.63 \times 10^{-3} \text{ m}^2 \text{ g}^{-1}$, taken from a similar study by Rana and Douglas (1961). The results are summarised in Table 6-2 below. In this table the time index constant ($\alpha$) and the corresponding time interval is shown. As a matter of interest the amount of alkali extracted ($Q'$) is also shown. This was calculated using Equation (6.1), (Equation 5.1 adapted).

Table 6-2; Summary of reaction parameters for a sodium silicate glass (Douglas and El-Shamy 1967) and untreated float glass (current work)

<table>
<thead>
<tr>
<th>Glass</th>
<th>$k_{Na,r}$ (mol Na m$^{-2}$ min$^{-a}$)</th>
<th>Time index $\alpha$ (-)</th>
<th>Time interval (min)</th>
<th>$Q'$ (mol Na m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 Na$_2$O-85SiO$_2$</td>
<td>$1.71 \times 10^{-3}$</td>
<td>0.513</td>
<td>25 - 300</td>
<td>$3.05 \times 10^{-2}$</td>
</tr>
<tr>
<td>Float glass (untreated)</td>
<td>$1.13 \times 10^{-6}$</td>
<td>0.46</td>
<td>4175 - 5802</td>
<td>$3.39 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

$Q = k_{Na,r} t^a$  

(6.1)

The corrosion constant ($k_{Na,r}$) measured by Douglas and El-Shamy (1967) for the time interval 25 until 300 minutes appears to be 1000 times higher compared to the value for the float glass sample which had been exposed to 30°C and 70% RH for the time interval 4175 until 5802 minutes (see Table 6-2). The dissimilarity of the corrosion constant value between the current data and that of Douglas and El-Shamy (1967) could be due to the different glass composition and experimental method used. These arguments are discussed below.

Douglas and El-Shamy (1967) studied aqueous corrosion, and replenished the leached solution frequently in order to ensure minimum glass composition changes caused by varying pH values. The availability of bulk water at the surface and the continual removal of leached sodium from the surface are thought to account for their high value of the corrosion constant. In the present work the leached sodium ions accumulate in the surface layer. There is no carbon dioxide or sulphur dioxide present in the gas stream and so no corrosion products form. The increasing concentration of sodium ions in the adsorbed water film may therefore have a retarding effect on the ion exchange – diffusion process. In addition, it is suspected that the float glass samples used in the present work are representative of a Type 2 surface (see Figure 2-6 in Chapter 2), as discussed above. This implies that selective leaching of alkali
occurs, leaving a silica-rich layer that causes the diffusion of ions to slow down for layers of thickness below 1 μm, (Hench 1982).

Douglas and El-Shamy (1967) used a sodium silicate glass. This glass is by nature of low durability because no lime is present in its composition, Clark et al. (1979). Furthermore, binary alkali-silicate glasses (like sodium silicate) have been suggested in literature to correspond to a Type 4 glass surface Hench et al. (1980). According to the authors this glass type does not have a high enough silica concentration to protect the glass from rapid dealkalization and network dissolution. According to El-Shamy (1973) glass is durable for a SiO₂ concentration exceeding 66.67 mol%. However, the sodium silicate glass used by Douglas and El-Shamy had a silica concentration of 85.4 mol% implying that the glass should therefore be durable. Nevertheless, the absence of calcium ions in the composition of the sodium silicate glass is very likely to be a contributor to the high value of the corrosion constant obtained.

6.1.3 Isotherms

In this work the water uptake as a function of %RH was measured for the range 0 - 70% RH, for crushed float glass Batch 1 (untreated) samples. The shape of the isotherms for Batch 1 samples are similar at the temperatures studied and appear to agree well with the BET theory, as shown in the BET plots see Figure 5-15, 5-16 and Figure 5-17.

Hysteresis in the isotherms is observed for Batch 1 samples, as seen from the value of the fractional mass uptake (µg g⁻¹) at 0% RH (Figure 5-12, 5-13 and Figure 5-14). This shows that some moisture remains adsorbed on the samples of crushed glass, suggesting that irreversible chemisorption has occurred on the sample. Chemisorption at the glass surface during the gravimetric experiments could have been possibly prevented by immersing the crushed float glass samples in water, for a length of time prior to the isotherm experiment. This would result in the activation of the first stage
Discussion

of corrosion *i.e.* the ion-exchange and simultaneously the hydroxylation of the glass. If the samples were then submitted to a given temperature and %RH the adsorption would occur by physisorption only because the surface is now said to be hydroxylated. Once sufficient adsorbed water is present on the surface, the ion exchange mechanism can begin. This would be an interesting study for future work.

However, the hysteresis could potentially be due to the presence of pores at the glass surface promoting capillary condensation. Quantification of these pores was attempted by N₂ adsorption. The results were inconclusive due to the very low pore volumes and the slow dehydroxylation of glass under vacuum which gave an apparent decrease in mass with increasing nitrogen pressure. For these reasons the approach was abandoned. Figure 5-45 shows the existence of a pore (circled in figure) which proved to be 4 nm in diameter on the surface of a float glass sample exposed to 30% RH prior to imaging. Pores are expected to form in the surface of glass during corrosion due to the ion exchange mechanism occurring in channels (Greaves 1985, see Figure 2-3 in Chapter 2).

The use of the BET model is questioned for water sorption isotherms as it assumes normal molecular packing. This assumption might not be correct, as the packing of water molecules on a glass surface is dependent on the position of the silanol groups. Further evidence of this is provided for example by Young (1958), who commented that water is believed to adsorb at the glass surface by cluster formation. Also according to Young, the measured specific surface area of silica by water sorption tends to be ¼ to an ⅛ smaller than if nitrogen is used. He attributed the difference in the values of surface area between measurements by water and nitrogen to be due to portions of the silica surface being hydrophobic.

The water uptake by float glass during the adsorption isotherm was expressed in terms of number of molecular layer \((n')\) and layer thickness \((l_l)\) in Figure 5-21. These results were compared with the data from Hagymassy *et al.* (1969). The latter authors measured adsorbed water on quartz at 25°C with a silica spring balance. They calculated the number of monolayers adsorbed by dividing the volume adsorbed by
the monolayer volume \( i.e. \frac{V}{V_m} \). The results for both float glass and quartz are shown in Figure 6-2 below.

![Figure 6-2 Number of molecular layers for a quartz sample exposed to 25°C, (Hagymassy et al. 1969) and for a Batch 1 (untreated) float glass sample with a particle size < 90 μm](image)

Figure 6-2 shows that the quartz sample adsorbs more water compared to float glass. However the difference between the two is marginal when considering that the water uptake is strongly dependent on the level of hydrophobicity, (Muster et al. 2001). It is well established that this depends upon the surface concentration of silanol (\( \equiv \text{Si–OH} \)) groups, Zhuravlev (1987). This in turn depends upon the exposure of the sample to high temperature (removal of silanol groups) or to water (formation of silanol groups).

At 50% RH it appears that the number of monolayers adsorbed on quartz and float glass is very similar (see Figure 6-2). The number of monolayers measured at this humidity is only 1.09 times higher compared to float glass, presumably because at this humidity the float glass surface has the same amount of silanol groups as the quartz sample. Furthermore, BET isotherms on quartz by Hagymassy et al. (1969) showed the BET constant to be 23; this is approximately 2.6 times higher the value at 30°C measured for float glass (see Table 5-6). From Equation 5.5 it appears that the \( c \) value obtained by Hagymassy et al. corresponds to a higher value of \( E_i \) i.e. 51575 J mol\(^{-1}\).
compared to the untreated float glass sample exposed to 30°C i.e. 43058 J mol⁻¹, see Table 5-8.

6.2 Zinc Treatment

In this dissertation crushed float glass samples with a specific surface area of 0.7 m² g⁻¹ were immersed in a zinc nitrate solution containing 100 ppm of zinc (0.00153 mol l⁻¹) at 60°C. The zinc concentration deposited on the crushed float glass samples was 7 atom% as suggested by the XPS results, see Table 5-23. In this section the effectiveness of the zinc treatment will be assessed by comparison of the results between the Batch 2 (zinc-treated) and the Batch 1 (untreated) float glass samples.

6.2.1 Zinc Mechanism

The limited amount of published evidence on the effectiveness of zinc points to a mechanism of zinc ion adsorption at the silanol groups, (Tait and Jensen 1982). Equation (6.2) (reproduced from Equation 2.29) below describes the proposed reaction mechanism of zinc ions on silica in which a hydrogen ion is released from the silanol group and is replaced by a zinc hydroxide species, Phan et al. (2004).

$$\equiv Si-OH + Zn^{2+} + H_2O \leftrightarrow Si-O^- (ZnOH)^+ + 2H^+$$  

(6.2)

Tait and Jensen (1982) propose that zinc protection operates by the adsorbed zinc ions blocking the silica lattice interstices thus inhibiting the ion-diffusion process. It can therefore be considered that zinc ions create a protective barrier. In addition, the substitution of the silanol groups for zinc ions is likely to render the surface more hydrophobic, as suggested by the lower water uptake for the zinc treated samples in Figures 5-12, 5-13 and 5-14. The decrease in water adsorption is therefore considered to be a contributing mechanism to the overall effectiveness of zinc treatment.

To check if the zinc-treated samples adsorb moisture similarly to silica (because no sodium is present) the float glass results for samples exposed to 20°C and to 50% and 70% RH were compared with the results of Collins et al. (2005). These are shown in Figure 6-3, below.
Figure 6-3: Adsorption curves for zinc-treated crushed float glass samples with a particle size < 90 \mu m (current work) at 20°C and 30%, 50% and 70% RH (these data were previously shown in Figure 5-2), and silica at 11% (a), 33% (b), 43% (c), 51% (d), 75% (e) and 85% (f) RH all at a temperature of 22°C. The dashed horizontal lines correspond to one, two and three times, etc., the monolayer concentration of 7.68 \mu mol m^{-2} as estimated by Collins et al. (2005) from the stable region of (c) and (d).

From Figure 6-3 clear differences in the mass uptake curves are observed between the zinc-treated float glass samples from the current work and the results by Collins et al. (2005), for a silica sample. The zinc-treated surfaces exhibit a higher water mass uptake compared to silica presumably because the sodium in the float glass samples is still able to go through a certain degree of ion-exchange in spite of the zinc treatment. Note also that Collins et al. had heat-treated their silica samples prior to adsorption. This is known to dehydroxylate the surface, rendering it more hydrophobic, as discussed in section 6.1.1.

The effect of %RH on zinc-treated float glass was also studied in this work using SIMS, after exposing samples to dry and saturated conditions for a two week period, see (Figure 5-56) and for comparison with the untreated samples, see Figure 5-55. The
extent of sodium depletion measured for the untreated sample was approximately 8 nm for the sample exposed to humid conditions. This is almost approximately 1.3 times the sodium depletion depth (i.e. 6 nm) measured for the zinc-treated sample exposed to humid conditions. Furthermore whilst a clear difference was seen between the untreated sample stored at dry and saturated conditions, this is not the case for the zinc-treated samples at these conditions. A sodium depletion of approximately 5 and 6 nm was measured for the sample stored at dry and saturated conditions respectively, see Figure 5-56. Hence this evidence supports the notion that zinc forms a protective barrier at the surface which blocks the sodium diffusion process. This mechanism has also been proposed by Wegst et al. (1948), Tait and Jensen (1982), Lewis et al. (1982), Caraval and Hatfield (1990).

The gravimetric results have shown an apparent anomaly that currently cannot be explained. The results at 30% RH and 20°C for zinc-treated float glass show a significant mass decrease with time until 3500 minutes where it appears to reach a stable weight (see Figure 5-2). The identical conditions for untreated glass show a continuous gain in mass see Figure 5-1. The same trend is seen when comparing the water adsorption isotherms for untreated and zinc-treated samples. A systematic decrease in mass was seen for the zinc-treated samples for a relative humidity between 30% and 40% RH, during the adsorption isotherms, see Figure 5-13 and Figure 5-14. No corresponding decrease was observed for the untreated sample. It therefore appears that this mass decrease on adsorption for zinc-treated samples around a relative humidity of 30% is a real effect. No evidence of this has been previously reported. This phenomenon requires further investigation.

A time index value (a) of \(0.24 \pm 5.22 \times 10^{-3}\) was measured for a zinc treated sample stored for a 12 day period at dry conditions for the time interval from 2.69 until 3.15 log min, see Figure 5-31. This agrees closely with the value of \(a = 0.25\) obtained by Tait and Jensen (1982) for alkali leached for a crushed sodium borosilicate glass in a solution of \(\text{ZnSO}_4\) of concentration 0.1 mol l\(^{-1}\) at 60°C. The sodium borosilicate samples used by these authors had an approximate specific surface area of 0.015 m\(^2\) g\(^{-1}\) and the data were collected over a total experimental time of 21 days. In this current work a lower amount of zinc in solution was used i.e. 0.00153 mol l\(^{-1}\) and
the crushed float glass had a specific surface area of 0.7 m$^2$ g$^{-1}$. The similarity of the results between the current work and that of Tait and Jensen (1982) suggest that the same corrosion mechanism is occurring, in spite of the many experimental differences. In addition, borosilicate glass is more corrosion resistant compared to soda-lime-silicate glass (Walters and Adams 1975).

### 6.2.2 Quantification of Zinc Treatment

The effect of zinc treatment on the glass surface was also quantified. This was done by expressing the mass uptake on a unit surface area basis, then fitting polynomials to the mass uptake curves, see Figure 5-22 and Figure 5-23 for the Batch 1 (untreated) and the Batch 2 (zinc-treated) float glass samples, respectively. The polynomial equations were differentiated and the flux value ($J'$) for both batches at $t = 3000$ minutes was calculated. The results are summarised in Table 5-11 showing flux values up to 11.8 times smaller for the zinc treated samples compared to the results for the untreated samples. The smallest but still noteworthy difference between batches was at 30°C; the flux values for the zinc-treated samples were 2.85 times smaller. The lower fluxes observed for zinc-treated glass give direct evidence of the effectiveness of this method of corrosion inhibition.

### 6.2.3 Storage Time

The data reproducibility for both untreated and zinc-treated samples, shows a clear difference in behaviour with storage time. For instance in Figure 5-29 the uptake curves of the untreated samples are of similar shape, whereas for the zinc-treated samples these showed clear differences, see Figure 5-30. The zinc-treated sample which had been stored for 150 days shows more than two times the mass uptake value at $t = 500$ minutes (see Figure 5-30) compared to the zinc-treated sample which had only been stored for 12 days. A greater influence of the storage time was also measured for the corrosion constant values ($k_r'$), see Table 5-13; i.e. for approximate values for $a$ of 0.25 the $k_r'$ values for the samples stored for 150 days were 2.2 times higher compared to the sample stored only for a 12 day period. At the same time the
zinc-treated samples showed the time index parameters to be similar for both storage times, i.e. there appeared to be no storage time influence on $\alpha$.

It appears that the zinc-treated samples age with storage time. Further evidence of this is obtained from the ion beam analysis data, which analyses samples down to a depth of around 1 $\mu$m. Zinc was only detected for the sample treated by Pilkington which had been stored for 2.5 years at dry conditions in the laboratory. This suggests that the zinc layer progresses into the glass over time, leaving the surface layer vulnerable to corrosion. Note that the SIMS results showed that zinc initially deposits in a thin surface layer of less than 1 nm as shown in Figure 5-57.

### 6.3 Effect of Temperature

The effect of temperature was studied for both Batch 1 (untreated) and Batch 2 (zinc-treated) float glass samples exposed to 15°C, 20°C and 30°C. It was established in Section 2.6.2 of the literature review, that the effect of temperature on diffusion through solids can be described by an Arrhenius-type relationship, (see Equation 2.21). In the current work, this was explored from the Arrhenius plot of the corrosion flux values ($J'$), see Figure 5-26. A reasonable degree of linearity was observed, especially for the zinc-treated float glass samples suggesting that an Arrhenius relationship is plausible. For the untreated samples the degree of linearity is lower as shown from the regression coefficient value. However, only three temperatures were considered and there is significant error, therefore further work is recommended in this area. It is interesting to compare values of the activation energy ($E_a$) obtained to values published for glass corrosion. For untreated glass the value of $E_a$ recorded in this present work was 50.9 kJ.mol$^{-1}$. This compares favourably with range of 44.5 – 66.4 kJ.mol$^{-1}$ published by Jiřička and Helebrant (2000) for float glass. Note that the value of $E_a$ obtained for zinc-treated glass was 122.3 kJ.mol$^{-1}$. The increase in activation energy relates to the lower dependence of corrosion flux on temperature, and this gives further quantification of the effectiveness of zinc treatment.

The effect of temperature on the corrosion flux values was also illustrated by plotting the corrosion flux values ($J'$) as a function of time for both Batch 1 and Batch 2 float
glass samples exposed to 15°C, 20°C and 30°C, see Figure 5-24 and Figure 5-25, respectively. Decreasing flux values with time were seen for both batches when exposed to 20°C and 30°C. Exposure of glass to higher temperatures results in increased sodium ion mobility therefore the sodium ions in the glass will become depleted more rapidly and consequently accumulate in the surface water film. It is proposed that this accumulation retards the diffusion of sodium due to the decrease in concentration gradient between the surface and the bulk. The use of a lower temperature such as 15°C, will result in lower rates of leaching of sodium and therefore lower rates of sodium accumulation in the adsorbed film. This argument could explain why, if the data are extrapolated at this temperature it appears that the corrosion flux values at 15°C will surpass the values at 20°C and 30°C, for both untreated and zinc-treated float glass samples.

6.4 Simulation

The simulation was developed to demonstrate that the mass uptake of water during glass corrosion could be modelled using basic mass transfer, adsorption, diffusion and reaction processes. At this stage it is therefore a proof of concept rather than a fully working model for the \textit{a priori} prediction of mass uptake.

The simulation is based on a number of assumptions that have been presented in Chapter 3. There is good agreement between the simulated and the gravimetric experimental results for short time experiments (up to 160 minutes), shown in Figure 5-35, 5-36 and Figure 5-37 for the untreated glass, and Figure 5-38, 5-39 and Figure 5-40 for the zinc-treated glass. Initial impressions therefore indicate that the listed assumptions are reasonable. Each assumption will now be discussed in more detail.

Assumption 1: \textit{The system is isothermal}. This assumption is valid because during the gravimetric experiment there is a good control of the temperature within ± 0.1°C but there is no control of temperature within the heap. However \( q \), \( E_a \) and \( E_l \) are small compared to the thermal mass. Using a typical value of 0.84 J g\(^{-1}\) K\(^{-1}\) for the specific heat capacity of glass, the maximum temperature increase due to heat of adsorption of
water is estimated to be only 0.5 °C. However this will be significantly lower due to heat loss from the sample pan by convection.

Assumption 2: *The bulk gas is assumed to be well-mixed hence the %RH is not a function of position but may vary with time.* This assumption is valid because the sample pan is exposed to a flowing air stream with effective control of the %RH within ±1% RH in the IGAsorp sample chamber. The sample pan is made from wire mesh, allowing good transport of water vapour into the heap.

Assumption 3: *Mass transfer from the gas phase to the glass surface is expressed by an external mass transfer coefficient following the Whitman film theory (Coulson et al. 1998 citing Whitman 1923). The external mass transfer coefficient is assumed to be based on a single system with a specific surface area that is based on the gross dimensions of the sample holder.*

The assumption of an external mass transfer coefficient based on the Whitman film theory assumes there is a quiescent film at the surface with a constant concentration gradient through the film. For the current glass-water system there is complexity of water vapour transport through the heap, compared to diffusion to the outer surface of the sample. It is anticipated that additional equations may be required to model mass transfer within the heap. This is a potential area for future development of the model.

The calculated mass transfer coefficient \( k_g \) based on the diffusivity of water predicted by the Chapman-Enskog equation (Equation 3.42) at 15°C was excessively large, leading to an unrealistically rapid initial uptake of water. Curve fitting the model to the experimental data gave a value for \( k_g \) that was four orders of magnitude smaller. This is realistic because the majority of the glass surface is within the heap which is much less accessible for diffusion compared to the scenario of the Chapman-Enskog equation that predicts a diffusivity from kinetic theory.

Assumption 4: *Adsorption at the glass surface follows the BET adsorption theory for water adsorbing on to glass hence this process is temperature and pressure dependent only.* The validity of the BET theory for glass-water systems has been discussed in literature by authors such as Gregg and Sing (1967), Collins (2005). The use of the
BET model is questioned for water sorption isotherms as it assumes normal molecular packing which might not be correct for water vapour sorption on glass, as the packing of molecules on a glass surface is dependent on the position of the silanol groups (water is believed to adsorb by cluster formation, Young 1958). Furthermore, the BET model accounts for physisorption only; this is why inert gases such as nitrogen are often used. It is believed for adsorption of water on float glass, physisorption and chemisorption are occurring simultaneously. The presence of chemisorption in the form of hydroxylation implies that use of the BET model to describe adsorption is not ideal, and future work could be directed at finding a more suitable adsorption model. However there is reasonable linearity in the BET equation plots in Figures 5-15 to 5-17, and Figures 5-18 to 5-20, supporting the use of the BET model for obtaining the amount adsorbed in the present work.

Assumption 5: *Equilibrium between the gas and the adsorbed water layer occurs at the glass surface instantaneously.* The kinetics of water vapour adsorption are much more rapid than the diffusion process of water into the glass, and therefore this assumption is felt to be reasonable.

Assumption 6: *The glass is assumed to be a homogeneous solid and the detailed elemental structure and the formation of a gel layer are not considered.*

The model appears to break down after approximately 200 minutes at 15°C, as shown by the poor fit to the gravimetric experimental results (see Figure 5-41). It is known from literature that the exposure of a glass to humid conditions initiates an ion-exchange at the glass surface and glass structural changes are to be expected, (Douglas and El-Shamy 1967). Therefore not considering the elemental glass structure might be too simplistic. Incorporating glass structure changes in the current simulation is likely to improve the simulation fit to gravimetric data at this temperature. Inclusion of the changes in the glass structure could be achieved using additional automata for the solid phase.

Assumption 7: *The water in the glass bulk diffuses undissociated.* There is uncertainty in the literature as to whether water diffuses in an ionised state or is undissociated,
(Bunker 1994). Without further evidence, it is considered that this is a reasonable assumption to make.

Assumption 8: *Water diffusion in the glass is a Fickian diffusion with an exponential temperature dependency.* The dependency of the amount of sodium extracted on the square root of time is a direct consequence of Fick's law. Experimental evidence of this has been published by Douglas and Isard (1949), and is also confirmed in the present work under certain conditions, (see Table 5-2). It therefore seems reasonable to assume that Fick's law applies. The assumption of exponential temperature dependency is also reasonable in that water diffusion has been shown to follow the Arrhenius equation (Doremus 1975, Holland 1964), as discussed in Sections 2.6.2 and 6.3 above.

Assumption 9: *A 1st order irreversible reaction of the form \( A + H_2O \rightarrow P \) is assumed where \( A \) represents a solid and \( P \) is the product of the reaction.* This reaction has been included inside the first glass node and is described in the simulation by four different parameters: diffusion constant \( (D_0) \), reaction capacity \( (R_c) \) i.e. the concentration of \( A \), activation energy \( (E_a) \) and the rate constant \( (k) \). The diffusion and the activation energy values were based on the work of Helmich and Rauch (1993) for silica. The reaction capacity was based on the concentration of the sodium measured by Staunton (2007) in float glass. The reaction rate constant was estimated by trial and error fitting to the experimental gravimetric results.

This is a very simplistic reaction scheme which serves the purpose of describing the chemical interaction between water and the glass without involving the complexities of the various reaction schemes and glass structure discussed in Section 2.4. Furthermore, the occurrence of chemisorption has been identified at the glass surface. Incorporation of this reaction in future work would be beneficial.

Assumption 10: *The solid reactant component \( A \) and component \( P \) are assumed to be incapable of diffusion.* For the purposes of the simulation it is important to have the reactant \( A \) stationary in the glass. It is assumed that the reactant is sodium as this has been identified as being the main component in glass corrosion reactions. However
sodium has also been identified as being the most mobile constituent of glass, exhibiting diffusion once an ion exchange reaction has occurred, Davison (2003), Fearn (2004). This assumption is therefore felt to be reasonable in that the sodium atoms are expected to be stationary before the reaction. However, the role of sodium ion counter-diffusion after the reaction is not currently accounted for in the simulation and could be addressed in future work.

Equation 3.13 is an assumption which is almost certainly not valid, for the amount adsorbed \( q \) is in excess of the monolayer capacity \( q_m \). Typically monolayer capacity is reached by about 30% RH and simulations are presented up to 70% RH. It may be more realistic to truncate \( C_1 \) in Equation 3.13 to the value obtained when \( q = q_m \), but the disadvantage of this would be an increase in complications involved for calculating the equilibration process in the CA.

**Sensitivity Analysis**

It appears from the relative sensitivity analysis that the simulation parameter which has the most influence on the final mass adsorbed value is the partial pressure. When \( p_0 \) is increased by 5%, the mass uptake increases by 14% indicating how carefully the RH must be controlled in the experiment, (see Table 5-20 in the Results Chapter).

Table 5-20 shows that a change in temperature of 5% has very little effect on the mass uptake. This is to be expected because whilst increasing the temperature will effectively reduce the mass adsorbed by reducing the BET constant (Equation 5.5), the temperature increase will also increase the vapour pressure of water from the Antoine equation (Equation 3.2). For a constant RH of say 70%, this results in a corresponding increase in the partial pressure of water in the bulk, \( (p_{o}) \). From Equation 3.1 the increase in \( p_{o} \) results in an increase in water flux that in turn gives an increase in water mass uptake. Therefore increasing the temperature results in a decrease in adsorption, and an increase in concentration driving force that cancel each other when combined.

From the sensitivity analysis it is clear that the parameters used for the glass bulk do not influence the relative final mass adsorbed because the relatively short time scales used do not allow sufficient time for diffusion to occur. Hence the total number of
nodes in the glass also is of no effect to the final mass adsorbed. Further work is recommended to explore the effects of diffusion at longer time-scales in the simulation.

**Zinc-Treated Samples**

It is reported in the literature that zinc deposits at the glass surface and forms a protective barrier for the diffusion of alkali from the glass bulk, Wegst *et al.* (1948), Tait and Jensen (1982), Lewis *et al.* (1982), Caraval and Hatfield (1990). Gravimetric experiments in the current work showed smaller mass uptake values for the zinc-treated samples compared to the untreated samples. Hence it is believed that zinc slows down the diffusion of water by possibly inhibiting reaction at the glass surface. Changes at the glass surface are believed to also occur. The parameters dominating the glass surface node are as follows: activation energy ($E_a$), reaction capacity ($R_c$) and rate constant ($k$). Hence the initial amount adsorbed by the zinc-treated samples was modelled assuming the reaction rate constant in the glass surface node is zero.

Good agreement was observed between the simulation and the gravimetric experimental results for zinc-treated samples, see Figure 5-38, 5-39, Figure 5-40, and Figure 5-42. The mass uptake for the zinc-treated sample which had been stored for 150 days and exposed to 20°C was simulated with the same simulation parameters used for the zinc-treated sample exposed to the same conditions which had only been stored for 12 days (see Figure 5-39). The simulation results were very different from the gravimetric results as shown in Figure 5.44. It is believed that the difference arises because the zinc-treated samples age with storage; conversely this is not seen for the untreated float glass samples (see Figure 5-29 and Figure 5-30). It was already suggested that a possible ageing effect occurs during storage of the zinc-treated samples (see Section 6.2.3).

A CA solution technique has been applied successfully to simulate glass corrosion. One of the advantages of this approach is that it can easily be adapted to include other mechanisms, and therefore its further use in the field of glass corrosion is recommended. As it stands, the current model lacks several features, including a diffusion coefficient which changes as the glass structure changes e.g. due to pore
Discussion

development. Similarly an automaton calculation to account for mass transfer through the basket and within the heap may improve the simulation considerably.

The chemistry of the corrosion process has so far been represented by a simple first order reaction. It is known that the chemistry of glass corrosion involves a number of possible reactions and the surface adsorption also involves a hydroxylation reaction. The CA model could therefore be improved by incorporating more representative chemistry. This could be extended to account for the effect of zinc treatment, once this mechanism is further understood.

In terms of the robustness of the model, care is taken at the data entry stage to ensure that the diffusivity ratio for the gas and the solid phase is below 1. Care was taken during the modelling of the adsorption node because this involved the solution of a polynomial equation using Laguerre's method. All the warnings detailed by Press et al. (2007) on the application of this numerical solution method were observed. For example in Laguerre's method two roots converge and disappear as a complex conjugate pair. All the recommendations of Press et al. (2007) were applied and proved to be useful.

Sensitivity analysis revealed that the dominant parameters influencing mass uptake relate to the gas phase. The effect of changing temperature was shown to have little effect due to the cancelling out of two competing effects; a decrease in adsorption, and an increase in concentration driving force whilst maintaining a constant relative humidity. The sensitivity analysis also showed that changes in the parameters relating to diffusion through the bulk glass had a negligible effect on the mass uptake.

Overall it is considered to have been an interesting and useful modelling exercise if not a completely successful one. The major conclusion from the modelling is that the automaton solution technique has proved to be successful and efficient, and potentially capable of extension to more realistic and detailed modelling assumptions.
7 Conclusions and Recommendations for Future Work

7.1 Conclusions

In the literature survey clear points for research were highlighted due to the lack of information in literature. These included the mechanisms by which stain inhibitors operate, and the effect of the adsorbed water layer on the corrosion rate. Furthermore, quantification of the effect of the zinc treatment in terms of adsorbed water had also not been previously published. The use of gravimetric analysis was identified as being suitable for the measurement of corrosion kinetics. Various surface analysis techniques were recommended to address the problem including PIXE, SIMS and XPS. Furthermore AFM emerged as the technique of choice for imaging of the glass surfaces.

The following objectives were therefore set;

- To measure directly the corrosion rate of float glass, using gravimetric analysis.
- To quantify the influence of zinc nitrate in the reduction of corrosion by comparison with untreated samples.
- To use surface analysis techniques to characterise the extent of corrosion by depth profiling.
- To develop a cellular automaton model for the simulation of glass corrosion.
- To test the suitability of the model by comparison with experimental data.

In the context of these objectives, the achievements of the current work can be summarised as follows:

A method for the direct measurement of the corrosion flux for crushed float glass was developed based on gravimetric water sorption and BET analysis of the sorption isotherms. The primary assumption for the measurement of the corrosion flux is that the mass uptake by the sample is purely a result of water adsorption to the surface, where the water adsorbed is replacing the water that has diffused into the bulk glass.
The mass uptake of untreated float glass samples was identified to be influenced by environmental conditions including %RH and temperature. Higher %RH gave higher water uptake, and higher temperatures resulted in higher corrosion fluxes. Saturated conditions resulted in higher amounts of sodium depletion as indicated by SIMS analysis.

Reaction parameters including the corrosion constant ($k_r$) and the time index ($\alpha$) parameters were measured for both untreated and zinc-treated float glass samples. Values for $\alpha$ of approximately 0.5 (within 11%) were identified at 20°C and at 30°C for certain time intervals. This is consistent with theoretical behaviour for water diffusing into the glass. However at 30°C, values for $\alpha$ of around unity were obtained (within 29.8%) suggesting diffusion through a layer of fixed thickness, according to Douglas and El-Shamy (1967).

Zinc treatment of the glass surface effectively reduces corrosion as noted from the smaller mass uptake values measured by gravimetric analysis. The smaller mass uptake for the zinc-treated samples has been attributed to zinc ions blocking the silica interstices, thus inhibiting the ion-diffusion process, (Tait and Jensen 1982). However the current work has shown that zinc treatment effectively reduces the amount of water adsorbed. It is therefore proposed that zinc ions combine with the surface hydroxyl groups thus rendering the surface less hydrophilic.

The effect of zinc treatment is also shown by SIMS analysis; an untreated glass surface showed much more sodium depletion after exposure to saturated air, compared to zinc-treated glass.

The corrosion flux values ($J'$) for the Batch 2 (zinc-treated) float glass samples are significantly lower compared to the results for the Batch 1 (untreated) samples. The corrosion flux for an untreated sample was 11.8 times higher that of a zinc treated sample exposed to 15°C, 9.25 times higher at 20°C and 2.85 times higher at 30°C. These results are direct evidence that zinc is effectively reducing the corrosion flux. It is interesting to note that the effectiveness of zinc treatment appears to decrease with increasing temperature.
A decrease in mass was measured for the zinc-treated samples isotherms during adsorption at 20°C, 40% RH and at 30°C, 35% RH and 40% RH. The mass uptake curves for these isotherm data points showed an initial short term increase in mass due to physisorption, followed by a sudden and systematic mass decrease to a lower equilibrium value. A mass decrease was also measured for the zinc-treated samples exposed to 20°C and 30% RH. No explanation can be currently offered to explain this phenomenon.

Surface analysis (SIMS) of a glass surface freshly treated with zinc revealed that the zinc resides in a very thin layer i.e. < 1 nm at the surface. However, ion beam analysis detected traces of zinc in an old sample at a depth of approximately 1 μm. This suggests that zinc diffuses into the glass over time and therefore the surface loses its protection. This argument is supported by the gravimetric data showing that a freshly treated glass surface (12 days old) has a significantly reduced level of water uptake compared to a surface that has aged for 150 days. It is interesting to note that the time index parameter (α) did not change with storage time.

From the three temperatures studied, it appears that the corrosion flux follows an Arrhenius relationship with temperature. Values of the activation energy (\(E_a\)) were obtained and compared to values published for glass corrosion. For untreated glass the value of \(E_a\) recorded in this present work was 50.9 kJ.mol\(^{-1}\). This compares favourably with range of 44.5 – 66.4 kJ.mol\(^{-1}\) published by Jiříčka and Helebrant (2000) for float glass. The value of \(E_a\) obtained for zinc-treated glass was 122.3 kJ.mol\(^{-1}\). This increase in activation energy gives further quantification of the effectiveness of zinc treatment.

A CA solution technique has been applied to model float glass corrosion. This technique was found to give simulation results that compared favourably to experimental data for mass uptake of water. The CA technique can readily be adapted to include other mechanisms and therefore it is recommended for further use in the field of glass corrosion. A sensitivity analysis revealed that the CA model was mostly influenced by parameters relating to the gas phase and surface reaction. The model was insensitive to parameters relating to the bulk glass phase, including diffusivity.
7.2 **Recommendations**

The following recommendations are suggested for further work:

More exposure temperatures should be used for the gravimetric and SIMS techniques in order to confirm the nature of the temperature dependence of the corrosion flux and the extent of sodium depletion.

The analysis of the float glass samples after exposure in the IGAsorp for a given time interval would be useful so that parameters obtained from gravimetric data can be related to specific changes in the glass structure.

Further investigation is needed into the adsorption behaviour of the zinc-treated samples to explain the anomalous mass decrease observed to occur at around 30% - 40% RH. The use of a surface analysis technique would also be beneficial at this stage to identify a possible molecular re-arrangement in the glass.

During gravimetric experiments, more attention needs to be paid to the exposure of the sample to laboratory air prior to an experiment.

Further work is required to confirm and quantify the suspected diffusion of zinc into the glass surface, resulting in an ageing effect. This could be done by repeating the ion beam analysis experiment at regular time intervals on zinc-treated float glass samples which were stored at dry conditions. A more detailed and systematic study of the effect of zinc ageing should be performed using gravimetric analysis and SIMS depth profiling to reveal the sodium depletion.

The simultaneous physisorption and chemisorption of water makes interpretation of water uptake difficult. It would be worthwhile to attempt to decouple the phenomena. Chemisorption could be completed by immersing the crushed float glass samples in water for a length of time prior to the isotherm experiment. The fully hydroxylated surface could be quickly dried and then subjected to water isotherm measurement in which only physisorption should occur.
Conclusions and Recommendations for Future Work

The Cellular Automaton model has been developed for proof of concept showing its potential to simulate the process of glass corrosion. In the light of this success, many improvements are recommended. These include:

- Running simulations for longer time-scales to explore the effects of the diffusion parameters
- Incorporation of a more reliable mass transfer coefficient that is able to represent the diffusion of water through the sample mesh and into the sample heap.
- Inclusion of a solid phase diffusion coefficient that is linked to changes in glass structure that occur as corrosion proceeds.
- Inclusion of a more detailed reaction scheme that can account for the various reactions that are implicated in glass corrosion, including a reaction to account for the chemisorption that occurs at the surface.
- Accounting for the counter-diffusion of the solid reactant (sodium and calcium ions) once ion exchange has occurred in the glass.
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APPENDIX A

BET THEORY
For convenience the BET equation is usually expressed in its linearised form, as shown below:

\[
\frac{p}{q(p_0 - p)} = \frac{1}{x_m c} + \frac{(c-1) p}{x_m c p_0}
\]  

(A.1)

When \(p/q(p_0-p)\) is plotted against \(p/p_0\) a straight line should result over the range of relative pressures of 0.05-0.30 if the BET model is applicable (Parfitt and Sing 1976). Upon fitting a linear trendline the gradient (s) and the intercept (i) are represented by Equation (A.2) and Equation (A.3) respectively, Gregg and Sing (1967).

\[
s = \frac{c-1}{x_m c}
\]  

(A.2)

\[
i = \frac{1}{x_m - c}
\]  

(A.3)

Solving the Equation (A.2) and Equation (A.3) for the gradient and the intercept simultaneously results in individual equations for the BET constant \(c\) and the monolayer \(x_m\). This is shown by Equation (A.4) and Equation (A.5) respectively.

\[
x_m = \frac{1}{s + i}
\]  

(A.4)

\[
c = \frac{s}{i} + 1
\]  

(A.5)

Once the monolayer value \(x_m\) has been determined, the specific surface area is calculated using the equation below:

\[
S = \frac{x_m}{M} \times N \times A_m \times 10^{-20}
\]  

(A.6)
Here $S$ is the specific surface area ($m^2 g^{-1}$), $N$ is Avogadro's constant ($6.02 \times 10^{23} \text{ mol}^{-1}$ in Atkins and Jones 1999), $A_m$ is the cross-sectional area of the adsorbed water molecule ($10.6 \AA^2$), $M$ is the molecular weight of the adsorbate ($18 \text{ g mol}^{-1}$) and $x_m$ is the monolayer capacity ($g g^{-1}$).

Other parameters which can be calculated from the BET theory are the energy of adsorption in the first layer ($E_1$) and the mean particle diameter ($d_{\text{particle}}$), see Equation (A.7) and Equation (A.8).

$$S = \frac{6}{\rho D_p} \Rightarrow D_p = \frac{6}{\rho S} \quad (A.7)$$

Here $S$ is the specific surface area ($m^2 g^{-1}$), $\rho$ is the glass density ($g m^{-3}$), $d_{\text{particle}}$ is the Sauter mean diameter assuming particles are spheres.

The BET constant ($c$) depends on temperature as follows:

$$c = \exp \left( \frac{E_1 - L_v}{RT} \right) \quad (A.8)$$

Here $c$ is the BET constant (-), $R$ is the Universal gas constant which is taken to be $8.314 \ (J \text{ K}^{-1} \text{ mol}^{-1})$ and $T$ is the temperature (K), $L_v$ is latent heat of vaporisation (kJ kg$^{-1}$), $E_1$ is the energy of adsorption in the first layer (kJ kg$^{-1}$).

**Adsorbed layer thickness**

To estimate the thickness of the adsorbed water layer the mass adsorbed was converted into a volume using the density of water and the BET specific surface value:

$$l_t = \frac{\rho_w}{S} \quad (A.9)$$

\footnote{Value quoted by Young (1958)}
Here $x$ is the mass adsorbed (g g$^{-1}$), $\rho_w$ is the density of water (g m$^{-3}$), $l_t$ is the layer thickness (m).

To obtain the number of molecular layers ($n'$) at a specific humidity the film thickness is divided by the approximate diameter of a water molecule, which Kalra et al. (2003) quote as 0.3 nm (a width of a monolayer), see Equation (A.11) below.

$$n' = \frac{l_t}{0.3 \times 10^{-9}}$$

(A.10)
APPENDIX B

ERROR ANALYSIS & RESIDUALS
Error Analysis

The BET slope shown in Figure 5-15 for an untreated sample exposed to 15°C for instance, can be expressed by Equation (B.1):

\[ y = mx + k \]  \hspace{1cm} (B.1)

Here \( y \) is \( p/p_0(p_0-p) \), \( x \) is \( p/p_0 \), \( m \) represents the BET slope and \( k \) the BET intercept.

The BET intercept is expressed by Equation (B.2) and the slope by Equation (B.3).

\[ k = \frac{1}{x_m c} \]  \hspace{1cm} (B.2)

\[ m = \frac{c - 1}{x_m c} \]  \hspace{1cm} (B.3)

The error in the slope can be expressed by Equation (B.4) and the intercept error can be expressed by Equation (B.5).

\[ m \Rightarrow \tilde{m} \pm se_m \]  \hspace{1cm} (B.4)

\[ k \Rightarrow \tilde{k} \pm se_k \]  \hspace{1cm} (B.5)

Here \( se_m \) and \( se_k \) are the standard error in the slope and intercept respectively, \( \tilde{m} \) is the slope value and \( \tilde{k} \) is the intercept value.

The error in the monolayer value, \( x_m \), and in the BET constant, \( c \), is required in the forms shown below respectively:

\[ x_m \pm se_{x_m} \]  \hspace{1cm} (B.6)
Substituting (B.1) into (B.2) Equation (B.8) is obtained.

\[ m = k(c - 1) \]  

(B.8)

After simplification of the equation above:

\[ c = \frac{m}{k} + 1 \]  

(B.9)

And therefore:

\[ c = \frac{m}{k} + 1 \]  

(B.10)

For the standard error in the BET constant the following equation is applied:

\[ \frac{se_c}{c} = \sqrt{\left( \frac{se_m}{m} \right)^2 + \left( \frac{se_k}{k} \right)^2} \]  

(B.11)

Similarly for \( x_m \):

\[ x_m = \frac{1}{k c} \]  

(B.12)

Therefore

\[ x_m = \frac{1}{k c} \]  

(B.13)

It follows that for the standard error in the monolayer value Equation (B.14) applies.
The values for the error in the BET constant \((c)\) and monolayer values \((x_m)\) are shown in Tables 5-3 for adsorption and Table 5-6 for desorption.

**Residuals**

In Chapter 5, Section 5.2.2 the logarithm of the fractional mass uptake was plotted as a function of the logarithm of time. For the determination of the time index value and the corrosion constant regions of linearity were fitted to the Figure 5-8 and Figure 5-9 by eye. In order to assess the true linearity of these regions the residuals were plotted. The equation estimated from the slope was used to estimate \(y_e\) which is defined by Equation (B.15).

\[ y_e = mx + c \]  

(B.15)

Now using the fitted values \(y_f\) which are represented by the values shown in the graphs for the logarithm of the fractional mass uptake as a function of the logarithm of time, see e.g. Figure 5-8. Note in this figure \(y_f\) is represented by \(x\), on the y axis. The difference between \(y_f\) and \(y_e\) was considered, as show by Equation (B.16).

\[ \Delta y = y_f - y_e \]  

(B.16)

Here \(\Delta y\) are the residuals.

The residuals for Batch 1 (untreated) are shown in Figures B-1, B-2, B-3 and for Batch 2 (zinc-treated) this is shown in Figure B-4, B-5, B-6 and Figure B-7. Note that Figure B-7 corresponds to a repeated experiment at 20°C for Batch 1 and Batch 2 samples, respectively.
Figure B-1 Residuals plot for Batch 1 (untreated) float glass sample, exposed to 15°C, corresponding to Figure 5-8.

Figure B-2 Residuals plot for Batch 1 (untreated) float glass sample, exposed to 20°C, corresponding to Figure 5-8.
Figure B-3 Residuals plot for Batch 1 (untreated) float glass sample, exposed to 30°C, corresponding to Figure 5-8

Figure B-4 Residuals plot for Batch 2 (zinc-treated) float glass sample, exposed to 15°C, corresponding to Figure 5-9
Figure B-5 Residuals plot for Batch 2 (zinc-treated) float glass sample, exposed to 20°C, corresponding to Figure 5-9

Figure B-6 Residuals plot for Batch 2 (zinc-treated) float glass sample, exposed to 30°C, corresponding to Figure 5-9
Figure B-7 Residuals plot for Batch 2 (zinc-treated) float glass sample stored at dry conditions for 12 days and exposed to 20°C corresponding to Figure 5-31.

The residual plots for the different batches showed in some cases a systematic curve indicating that the underlying data are in the form of a curve as there is no random distribution for the fitted line as shown in Figure B-6. In other cases a random distribution of the data showed the digitization error in the IGAsorp instrument, see Figures B-4 and Figure B-5. A mixture of digitization and systematic curves is found in Figure B-1, B-2, B-3 and Figure B-7.
APPENDIX C

MODEL
The following flow charts describe the parameters used and the order these were entered for the simulation. Four flow charts are shown below these include general parameters, gas phase and solid phase, diffusion and reaction parameters.

Figure C-1 Flow chart for general system parameters
Enter gas mass transfer coefficient \( k_g \) (mol s\(^{-1}\) kPa\(^{-1}\) m\(^2\))

Enter gas film thickness \( \delta z_g \) (m)

Enter number of nodes in gas film \( N_{n_{gas}} \geq 2 \) (-)

Calculate gas node thickness (m)
\[
gas _{-} dz = \frac{\delta z_g}{N_{n_{gas}} - 1}
\]

Enter number of nodes in solid \( N_{n_{glass}} \geq 5 \) (-)

Enter distance step length in solid, this is also the thickness of a solid node \( \delta z \) (m)

Enter integration step length \( \delta t \) (s)

Calculate \( Da_{gas} = \frac{(\delta z)^2}{4\delta t} \)

Calculate \( Da_{sola} = \frac{(\delta g)^2}{4\delta t} \)

Calculate relative mass transfer coefficient (-)
\[
k_{g_{relative}} = \frac{k_g 4\delta t RT}{gas _{-} dz}
\]

Calculate \( k_{g_{frac}} = \frac{k_g}{k_{g_{relative}}} \)

Use \( \frac{kg _{-} old}{kg _{-} frac} \)

Figure C-2 Flow chart for gas phase and solid phase parameters

Figure C-3
Enter diffusion constant at glass surface $D_{0,gs}$ (m²s⁻¹)

Enter activation energy at glass surface $E_{a,gs}$ (kJ kmol⁻¹)

Calculate diffusion at glass surface $D_{gs}$ (m²s⁻¹) using Equation (3.13)

Calculate $D_R = \frac{D_{gs}}{Da}$

Go back reduce $\delta t$ (s)
OR increase $\delta z$ (m)

Is $D_R \leq 1$?

NO

Do the same for the glass bulk

Enter diffusion constant in the glass bulk $D_{0,bg}$ (m²s⁻¹)

Enter activation energy in the glass bulk $E_{a,bg}$ (kJ kmol⁻¹)

Calculate diffusion in the glass bulk $D_{bg}$ (m²s⁻¹) using Equation (3.13)

Calculate $D_R = \frac{D_{bg}}{Da}$

Go back reduce $\delta t$ (s)
OR increase $\delta z$ (m)

Is $D_R \leq 1$?

YES

Figure C-3 Flow chart for diffusion parameters

Figure C-4
Figure C-4 Flow chart for reaction parameters
APPENDIX D

ISOTHERM KINETICS
Figure D-1 below shows the adsorption kinetics of a Batch 2 (zinc-treated) float glass sample exposed to 30°C and 35% RH. The mass decrease measured at this temperature appears to be real and is not due to a sudden fluctuation in temperature or %RH.

Figure D-2 also below shows the desorption kinetics for a sample exposed to 30°C and 60% RH. The mass increase is believed to be due to equilibrium not having been reached at this humidity.
Figure D-1 Adsorption isotherm kinetics for Batch 2 (zinc-treated) float glass sample exposed to 30°C and 35% RH, from Figure 5-14 in Chapter 5
Figure D-2 Desorption isotherm kinetics for Batch 2 (zinc-treated) float glass sample exposed to 30°C and 60% RH, from Figure 5-14 in Chapter 5