

**Department of Applied Chemistry**

**Degradation of E-glass Fibre in Selected Organic Acids**

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**This thesis is presented for the Degree of  
Master of Science  
of  
Curtin University of Technology**

**January 2008**

## **Acknowledgements**

The student wishes to acknowledge the support and guidance of Dr Lynne Jones (project supervisor) and the funding provided by the School of Applied Chemistry of Curtin University and technology. Further acknowledgement goes to David Pritchard (Applied Chemistry, Curtin University of Technology) for the time and assistance he contributed in the analysis of cation by AAS (Atomic absorption spectra) and ICP\_OES (inductively coupled plasma optical emission spectroscopy). Appreciation further goes to Celeste Wilson (Marine and Water Research Laboratory, University of Murdoch) for the contribution in the cation analysis. Many thanks also go to Keith Wenn (Applied Chemistry, Curtin University of Technology) for supplying analytical reagents, equipments, and apparatus as well as for the time he contributed.

## Abstract

E-glass has been widely used as a reinforcing material for years, especially as a plastic reinforcer in the production of GRP (Glass Reinforced Plastic). Failure of GRP materials under stress came in to the picture quite recently. Since then studies have been conducted in an attempt to understand the causes and the underlying behaviour.

Except for the last section of the research (analysis using a kinetic approach) where glass fibre was cut out to weigh approximately 1.0g, standard sized specimens were soaked in the required acid solutions of desired concentrations for varying temperatures and time frames. Wherever tensile strength retention was measured, LLOYD instrument was employed. Leaching of the cations were analysed using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES and also know and ICP-AES).

The scope of this project can be divided in to four sections; first section involved investigating the effects of malonic acid. The study of malonic acid was narrowed to investigating the trend in strength retention. A rapid strength loss was observed initially followed by a much steady decline in the strength. However the continuation of the loss of strength was unmistakable throughout the time period of exposure. Furthermore, temperature can be observed as a facilitating factor in this degradation reaction.

Secondly the corrosive effect of glyoxylic acid on E-glass fibre was studied. This was explored at two different temperatures for two specific time frames using various

concentrations of the acid of interest. The influence of this acid on the glass fibre was found out in terms of strength retention and loss of cations from the glass matrix. The mildness of this acid was accentuated by the fact that 70% or more of the strength was retained at all the conditions employed. A minima in strength retention was observed at 2M acid concentration similar to the trends observed in the past (Betz and Jones 2003 and Jones and Chandler 1986). Leaching of cations reflected this trend. The large strength retention could be related to the fewer amounts of Ca and K leached from the glass matrix (Kumosa and Qui, 1997). Similar to malonic acid, an unusually large amount of B was leached out that could be due to the favourable orientation of the anion with the trivalent ions during the complex formation. Yet again temperature was found to enhance the degradation process.

Next the extent of passivation (if any) showed by malonic acid was investigated using E-glass fibre pre-treated in 5M malonic acid and post treated in known corrosive acids hydrochloric acid and oxalic acid. Passivation of malonic acid was put to test through examination of strength retention of the fibres under these conditions. This segment was carried out as an extension of a finding (a behaviour synonymous to passivation) shown by malonic that surfaced the previous year by the present researcher. Increasing the pre-treatment time showed a great improvement in the retained strength for all the post-treatment acid mediums. Furthermore, while Jones and Betz (2004) featured 20-40% strength retention within a short time frame in 3M HCl, the immense amount of strength retention (60-70%) preceding pre-treatment should definitely be noted. Similarly strength retention of about 80% was observed when post-treated with the severely corrosive oxalic

acid. Hence it is clear that passivation can be induced through prolonged pre-treatment in 5M malonic acid that could inhibit the attack of corrosive acid at least for a period of time.

The last fragment of the study focussed on understanding and working out the mechanism behind the reactions between the E-glass fibre and acid medium in terms of kinetics. The acids utilized were 1.5M malonic acid and 3M glyoxylic acid and the assessments were made through the analysis of the weight changes brought about by the acid medium at various temperatures and time frames. In addition leaching patterns of cations were evaluated as this could contribute in achieving the objective. Maximum weight loss reached 4% in glyoxylic acid while that for malonic acid exceeded 20%. The general trend was that the glass fibres lost weight in both acids for a period of time followed by an evident weight gain. Furthermore the weight loss results fit the first order rate law. While the leaching of cations reflects the weight loss for the shorter time frames, steady loss of ions was visible even for the longer time frames where the weight has increased. The weight gain could be explained in terms of binding of anions to certain cations on the glass surface, accounting for the hindrance in the loss of cations at the longer time frames as well. About 50% of weight loss was associated to Ca while 20% was to Al, leaving 6% to B where as the rest of the ions had shown almost insignificant contribution to the weight loss.

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## **1 Introduction**

### ***1.1 Introduction to E-glass fibre, their uses and past studies***

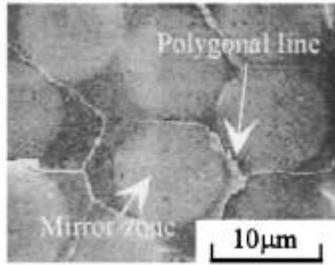
E-Glass fibre has been known as the major reinforcing material in the manufacture of glass reinforced plastic (GRP) composite in Australia. During the eighties and early nineties there was a substantial growth in the use of GRP to meet the demand of lightweight, high strength and corrosion resistant materials for the manufacture of domestic appliances, automotive, offshore structures, sports goods, and aircraft in industries (Jihan, Siddiqui and Sweet, 1997) . The high specific modulus and strength together with the good corrosion resistance of these materials lead these GRP materials to be used as a structural material in wet environments (Shen and Springer, 1977 and Ellis and Found, 1983). As a construction material GRP works well in conditions of prolonged contact with harsh chemical conditions as well as heightened temperatures without corroding or swelling, however it is not true that GRP materials are totally inert to chemical attacks (Sapalidis, Hogg and Youd, 1997).

Failure of GRP became apparent in several occasions over the past two decades (Hogg and Hull., 1980 and Aveston et.al., 1981). Such failures have been associated with the corrosion of the materials, especially those subjected to mechanical stress under strongly acidic environments (Hogg et.al., 1980 and Garg, 1983). According to Sapalidis et.al., 1997, the causes of environmental degradation of GRP material are five: (i) strength loss of the reinforcing fibres due to stress corrosion, (ii) loss of adhesion and interfacial bond strength due to the degradation of the fibre matrix interface, (iii) chemical degradation of

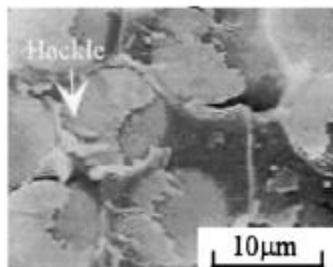
matrix material, (iv) how the matrix modulus and strength depends on the time period and temperature, and (v) accelerated degradation due to combined effect of temperature and chemical condition.

According to Kumosa and Qui (1997) GRP composites consists of three elements; the glass fibre, the resin matrix and the fibre/glass interphase. The resin matrix protecting the fibres normally appear to be unaffected by the strongly acidic environment (Norwood and Farebrother, 1979). However any defects or damage to this shield could expose the glass fibres to the harsh acidic media, allowing rapid corrosion which may be catastrophic (Jones and Chandler, 1984).

In a recent study, Kawada and Srivastava (2001) explain that in GRP, the majority of the load is carried by the fibres, and a corrosive environment could cause failure of fibres at loads much below the normal failure strength. Kawada and Srivastava (2001) further believe that the acids could only reach the glass fibres through microcracks, crazes or similar voids in the resin matrix which are formed as a consequence of stress intensification of a growing stress corrosion crack. Figure 1a and 1b shows glass fibre corrosion in two stages as studied and presented in the paper by Kawada and Srivastava (2001). These figures show fracture surface of an E-glass reinforced plastic, plastic in this case being bisphenol-vinyl ester.



*Figure 1a:* Fracture surface of GRP - Stage 1(Kawada and Srivastava, 2001)



*Figure 1b:* Fracture surface of GRP - Stage 2 (Kawada and Srivastava, 2001)

Glass fibre is known to suffer spontaneous cracking once exposed to acidic media (Norwood and Millman, 1979). This occurs due to the replacement of cations of the glass matrix by the protons of the acid, a reaction known as the ‘ion-exchange reaction’ (Hojo and Tsuda, 1979). Early researchers relied on this theory where they were led to assume the correlation with the strength of an acid in the medium or the hydrogen ion concentration with the corrosive effect on E-glass (Metcalf and Schmitz, 1972, and Friedrich and Mater 1981). However, follow up studies revealed information which proposed the anions of the acid to have a significant role in the corrosion process (Jones and Chandler, 1984a). In fact the anions capable of forming a negative or neutral complex with the cations in the glass pose a more deteriorative effect (Jones and

Chandler, 1985). Kumosa and Qui (1997) ascribed the severity of corrosion to the type and concentration of the acid, along with the composition and fabrication of the fibre.

The failure of E-glass reinforced composite materials that were being used as insulators on high voltage transmission lines was reported by Jones et al. (1983). These composites were subjected to high electrical and mechanical stress, but were not exposed to any acid directly. It was therefore proposed that the formation of low molecular weight organic acids, arising from the degradation of the polymer resin via partial discharge activity under such conditions, was responsible for the corrosion of the glass fibres themselves (Jones and Chandler, 1985). The corrosion and discharge activity could take place in the tiny air gaps within the composite or at surface asperities in the rod (Jones and Chandler, 1985). Generally the polymer coating serves as a protective layer; however in such a situation it is a contributing factor for corrosion.

In the past studies, two of the methods have been mainly administered to examine the behaviour of E-glass under the influence of acids (Lewis and Bedder, 1984). One is to measure the failure time when samples are subjected to a sustained load in an acidic environment (Scrimshaw, 1980 and Roberts, 1978), while the other method involves soaking stressed or unstressed fibres in acid environment followed by constant-rate-of-strain tensile testing (Torp and Arvesen, 1979 and Roberts, 1978).

The later method was employed in this paper. This method is rapid, simply providing a picture in comparison to the unstressed glass fibres, giving more of a relative

measurement which however does not present the actual scenario (Lewis and Bedder, 1984). The former method is a better representation of reality yet time consuming and likely to give scatter in failure times (Lewis and Bedder, 1984). A study by Aveston et al. (1980) showed that, in a multi-filament test, the maximum load the fibres can withstand has no correlation with variation in scatter observed in individual fibres. Nevertheless, Hull (1981) has stated the strength of a bundle of E-glass fibre to be within 65%-80% of mean individual fibres. Furthermore, the tensile strength of the bundle is prone to fall from the mean individual fibre strength, in the case of non-uniform stressing of individual fibres in the bundle (Hull, 1981). However, the fibres in the composite have the matrix for stress transfer effect which increases the strength in the order of two or four times the mean individual fibre (Hull, 1981). Hence the results may fail to produce the exact values.

Various studies conducted in the past revealed a unique behaviour of some acids. In these circumstances the acid appears to have a severe corrosive effect on the glass fibre at a specific concentration while at higher or lower concentrations very little or no strength loss of glass fibre is observed. These studies include the case of perchloric acid discussed by Jones (1987), behaviour of hydrochloric and hydrobromic acid studied by Jones and Chandler (1985) and the behaviour of malonic acid as described in the postgraduate diploma thesis (Effect of Malonic acid on the corrosion of E-glass fibre in glass reinforced plastic, 2004) by the present researcher.

## *1.2 Structure of E-glass fibre*

The high tensile strength and the low expansion properties are the key factors that make glass fibre a suitable material to reinforce plastic (Pfaender 1996, p. 168). The material 'glass' is a collective term describing a vast number of materials of varying composition in glassy state (Pfaender 1996, p. 168). Some of these include: sodium silicate glass (Figure 2), lead glass, soda-lime glass and special glasses of varying composition of numerous elements for desired use (Pfaender 1996, p. 23-25).

The glass fibre known today was invented in 1938 by Russel Games Slayter, for use as an insulating material (Kruschndl, 2006, p.1 of 1). According to Pfaender (1996, p.168), glass fibre is explained as a collective term for glasses drawn in to fibres of diameter between one tenth and a few thousandths of a millimetre, hence describing the structures and composition of glass becomes too wide to be discussed in this paper. The chemical composition of E-glass fibre seems to vary from manufacturer to manufacturer. Table 1, gives the composition of E-glass fibre employed in this research, kindly supplied by ACI Fibreglass (Belmont, WA, Australia).

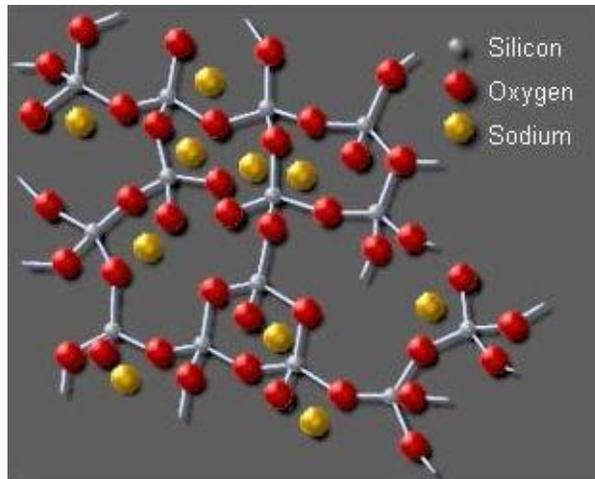


Figure 2: Structure of Sodium Silicate glass (Pfaender 1996, p. 19)

The general essential molecular building blocks of glass are tetrahedral  $\text{SiO}_4$  which are spatially cross linked to each other as shown in figure 3a.

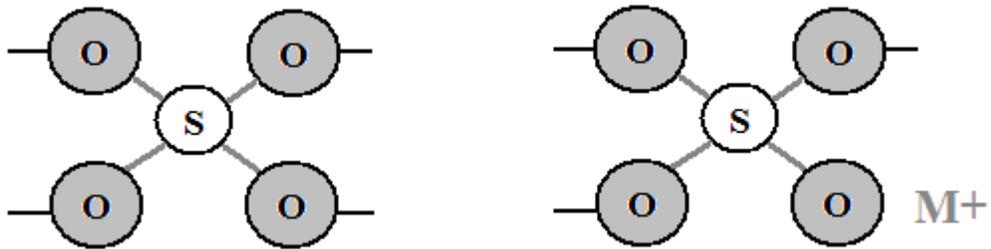


Figure 3: a) Structural units with each oxygen shared twice.

b) Interaction of Alkali ion with oxygen.

Table 1. Chemical composition of E-glass (wt%)

$\text{SiO}_2$	$\text{CaO}$	$\text{Al}_2\text{O}_3$	$\text{B}_2\text{O}_3$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{Fe}_2\text{O}_3$
52.10	23.90	14.86	4.29	1.78	1.06	1.02	0.39

It can be seen from Table 1, that the elements Aluminium and Calcium are present in highest quantity beside the silica network. When Alkali metals are added to the matrix, ionic non-bridging oxygen atoms are formed as shown in Figure 3b. Such is the case with all metals present in the glass such as Na, K, Fe, Ca, Al, and Mg. Boron is however different as it resides in the silica matrix. Locher and Martin (2002) in their lecture on ‘the structure of glass’, explain the bonding of Boron to be similar to the Silicon atoms although possessing a net charge.

The character of the elements and the type of bonding they exhibit in the glass matrix play a significant role in the leaching of these elements during corrosion, and the mechanism with which they are leached. According to Kumosa and Qui (1997), boron ions reside in the silica network and are believed to have a stabilizing effect. They further ascribe calcium as network modifier and regard these ions to exist as interstitial ions in the glass matrix. Aluminium ions are said to occupy either holes between the silicate tetrahedra or to join the silica network in the presence of enough alkali that could neutralize the negative charge on the tetrahedral aluminium ion (Holloway, 1973).

### ***1.3 Mechanism of Corrosive attack***

At present the chemical corrosion process of E-glass fibre especially in acidic medium is well established (Harris, Noble and Owen, 1984 and Jones and Chandler, 1985).

At first, the deteriorative effect of acidic conditions on glass fibre was primarily linked to the acidic strength of the medium. The proposed mechanism was an ion exchange

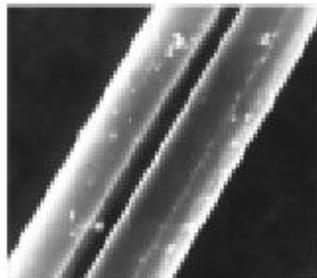
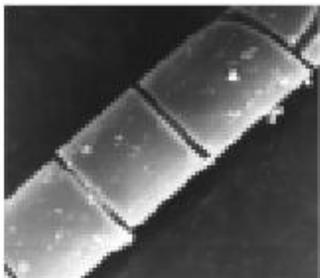
reaction where the cations on the glass surface were replaced by the protons from the acidic medium (Jones and Chandler, 1984b). The ion-exchange mechanism is said to be governed by diffusion process. Jones and Chandler (1984b) also suggested the rate limiting step to be the diffusion of ions through the solid phase (particle controlled diffusion) due to the compact nature of glass.

The general reaction may be written as:



(Metcalf and Schmitz, 1972 and Friedrich, 1981), where bar indicate the species associated with the glass phase. The differences in size of the much smaller protons compared to the cations they replace from the glass surface, induce tensile stresses on the surface, which according to Jones and Chandler (1984b), could become large enough to promote cracking. As a result the composite material may fracture under these conditions, even under relatively low mechanical stress (Kumosa and Qui, 1997) or worse it could crack spontaneously even in the absence of a mechanical stress (Jones and Chandler 1984b).

The fibres have been known to develop spiral or axial cracks on the surface as part of corrosion. Kumosa and Qui (1997) proposed an ion-depletion-depth model in an attempt to explain the fibre surface cracking. Their findings showed a likely correlation of the depletion of the larger ions from glass to axial cracks and rather than to spiral cracks.



*Figure 4a: Spiral cracks (Kumosa, 2001)*      *Figure 4b: Axial cracks (Kumosa, 2001)*

It was also shown around 1984 and 1985 (Jones and Chandler, 1986) that glass fibres exposed to organic acids were also severely corroded despite their weaker acid strength (hydrogen ion concentration) in comparison with mineral acids. Two theories were proposed to explain the corrosive effect of organic acids: where certain anions could form insoluble salts with leached metal cations, and where they could associate with these cations to form insoluble complexes of either neutral or anionic nature (Jones and Chandler, 1985). Here it is the anion of the acid that plays a significant role by forming complex ions or insoluble species with the cations in the glass. This will effectively reduce the  $M^+$  ions in equation (1), and would drive the forward reaction according to Le Chatelier's Principle, hence enhancing the depletion or corrosion of the glass. (Jones and Chandler, 1986). The corrosive effect has been principally attributed to the leaching of the larger non-silicious  $M^+$  ions, calcium and aluminium (Kumosa and Qui, 1997).

However the corrosion was found not to be proportional to an increase in concentration of the organic acids oxalic and mesoxalic acid, and in fact, for these two acids, a strength retention minima (or corrosion maxima) was observed by Jones and Chandler (1985).

The explanation put forward was: at the lower concentrations, the hydrogen ion concentration is too low to favour the ion-exchange reaction. At the higher concentrations, the anions present are thought to bind on to certain metal cations on the glass surface, hence preventing further dissolution. A similar effect has been observed with hydrochloric acid (Jones and Chandler, 1986).

Lastly according to Kumosa (2001), the tendency of an ion to deplete is highly related to the character of the ion, especially to its bond energy in the glass, hydrated volume and valence state. The extent of corrosion further depends on the type and concentration of the acid, the glass composition and also the fabrication process of the fibre (Kumosa, 2001).

#### ***1.4 Acids Utilized in the Analysis***

Generally weak organic acids would not be expected to have much corrosive effect on glass fibre with respect to their acid strength. However, a study conducted by Jones and Chandler (1986) showed oxalic acid and mesoxalic acid to have corrosive effect on glass fibre. Therefore studying the effects of similar acids could be very beneficial.

As stated in 'Basics on Degradation' (2008, p.1 of 2), when polymers are exposed to electric discharge, light, heat or radiation, chemical reactions are initiated in the polymer which results in a change in the chemical composition, physical properties, as well as the molecular weight of the polymer. As hydrogen and carbon are the main constituents of polymers, the ultimate products of degradation in an oxidating environment are carbon

dioxide and water. However during the degradation, the carbon back bone of the polymer chain is broken from various places at the intermediate stages enabling a variety of organic acids similar to the following type to be formed (Jones and Chandler, 1986)



Where  $n = 0, 1, 2, \text{ etc}$

The organic acids utilized in this research are acids suspected to be formed in the degradation process of plastics.

#### ***1.4.1 Malonic acid***

According to Chemical Land21, (2008, p.1 of 3), malonic acid also known as propanedioic acid, is a dicarboxylic acid of the formula  $\text{HOOC} \cdot (\text{CH}_2) \cdot \text{COOH}$  (refer Figure 5. for the structure). The acid is soluble in water, alcohol and ether though too unstable for many applications. This is regarded as an acid of relatively weak strength, with  $\text{pK}_a$  of 2.81 (Jones and Chandler 1986). Jones and Chandler (1985) considered malonic acid as one of the likely products of the ultraviolet light induced degradation of the polymer used to make GRP. These researchers came to the conclusion that although malonic acid form complexes with cations, the dissociation is insufficient to provide a hydrogen ion concentration to bring about rapid leaching of the cations. However it was still found to cause severe corrosion to glass fibre after prolonged exposure.

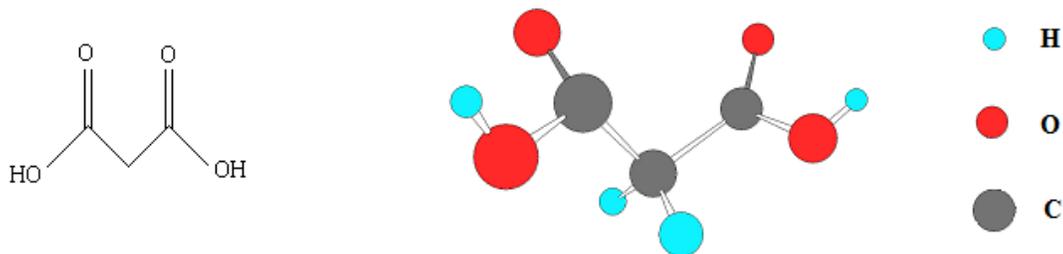


Figure 5: Structure of Malonic acid

#### 1.4.2 Glyoxylic acid

Glyoxylic acid (refer Figure 6. for the structure) has a molecular formula  $\text{OCHCOOH}$  and it is the smallest known keto-acid (Sciencelab.com, 2005, p.1 of 1). This acid is known to possess dual functions making use of its carboxylic acid group and aldehyde group. Chemical land 21 (2008, p.1 of 3) further claims that glyoxylic acid is known to be found in human body as a primary precursor of oxalic acid and as an intermediate in the conversion of glycolic acid to glycine. In the Industrial field, this acid is used as a starting material in the production of other chemical products such as aroma compounds, pharmaceuticals and polymers (Chemical land 21, 2008, p.1 of 3). Jones and Chandler, (1986) explains glyoxylic acid as an organic acid with a relatively weak strength, with a  $\text{pK}_a$  of 3.46.

Previous analysis of the corrosive effect of glyoxylic acid on glass fibre by Jones and Chandler (1986) showed this acid to have a mild deteriorative effect on glass fibres after a 7 and 30 days exposure, compared to acids such as oxalic acid and mesoxalic acid.



Figure 6: Structure of glyoxylic acid (CS ChemOffice 2000 Ultra – Software)

### 1.4.3 Oxalic acid

Oxalic acid (refer Figure 7. for the structure), also known as ethanedioic acid is a colourless, crystalline and toxic organic compound with the formula HOOC<sub>2</sub>COOH (Chemical land 21, 2008, p.1 of 3). This compound is known to be the only chemical compound where two carboxyl groups are directly joined together. In nature it exists in the form of its metal salts in many plants (Chemical land 21, 2008, p.1 of 3). As Day, Whalen, King and Hust et.al (2004) describes, oxalic acid is one of the most aggressive alkane acids with a pK<sub>a</sub> of 1.23, and hence it is used as a bleaching agent, rust remover as well as in water treatment.

As oxalic acid would be the most highly oxidized species next to carbon dioxide and water vapour, Jones and Chandler (1986) suspected oxalic acid to be a predominating species in the polymer degradation process. This theory was somewhat supported by McMohan (1968) and Mayoux (1976) as they showed the production of oxalic acid in appreciable quantities through electrical discharge activity on polyethylene. Oxalic acid was found to have a severe corrosive effect on the glass fibre even after exposure to this acid for only 7 days (Jones and Chandler, 1986).

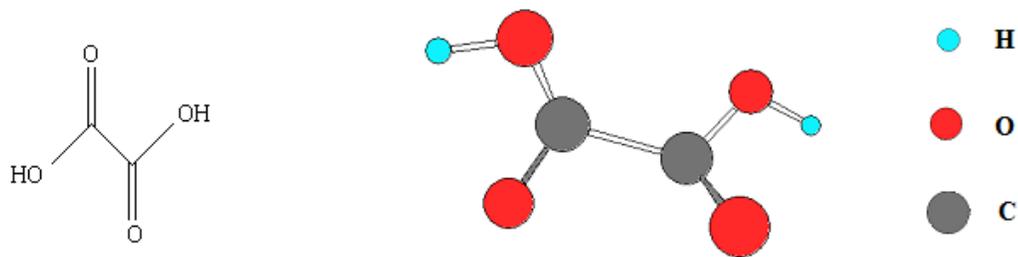


Figure 7: Structure of oxalic acid

#### ***1.4.4 Hydrochloric acid***

Hydrochloric, also known as muriatic acid (as a historical name) is an aqueous solution of Hydrogen chloride gas (Net Industries, n.d., p 1 of 1). Crystal (n.d., p.2 of 5) claims that this highly corrosive acid was discovered by an Iranian-born alchemist by the name Jabir ibn Hayyan around the year 800. The Alchemists of the time found this acid to be very useful in their work as it proved to be a good solvent (Net Industries, n.d., p 1 of 1). This is the only inorganic acid utilized in this research and is known to have a considerable corrosive effect on E-glass fibre (Jones and Betz, 2004). The chloride ions are believed to form complexes with some of the cations leached out from the matrix and clear corrosion maximum was observed by Jones and Chandler (1985a) at a concentration of 3M hydrochloric acid.

### ***1.5 Aim of the Project***

The scope of this project is to investigate the mechanical properties of, and cation leaching from, E-glass fibres under the influence of malonic and glyoxylic acids in varying conditions of concentration and temperature. Furthermore, in the light of previous research; this research investigates the passivating effect of malonic acid, by pre-treating glass fibres with this acid prior to exposure to hydrochloric and oxalic acids. Since malonic, glyoxylic and oxalic acids are organic acids which are likely products of electrical or ultraviolet light induced decomposition of the plastic resin, it is important to study their effects on E-glass fibre. The glass fibre was exposed to these acids in various conditions for various amounts of time. Mimicking these situations could possibly illustrate the effectiveness of the presently used resin or prove the need for its modifications for the future.

## **2. Experimental Procedure**

### ***2.1 Analysing the Corrosive effect of Malonic and Glyoxylic acid***

#### ***2.1.1 Preparation and Corrosion of E-glass fibre***

Samples of E-glass fibre of the composition described in Table 1 were cut into 200mm strips from an E-glass roving kindly supplied by ACI Fibreglass, Belmont, WA, Australia. The ends of the strips were glued using contact cement glue for ease of handling. Test tubes were filled to a depth of 50 mm with either glyoxylic or malonic acid of desired concentration and 6 strands of glued E-glass fibre samples were placed in it to ensure the exposure of 100mm length of glass fibre to the corrosion medium. The test tubes were sealed with para-film to prevent the evaporation of solution, then placing in a water bath of selected temperatures for the desired period of time. Controls were made for each experiment by immersing six glass strands in deionised water at each temperature. All experiments were run in duplicate in an attempt to reduce errors.

The above procedure was carried out for two different sets of experiments.

The first involved glyoxylic acid, where the glass specimens were treated in varying concentrations ranging from 0.5M-3M acid at temperatures 20°C and 30 °C for time periods of 20 and 35 days.

The second was carried out for varying time frames ranging from 4 hours to 30 days at temperatures of 20, 30, 40 and 50°C using 1.5 M malonic acid

### ***2.1.2 Post-treatment of E-glass fibre***

At the end of the desired time period, glass fibres were removed from the test tubes, rinsed with deionized water and air dried by leaving them on paper towels overnight. Tensile strength analysis was performed as detailed in 2.4. The resulting solution in the test tube, including the rinsing of the fibres, was made up to 50 mL for analysis. Cation analysis was carried out for these solutions as described in 2.5.

## ***2.2 Analysing the Passivating effect of Malonic acid***

### ***2.2.1 Preparation and Corrosion of E-glass fibre***

In this investigation, the fibres were pre-treated in 5M malonic acid at room temperature for 10, 20 and 30 days. At the end of the time periods, glass specimens were removed and rinsed in deionised water before allowing them to dry overnight on paper towels. The resulting solutions in this case were discarded.

Once fully dried, six specimens of glass fibre were again immersed in a test tube containing the corrosive acid of interest. The acids utilised in this case were; a saturated, (0.9 M) solution of oxalic acid, 1M and 3M hydrochloric acid. The specimens were treated for time periods ranging from 4 hours to 4 days for oxalic acid, and from 4 hours to 10 days in both hydrochloric acid concentrations. As before controls were set up and duplicates were made for each condition. Samples were removed, rinsed, dried and tensile tested as previously described.

## ***2.3 Analysing the Kinetics involved in the corrosion process of E-glass fibre in acid mediums***

### ***2.3.1 Preparation and Corrosion of E-glass fibre***

Samples of E-glass fibre were cut from the roving into approximately 1300mm strips weighing approximately 1.00g. Each sample was weighed accurately before being immersed completely in either 1.5M malonic acid or 3M glyoxylic acid. Treatment was carried out for varying time frames ranging from 4 hours to 30 days at temperatures 20, 30, 40 and 50°C. Controls in deionised water were set up for each temperature, and each experiment was performed in duplicate.

### ***2.3.2 Post-treatment of E-glass fibre***

Glass fibres were removed at the end of the time periods, rinsed with deionized water and air dried by leaving them on paper towels overnight. A 50 ml solution was made up using the residual solution and fibre rinses were made up to 50 mL. Solutions were analysed for the cations present as described in 2.5. Once fully dried the specimens were individually reweighed.

## ***2.4 Tensile testing of E-glass fibres***

Tensile testing was performed using LLOYD Instrument L600R fitted with a 1000N load cell with the software version 4.43 (research grade). Flat rubber pads were used to clamp

the fibre ends to minimize damage to the specimen. Care was taken to clamp the ends tightly enough to prevent the slippage of the specimen while testing.

The rate of extension or crosshead speed was set to 2mm/min, and the test length was 100mm (the length that was exposed to the medium). All the settings in the LLOYD instrument are given in Appendix A. The fibres were ‘pulled’ while the load was gradually increased until it fractured and the failure load (which is the maximum load the fibre specimens could withstand) was noted.

This part of the experiment was observed to contain the largest source of error. Some unacceptable flat lying and extended peaks were observed on the force extension graphs for reasons such as failure of stressed specimens. One other reason was fibre slippage as shown in Figure 8a. An ideal force extension plot should exhibit brittle fracture as indicated in Figure 8b (Betz, 2002). Nevertheless, the collected data was limited to those fibres which produced satisfactory force-extension graphs.

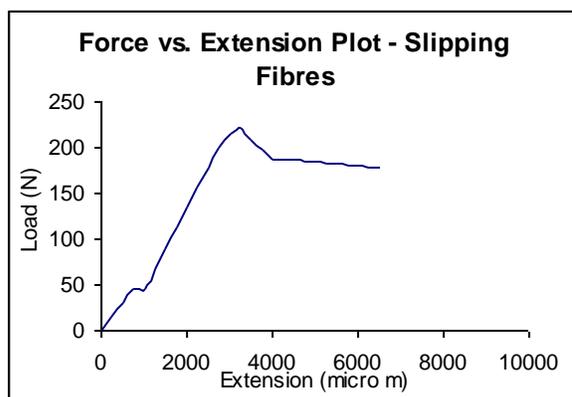


Figure 8a.

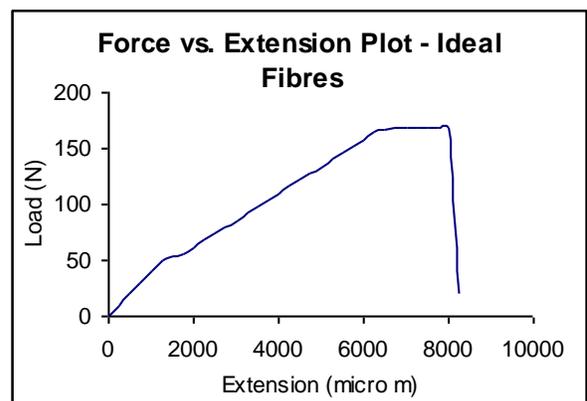


Figure 8b.

### ***2.5 Measurement of Ions leached from the glass matrix***

The cations present in the residual solution were analysed using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES and also known as ICP-AES). The samples were run on Varian Vista ICP-OES machine with an axial view. Analysis was carried out simultaneously with measurements recorded in radial mode. Samples were introduced through a series of compartments comprising of a Seaspray nebulizer, glass cyclonic spray chamber and a Teflon transfer line.

*Table 2:* The condition employed for all the elements as it was a multi-element analysis.

<b>Parameters</b>	<b>Condition Employed</b>
Wash time (1% nitric wash out at max. speed)	20 Seconds
Sample Flush Time (Sample pumped at max. speed)	18 Seconds
Stabilization delay ( Pump set to normal speed)	25 Seconds
Replicate delay time ( Normal Speed)	10 Seconds

Calibration was made using multi-element standards 0, 0.5, 1, 10, and 50 mg/L in 1% nitric acid. Since leaching was observed to be high for elements, extra standards were included for Ca, Al and B. For each sample, the instrument records three replicates with a default setting subtracting the background from the side of the peaks for each line using the peak area mode. After every 20 samples, 1 duplicate and 1 standard addition was analysed. To avoid inaccuracy by drift, standards were run in every 10 samples throughout the analysis and sample re-runs were performed after recalibration if any drift was observed.

### **3. Results and Discussion**

#### ***3.1 Analysing the Corrosive effect of Malonic acid***

##### ***3.1.1 Tensile Strength Retention***

Although Pfaender (1996, p. 168) explained the high tensile strength of glass fibres as one of the two key properties that make glass fibre suitable to reinforce plastic, the loss of this property due to corrosion of the fibre has been raised on several occasions. Hence it becomes very important to understand this behaviour of glass fibres and if at all, ways of preventing this.

Researches involving the investigation of the tensile property of E-glass fibre under the influence of acids at various conditions have been carried out before. In such investigations, the mechanical strength results have been illustrated in the past as the “% strength retention” of the glass fibres (Betz, 2002). This was calculated by comparing the maximum load the corroded fibre could withstand without breaking, to that of the control specimens (which were kept in deionized water). This procedure was followed to produce figure.10 and similar strength retention figures.

These findings revealed a unique character of malonic acid where a strength retention minimum was found around 1.5 M malonic acid. Strength loss appeared to be most at this concentrations and least at higher and lower concentration extremes. This trend has been revealed in pervious studies as well. The study by Jones and Betz (2002) showed HCl to

have a strength retention minimum at 3M, and another study by Jones and Chandler (1985) showed mesoxalic acid to possess a strength retention minimum at 1M. As no traces of insoluble salts were observed, this suggests the formation of stable complexes between the leached cations from the glass and malonic acid. This is a factor believed to affect the strength of the fibres (Jones and Chandler, 1984a). Mesoxalic acid is thought to form complexes particularly with trivalent ions such as Al and Fe due to the favourable orientation of its carboxylic groups (Figure 9a) (Jones and Chandler 1985), hence malonic acid which acquires a similar structure (Figure 9b), could exhibit a similar complexing behaviour as it too shows severe leaching of both Al and Fe.

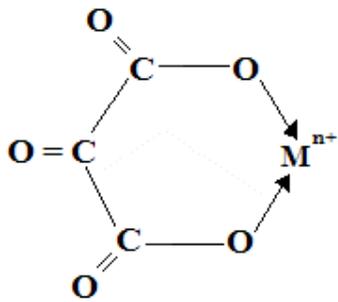


Figure 9a: Mesoxalic acid

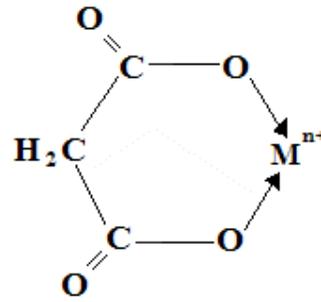


Figure 9b: Malonic acid

One section of the previous study focused on the strength retention in fibres treated with 1M malonic acid at varying temperatures and time frames. Lister and Renshaw (1990, p. 171) have stated that ‘a rough rule of the thumb which applies to many reactions at room temperature is that a 10°C rise in temperature approximately doubles the rate of the reaction’. This nicely accounts for the severe strength loss of the glass fibres as the temperature of exposure escalated.

However a decline in strength was visible as the time of exposure increased. The study however failed to reveal the real trend for prolonged time frames (figure 27-30, Appendix B). With the light of the previous research, the present study was carried out at this

specific concentration of 1.5M malonic acid where the effect of the acid was at its maximum. The aim of this portion of the study was to reinvestigate how the strength retention of the fibres varies with changes in temperature and time, especially for the longer time frames.

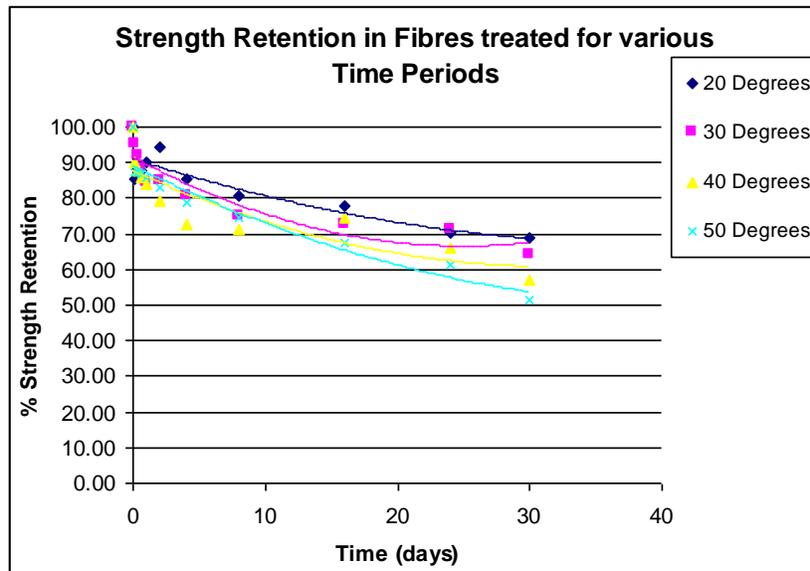


Figure 10: Strength Retention in glass fibres treated in 1.5M Malonic acid at different temperatures with varying time

In the illustration in figure 10, all four plots appear similar in that, the strength decreases rapidly during the initial time period followed by a steady decline in the rate of strength loss (denoted by the gradient) after longer periods of contact with the acid. Similar to the previous findings, the role that temperature plays in the rate of reaction can also be observed from these figures, as well in that the strength loss is minimal for fibres subjected to 1.5M acid at 20°C while the least amount of strength seemed to be retained for fibres treated at 50°C (Lister and Renshaw, 1990, p. 171). Furthermore it is clear from this plot how the strength retention varies with time during prolonged exposure to the

present corroding medium. As expected, the results show the fibres to have retained less and less of its strength as the time of exposure lengthened. An ion exchange reaction has been proposed by Jones and Chandler (1984b), where they suggested the hydrogen ions of the acid to replace the cations in the glass matrix. The kinetics of a chemical reaction in a solution is significantly affected by the motion of the molecules in liquid state (D.W. Oxtoby and N.H. Nachtrieb, 1990, p.662). This ion exchange reaction is suggested to be a mechanism governed by diffusion (Jones and Chandler 1984b). Hart (2001, p. 42) explains that diffusion in liquids is a slow process hence the time of exposure has a significant effect on the strength loss of the fibres.

### ***3.1.2 Leaching of Cations***

A comparison of percentages of the cations leached out was carried out in the previous years study (table 8; Appendix –C), from which it was gathered that the non-silicious components of E-glass came up to about 45% of its total weight. Since Ca and Al oxides alone make up around 35% by weight of the glass, leaching of these two ions has been long associated as a major cause of acid corrosion (Kumosa and Qui, 1996). The finding exhibited similar behaviour which explained the corrosion by malonic acid mainly in terms of Ca and Al. Cation analysis carried out showed a direct correlation with the corresponding tensile strength plots and the leached cations. The strength loss appeared to be a consequence of leaching of cations, especially to that of Ca, Al from the glass matrix. Both Ca and Al are believed to readily form stable complexes with the malonic acid similar to that proposed for mesoxilic acid (figure 9a and 9b) as there structures

show a clear resemblance with that of mesoxilic acid. In addition to Ca and Al, it should be noted that B showed a very unusually high percentage (about 96.66%) of leaching from the glass matrix. Boron is known to exist in the silica network and is believed to have a stabilising effect and have not been found to show significant leaching in previous studies (Jones and Betz, 2003). However, as boron is a member of group three, the possibility of it forming complexes with malonic acid was proposed in the study. Although cation analysis was not performed in the present investigation of malonic acid, with clear correlations observed between the tensile strength loss and cation leaching in the previous year's research, leaching of cations have been strongly expected to match the findings of the tensile strength retention.

### ***3.2 Analysing the Corrosive effect of glyoxylic acid***

#### ***3.2.1 Tensile Strength Retention***

Strength retention in glass fibres exposed to glyoxylic acid has been briefly explored previously by Chandler and Jones and Chandler (1985b). They discovered this acid to have a much less deteriorative effect on the fibres compared to oxalic and mesoxalic acids, whereas it appeared to be in a similar range in corrosiveness as malonic acid. Tensile properties of the E-glass was analysed after exposing the samples to 3M glyoxylic acid for 20 and 35 days at 20°C and 35°C to produce the results in figure 11a and 11b.

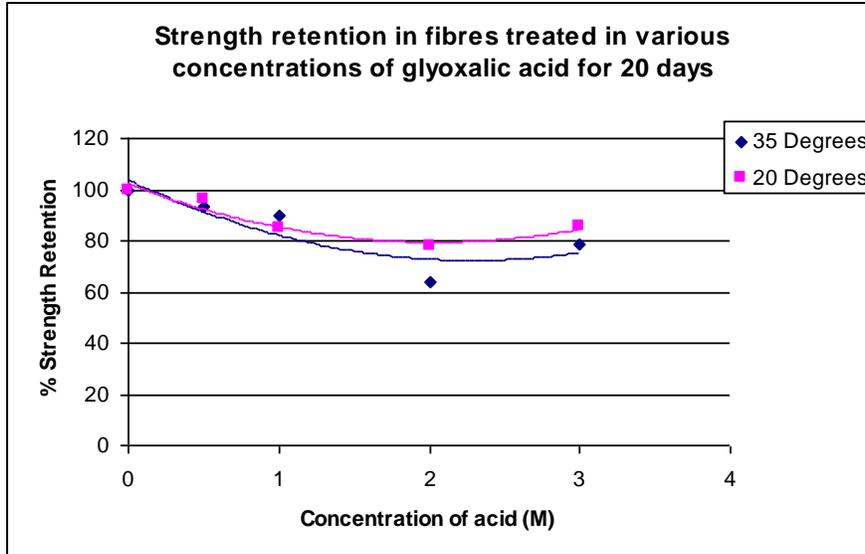


Figure 11a: Strength retention in glass fibres treated in various concentrations of glyoxylic acid at 20 and 35°C for 20 days.

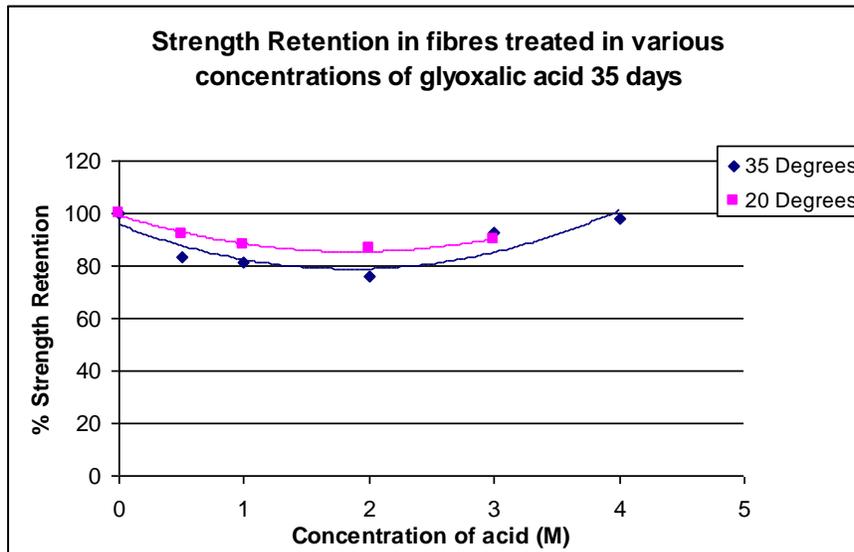


Figure 11b: Strength retention in glass fibres treated in various concentrations of glyoxylic acid at 20 and 35°C for 35 days.

The very first observation that should be noted from these figures is that the glass fibres retained 70% or more of its strength after exposure to glyoxylic acid for the time periods

and temperatures employed in this research. This confirms the results discovered by Jones and Chandler (1985). In fact it appears to have an even less corrosive effect on the glass fibre when compared to malonic acid. It can also be observed that the glass fibres retained more strength when they were exposed to glyoxylic acid at 20°C compared to the higher temperature of 35°C. The role of temperature behind the chemical kinetics clearly explains the increase in the rate of reaction alongside the rise in temperature (D.W. Oxtoby and N.H. Nachtrieb, 1990, p.662). Although this relationship is apparent additional work could be done to explore this correlation further using more temperature ranges.

Looking at the relationship between the glyoxylic acid concentration and tensile strength retention, an important point to note is the minima observed around 2M glyoxylic acid for all the experimental conditions employed. This observation is similar to the trend observed in the previous analysis of malonic acid as well as HCl, oxalic and mesoxalic acids discovered by Jones and Betz (2003) and Jones and Chandler (1986) respectively. The reason for the minima in the present results for glyoxylic acid can be explained with similar reasoning as that for malonic acid, mesoxalic acid and oxalic acid. As the acid is relatively weak, the H<sup>+</sup> ion concentrations are too low at lower acid concentrations to bring about the ion-exchange reaction. At the higher acid concentrations, the anion of the acid is said to bind to certain cation on the glass surface preventing further dissolution hence inhibiting corrosion (Jones and Chandler, 1985). Lastly, although only two time frames were employed for this study a difference between the strengths for these time frames can be interestingly noted. Figure 12a and 12b exhibits this correlation.

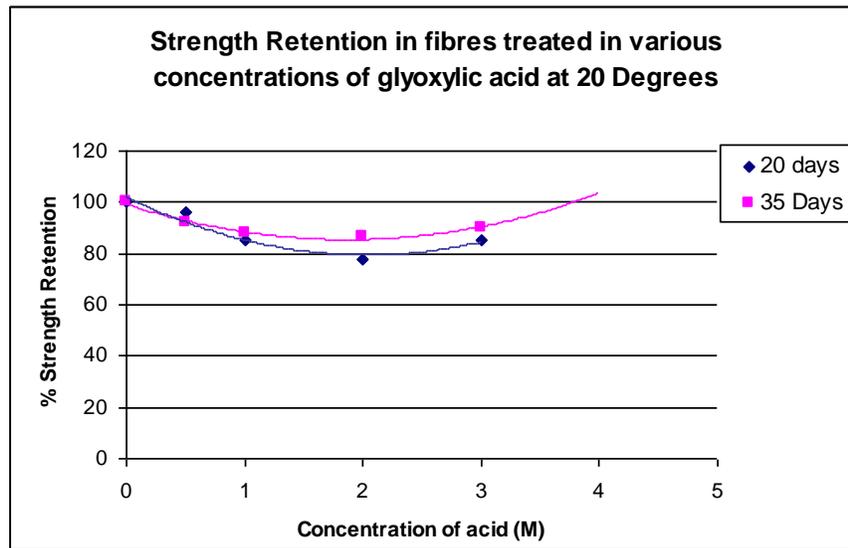


Figure 12a: Strength retention in glass fibres treated in various concentrations of glyoxylic acid at 20°C.

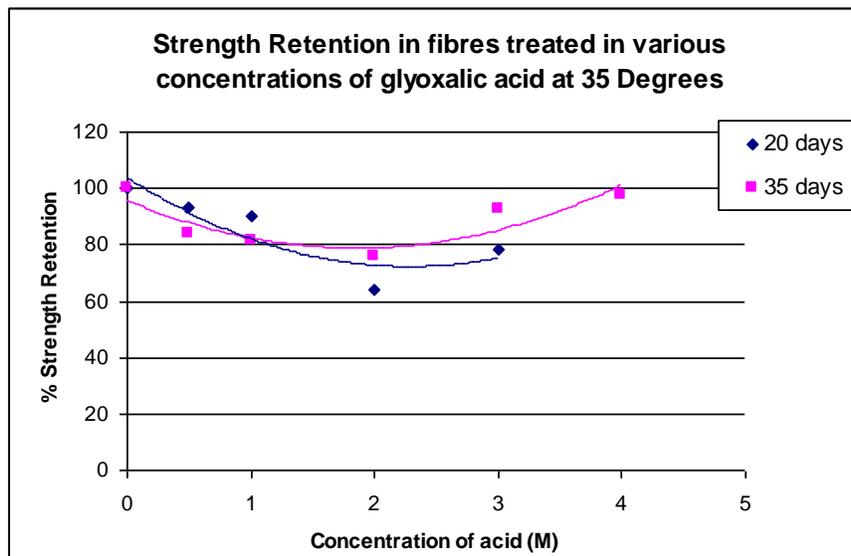


Figure 12b: Strength retention in glass fibres treated in various concentrations of glyoxylic acid at 35°C.

An interesting note that can be made from figure 11a is that the longer time frame (35 days) allowed the retention of more strength compared to the shorter time frame (20 days). However, at the higher temperature (figure 12b) the fibres treated for 20 days seemed to have retained more strength at concentrations below 1M while those treated for 35 days retained more strength at higher concentration of glyoxylic acid. Although these results may fall in the range of experimental uncertainty, further investigation needs to be carried out preferably using larger range of closer time frames in order to reach a definitive conclusion.

### *3.2.2 Leaching of cations*

Investigating the leaching patterns of ions from the glass matrix at various conditions could provide information vital to understand the corrosion process. The accepted mechanism for years has been the ion-exchange process where the hydrogen ion from the acid replaces the cations from the glass matrix (as shown in equation 1). Here the H<sup>+</sup> ion is regarded to be playing the important role and to be the determining factor for the extent of this process.



The anion of the acid has also been found as an important factor in leaching of the cations. The cation could either form insoluble salts with the anion or they could form neutral or anionic species that is believed to favour the forward reaction (Jones and Chandler, 1985)

Figures 13a and 13b shows the variation of ions dissolved in the solution for experiments conducted at 20°C for 20 and 35 days for varying concentration of glyoxylic acid (refer figures 27 and 28; Appendix-D for similar plots for experiments conducted at 35°C for 20 and 35 days).

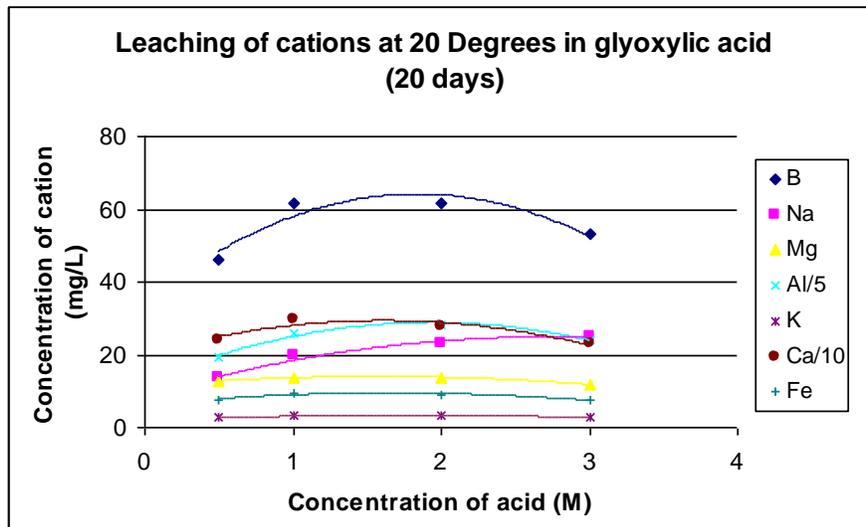


Figure 13a: Leaching of ions at 20°C for 20 days

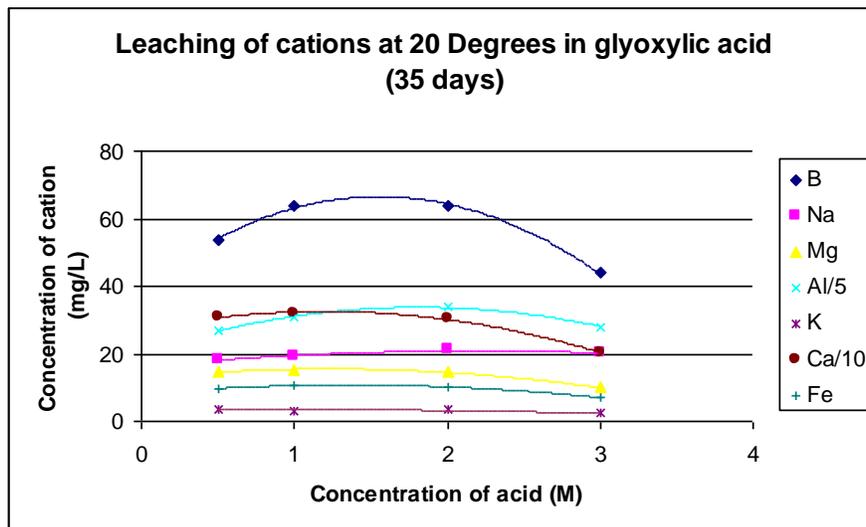


Figure 13b: Leaching of ions at 20°C for 35 days

To illustrate the trend in all elements, on the same graph, Ca and Al have been reduced by factors of 10 and 5 respectively. These plots illustrate how each of the seven ions in the glass matrix is leached out at each temperature while the acid concentration of the corroding medium is gradually increased. All seven ions were present in the residual solution suggesting that all seven cations have been leached out from the glass matrix, however the general trend based on these plots are that the leaching of all seven ions; B, Na, K, Fe, Mg, Ca and Al were increasing at a steady rate (denoted by the gradient of the graphs) as the concentration of glyoxylic acid increases to 2M, beyond this concentration however, a steady decline in the cation concentration was observed. A contradiction to this trend is recognised for the plot made for the conditions 35°C and 35 days especially for Ca, B and most of the ions while Al seem to show its highest ion concentration at 2M glyoxylic acid similar to the other plots. It should be noted here that ICP-MS is not usually adapted for the analysis of Ca ions although it was utilized in this situation. Furthermore it is highly unlikely for ICP\_OES to produce results with large deviations, as standards were run in between to check its performance and where necessary the samples were re-run. However, cation analysis could be redone or analysed using another procedure for these solutions in the hope of overcoming this inaccuracy.

Based on the general trend, it can be observed that B, Al and Ca are leached out at a higher rate and reached a much higher maximum concentration in the left over solutions compared to the rest of the cations. In fact the highest is shown by Ca and Al followed by B. These results reflect that of the previous findings where Ca and Al leaching coincides with the strength loss (Kumosa and Qui, 1997). In order to further explore the leaching

shown by the cations, the percentages of the cations leached were calculated for one of the conditions used (E-glass exposed for 20 days at 35°C for 2M glyoxylic acid).

*Table 3:* The percentage leaching of cations at 35°C exposed for 20 days for 2M glyoxylic acid.

Cation	Concentration (mg/L)	Mass in 50ml solution	Mass of ion in 0.8g fibre (mg)	Relative wt (%) Cation leached
Al	203	10.15	63	16.11
B	114.5	5.725	10.6	54.0
Ca	422	21.1	136.6	15.44
Fe	13.65	0.6825	2.16	31.59
K	4.425	0.2213	7.04	3.14
Mg	19.9	0.995	8.56	11.62
Na	27.4	1.37	6.08	22.5

From the table it is clear most leaching was shown by B followed by Fe and Na unlike the expected Al and Ca. Here again B revealed its unusual leaching behaviour which was exposed recently with malonic acid that contradicted the behaviour B exhibited with mineral acids. Boron showed 95.66% of its ions to have leached out from the matrix for malonic acid in the previous research. The percentage has fallen for glyoxylic acid as expected. Strength retention results showed this acid to have a less corrosive effect on the glass fibre compared to malonic, oxalic or even mesoxalic acid. Although this percentage is low compared to malonic acid, it is still high enough and contrasting against most of the previous findings. This extreme leaching of B is regarded as unusual especially as B

is believed to exist in the silica network and thought to have a stabilizing effect (Kumosa and Qui, 1997).

As discussed before, malonic acid is believed to form stable complexes with the cations similar to those proposed for mesoxilic acid by Jones and Chandler (1985b). Although the structure of glyoxylic acid is slightly different, similar complex formation is highly likely (figure.14), as the complex formation is believed to be particularly favourable with trivalent ions due to the favourable orientation between the two. This explains the high percentage leaching shown in Fe and B (Jones and Chandler, 1985b) and same could be said for Al although it showed a smaller amount of leaching than was expected. Iron is known to form soluble complexes with the corroding medium which further explains the high levels of leaching from the glass matrix (Jones and Betz, 2004).

As for Ca, which occurs as interstitials (Kumosa and Qui, 1997) rapidly diffuses through the silica network and exchange with the H when exposed to acidic medium. However Ca too showed a smaller percentage than was expected possibly due to the mild corrosive effect shown by this acid.

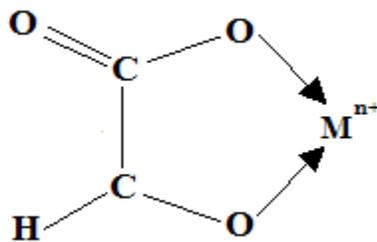


Figure 14: Structure of possible complex formed between cations and glyoxylic acid

The basic trend is consistent with that exhibited by the tensile strength retention. In Figures 11a and 11b the strength retention decreased steadily until 2M glyoxylic acid after which an increase in strength retention was observed. Although one plot shows minor contradiction which should be further analysed for clarification, it can be concluded that these two sets of results collectively suggest a correlation between the rate of cation dissolution from glass matrix and loss of tensile strength of the glass fibre. Kumosa (2001) associated the strength loss of these fibres to the loss of Ca and Al ions from the glass matrix as their compounds make up 35% of the glass fibre. As the percentages of these two cations leached was minute compared to the previous findings, it clearly explains the reason for the large amount of strength retained in the fibres that were treated in glyoxylic acid.

### ***3.2.2.1 Leaching of cations at varying temperatures and time frames***

Only two different temperatures and time durations were employed in this study, however analysing how the leaching of cations varies with these two factors could be beneficial as under natural conditions the fibres could be exposed to any of these temperatures for any time period.

The effect of temperature on leaching of most of these cations showed a clear trend. Figures 15a and 15b exhibit how boron leaching varies with temperature for both time durations (similar plots for the rest of the cations in figures 29- 40; Appendix-E).

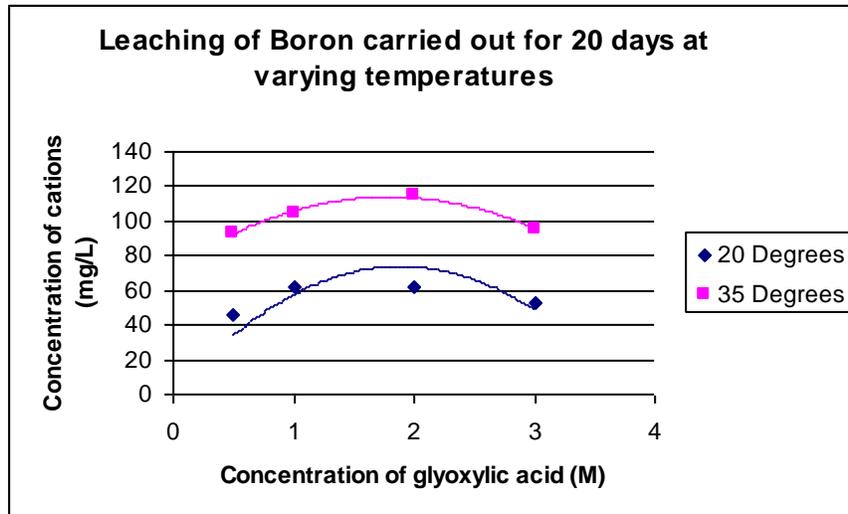


Figure 15b: How B leaching varies with temperature when carried out for 25 days

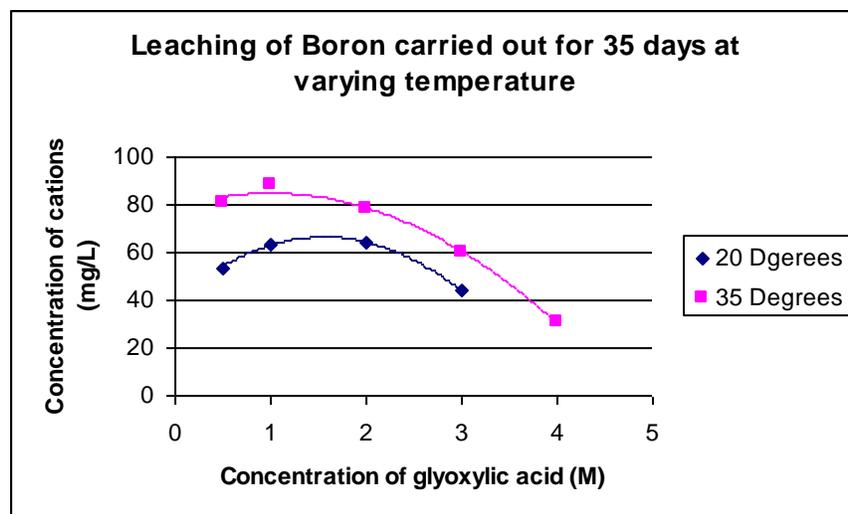
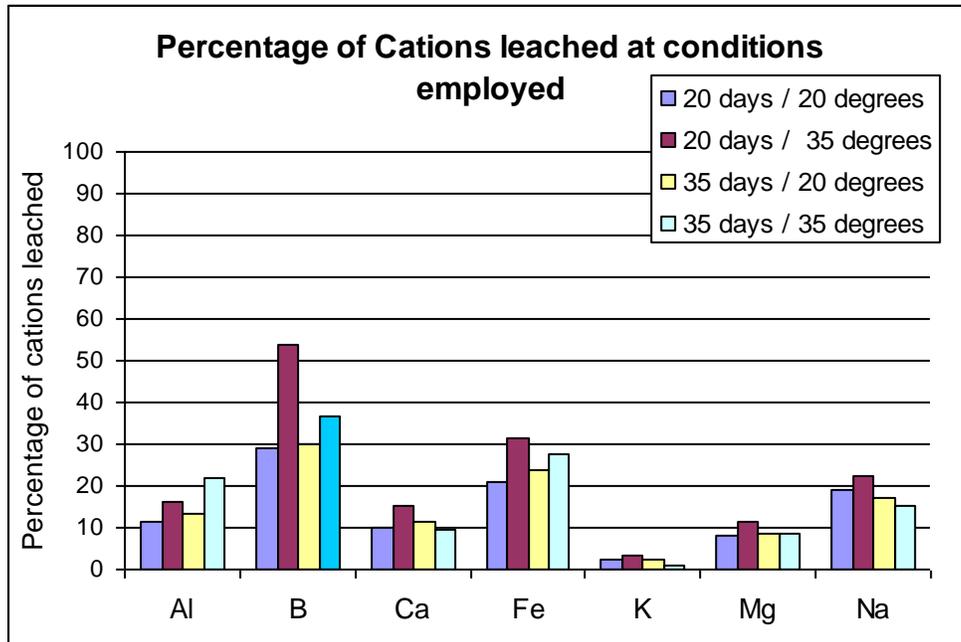


Figure 15b: How B leaching varies with temperature when carried out for 35 days

Firstly it should be noted that the leaching of B is higher at 35°C throughout the concentration range of glyoxylic acid employed compared to the lower temperature. A similar trend is displayed by the rest of the cations where the leaching of the ion appeared to be more at the higher temperature. The reason for this lies in the simplest chemistry involving the kinetic theory. According to an article on ‘activation energy’, (Purdue

University, 2004, p.1 of 6), the rate of a chemical reaction usually depends on the temperature at which it is performed, the higher the temperature the larger the number of collisions is expected to be. The second observation is that the concentration of leached ions reached a maximum at around 2M glyoxylic acid. This behaviour was well explained for perchloric acid by Jones (1995) and it suffices for glyoxylic acid. It was stated by Jones(1995) that at the lower acid concentration, the ion exchange reaction would be extremely slow owing to the low concentration of H ions , on the other hand at higher acid concentrations the anion of the acid could bind to certain cations on the surface slowing down the rate of reaction. However the plots do not show this to be true for all the cations at these conditions. Re-analysing the cations could either confirm or reject the second observation made, if confirmed establishing a similar correlation between the tensile strength loss and the amount of cations leached from the glass matrix as in the previous research.

The bar chart on figure.16 further elaborates the effect temperature on the leaching of cation on both time durations employed.



*Figure 16:* Percentage leaching of cations at both temperatures and time periods employed

From this plot, the effect of temperature is very clearly shown by all seven cations when treated for 20, while only Al, B and Fe followed this trend when the treatment time was 35 days. Reanalysing the rest of the ions could produce matching data proving the temperature to be an enhancing factor in the corrosion of E-glass fibre.

A second set of plots was further made to establish the relationship between the duration of exposure of glass specimens to the corroding medium and the leaching of cations at these conditions. Two of these plots are shown in figures 17a and 17b (similar plots for the rest of the ions and condition in figure 41-52; Appendix-F)

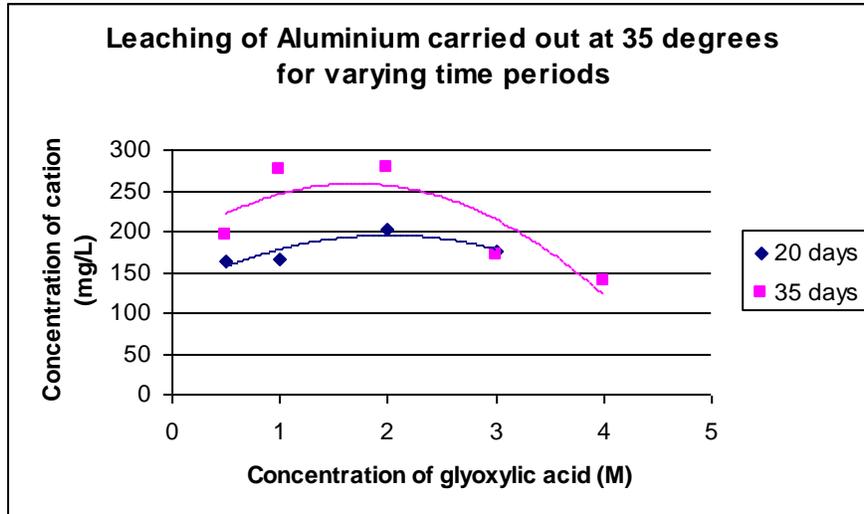


Figure 17a: How Al leaching varies with time at 35°C

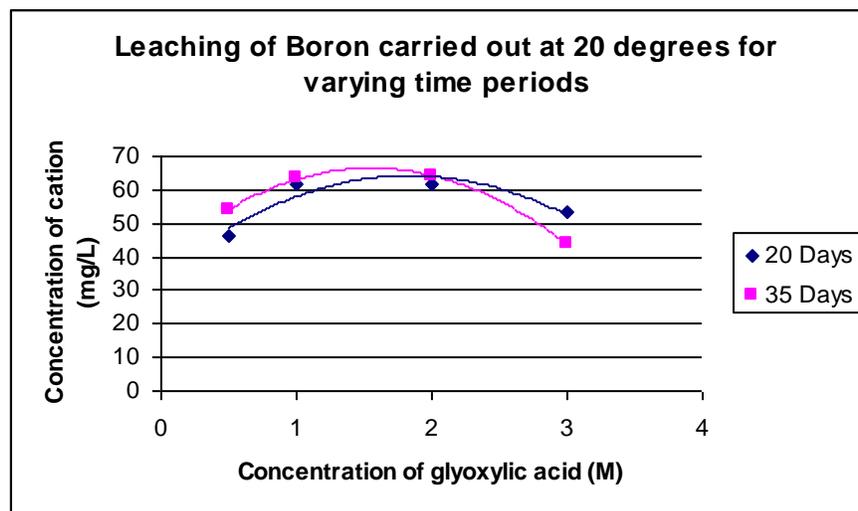


Figure 17b: How B leaching varies with time at 20°C

It was only the leaching of Al that showed a clear trend where more ions appeared to have leached at longer exposure times at both temperatures. The only other ion showing this was Ca at 35°C. The rest of the plots failed to exhibit a consistent trend with most of the plots showing concentration of the cations overlapping at various glyoxylic acid concentrations. It is further observed that the maxima were not observed around 2 M

glyoxylic acids for all the conditions. Further work needs to be carried out for a better understanding of how time effects the glass fibres exposed to glyoxylic acid.

### 3.3 Analysing the Passivating effect of malonic acid

Malonic acid, although known as a mild organic acid, is known to corrode E-glass fibre (Jones and Chandler, 1986) and studies have been carried out in the past to analyse its effects. Figure 18 reveals the results of a further attempt to analyse the effect of malonic acid by the present researcher.

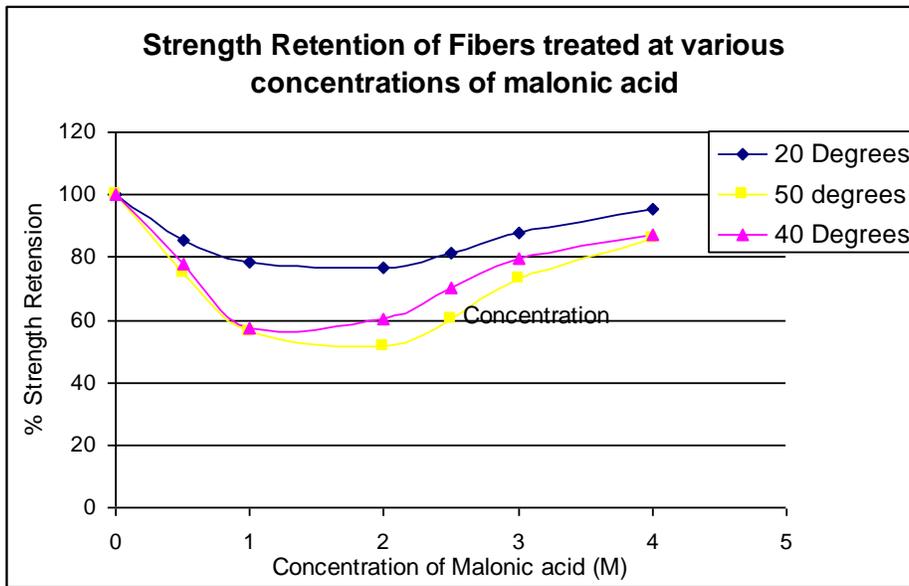


Figure 18: Tensile strength retention in fibres treated various concentrations of malonic acid.

In the figure, a strength retention minimum is observed around 1.5M of this acid. An interesting observation that cannot be overlooked is that the E-glass appeared to retain more and more of its strength as the concentration of malonic acid was increased from 1.5M to reach almost 100% strength retention around 4M malonic acid. Binding between

the malonate ion and the cations of the glass at the surface could be hindering further diffusion of cations and diminishing the ion exchange reaction resulting in the inhibition of strength loss (Jones, 1995). This interesting observation requires further investigation which might prove to be beneficial in this field of study. The aim of this portion of the research was to analyse the passivating effect of malonic acid. Hence with the light of this result, 5M malonic acid was employed for pre-treatment of E-glass fibre in the present research. The specimens were then post treated with HCl and oxalic acid for investigation purposes as the effect of these acids on E-glass fibre has been previously studied. The corrosive effect of hydrochloric acid on E-glass pre-treated in 5M malonic acid (for various time periods) is illustrated in Figure 19a and 19b.

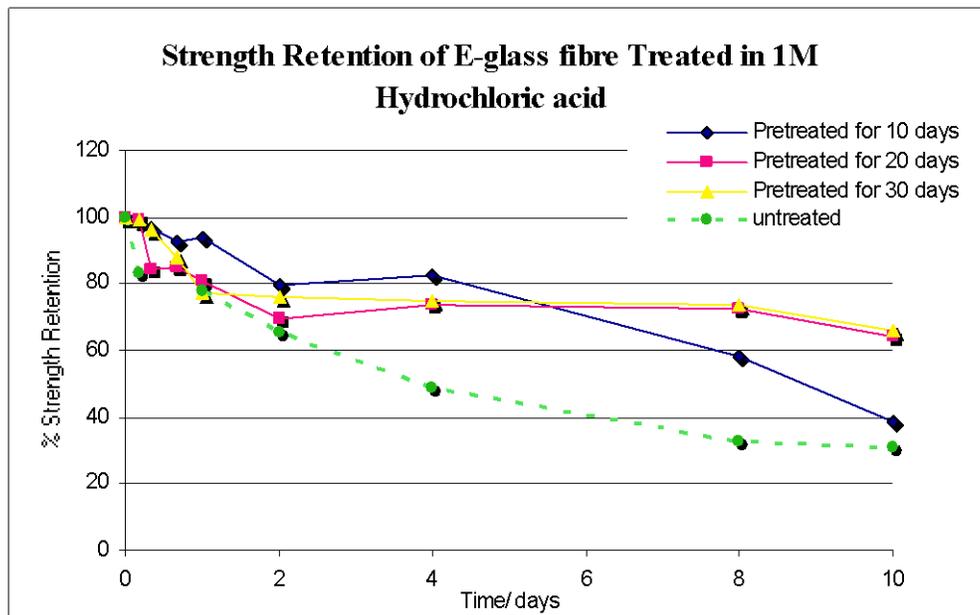


Figure 19a: Strength Retention in fibres after exposure to 1M HCl with and without pre-treatment in 5M malonic acid

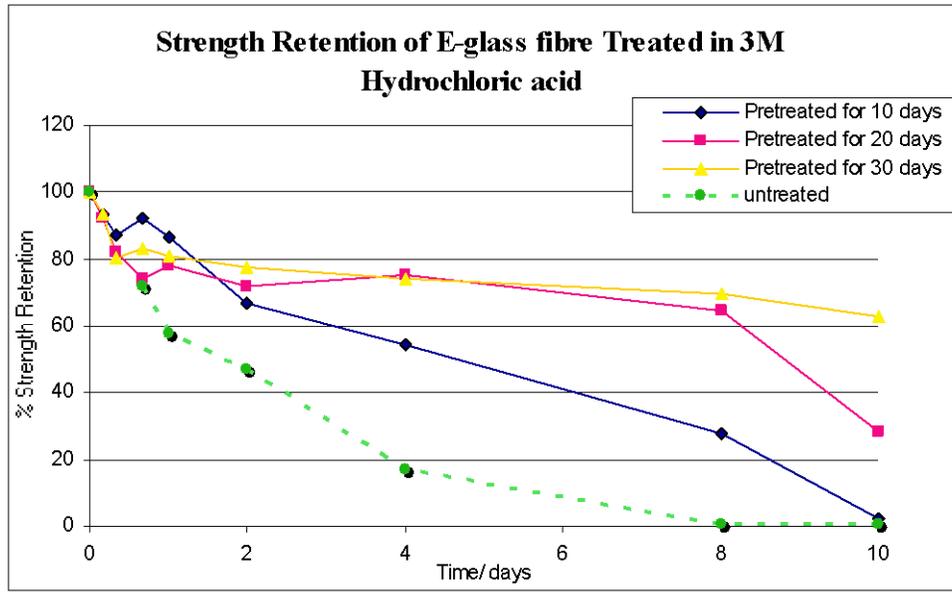


Figure 19b: Strength Retention in fibres after exposure to 3M HCl with and without pre-treatment in 5M malonic acid

These two concentrations of hydrochloric acid utilized in the present study have been explored previously by Jones and Betz (2002). According to Jones and Betz (2002) the two concentrations of acid employed would not show significant difference in corrosiveness as the operating temperature was room temperature within a short duration of time (figure 53; Appendix-G), however increasing the time clearly shows a decrease in the retained strength when exposed to 3M HCl (figure 54; Appendix-G).

The aim of this section of the research was to explore the passivating effect (if any) of malonic acid. A vast difference in strength retention can be observed between the fibres pre-treated in malonic acid and the fibres not exposed to this acid (untreated) proving that malonic acid creates a passivating effect on the glass fibres. Secondly the considerable effect of increasing the pre-treatment time duration from 10 to 20 days on the strength retention should be noted. However the increase from 20 to 30 days time duration does

not seem to show significant difference in strength retention within shorter time frames of exposure to the corrosive acid. The cause of passivation effect (which is most likely due to the binding of malonate ion to particular cations at the glass surface) seems to have taken place by the time the fibres were exposed for 20 days hence lengthening the time does not prove to be significantly advantageous. However increasing the time of exposure to HCl could better show the effect of increasing the pre-treatment time.

For the fibres exposed to 1M HCl after being pre-treated in malonic acid for 10 days, a gradual and steadier strength loss is observed as the time of exposure increased. This trend can be seen to continue until 8 days after which a much rapid rate in strength loss can be observed. Furthermore it should be noted that about 70% of the strength was retained within the 8 days of exposure to 1M HCl, while 0% strength retained when directly exposed to this acid.

When the concentration of HCl exposed was increased to 3M, a very rapid rate in strength loss can be seen during the initial hours of exposure (denoted by the gradient of the plot). However from 16 hours of exposure onwards a much slow and steady strength loss can be observed until the duration of exposure to corrosive acid lengthened to 8 days. Beyond 8 days the rate of strength loss can be seen to increase yet again. It should be noted here that unlike in the case of 1M HCl, only about 40% of strength is retained in the fibres within the 8 days of exposure to the most severe acid medium of 3M HCl. Nevertheless it should be noted that the fibres pre-treated in malonic acid retained a significant amount of strength compared to the untreated fibres.

For the pre-treatment time duration 20 and 30 days, a rapid loss of tensile strength is observed initially when exposed to both concentrations of HCl. This rapid loss of strength continues until 1 day when exposed to 3M HCl, while it goes on for 2 days in the case of 1M HCl. For both concentrations, the rapid strength loss is however followed by a very slow and much steadier rate of strength loss until the exposure time reached 8 days beyond which the rate appears to change for a second time. It is very interesting to note that around 70% of the strength is retained in the fibres throughout the period of exposure in the corrosive acid except for the experiment where the specimens were pre-treated for 20 days and exposed to 3M HCl and kept for over 8 days.

Corrosion of e-glass fibre is a complicated process involving the role of the acid as well as the strength of the acid (Kumosa and Qui, 1997). The reason for the passivation is presumed to be linked to the ability of the anion of the acid to form complexes with some cations of the glass on the glass surface (Jones and Brunt, 2004). The initial loss of strength on the exposure to the severe corroding acid medium can be understood despite the passivation due to the destructiveness nature of the acid. Based on the presumption of anion binding, the surface bound malonate ion can be observed to inhibit corrosion initiated by HCl only to a certain time period (8 days). An onset of corrosion is observed as a result of the removal of malonate ions from the surface, as it was observed for perchloric acid (Jones and Brunt, 2004).

The corrosive effects of HCl have been studied previously by Jones and Betz (2004) where they discovered 3M hydrochloric acid to have severe corrosive effect on glass fibres on prolonged exposure (figure 54; Appendix –G). Their research explored the effect of 3M hydrochloric acid on E-glass fibre within a short time frame, however from the figure it is apparent that between temperatures 20 and 30 °C only 20-40% strength of the glass is retained by the time the fibres were exposed for only 3 or 4 days. In addition to the above findings, the strength retention results produced by the untreated fibres in figure 19a and 19b, clearly illustrates the immense amount of strength retained in the fibres pre-treated in 5M Malonic acid (especially for 20 or 30 days) which otherwise would have been lost in the corrosive HCl solution. Future work needs to be carried out to analyse the passivating effect of malonic acid from various aspects as this procedure could prove to be beneficial in this field.

Jones and Chandler (1986) suspected oxalic acid as a predominating species in the polymer degradation process. This acid was found to have a severe corrosive effect on the glass fibre even after 7 days of exposure (Jones and Chandler, 1986). Hence the time frame in the present study was limited to only 4 days as shown in figure 20.

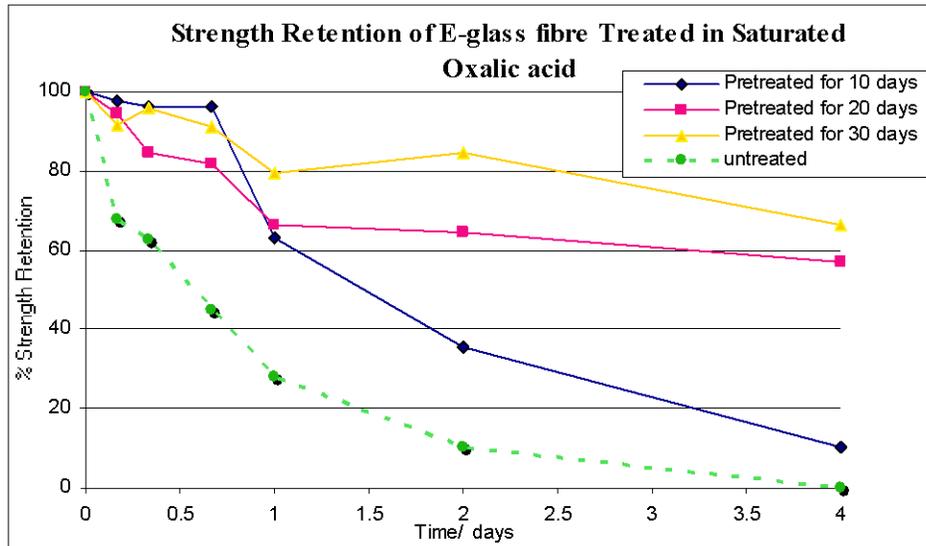


Figure 20: Strength Retention in fibres after exposure to saturated oxalic acid with and without pre-treatment in 5M malonic acid

The existence of passivation through pre-treatment in malonic acid can be clearly observed. However, the inhibition produced through 10 days of pre-treatment appears to be extremely short lived with the destructiveness of the acid taking over shortly after exposure to oxalic acid. While a striking retention of strength can be observed for 20 days pre-treatment and more so for 30 days pre-treatment. The strength loss immediately after exposure is apparent although not as severe as what was observed for HCl. However 60% strength retention can be observed when pre-treatment time was 20 days while almost 80% is reached when it was increased to 30 days. These values for strength retention are significant improvements compared to 0% strength retention in fibres directly treated in oxalic acid for the same time duration. Clearly lengthening the pre-treatment time allowed stronger binding or better adherence of the complexes to inhibit the corrosion significantly. Further work needs to be carried out focusing of the effect of lengthening

the pre-treatment time beyond 30 days and lengthening the treatment time in oxalic acid to investigate the duration of the inhibition induced by malonic acid.

Unlike perchloric acid (figure 55; Appendix-H) which showed to have a short lived inhibition effect on the glass fibre (Jones and Brunt, 2004), about 60 – 80% of strength retained throughout the exposure time for all the conditions when the pre-treatment was carried out for 30 days in 5M malonic acid. It is highly likely that malonic acid could inhibit the corrosion of E-glass fibre to a greater extent and could prevent the attack of destructive acids. Hence it is vital to further explore this aspect using longer pre-treatment time frames to analyse the possibilities of malonic acid protecting the glass fibres exposed to corroding mediums for prolonged time periods.

### ***3.4 Analysing the Kinetics involved in the corrosion process of E-glass fibre in acid media***

#### ***3.4.1 Weight change in fibres treated in 1.5M malonic acid and 3M Glyoxylic acid at varying temperatures and time frames***

This section of the research was mainly focused on analysing the weight loss and leaching of cations from E-glass fibre in relation to the time of exposure when the fibres were exposed to 3M glyoxylic acid and 1.5M malonic acid. The aim of this portion of the study was to put forth a better understanding behind the degradation process between the acid and the glass fibre. To some extent it is believed that the weight change could show the rate of reaction throughout the time period of analysis. This aspect was briefly looked

at by Kumosa and Qui (1996) where they analysed the effects of oxalic, hydrochloric, nitric and sulphuric acids at various concentrations. Their research revealed oxalic acid to have caused most weight loss in E-glass fibre compared to the mineral acids employed in the study. Furthermore they discovered that as a general trend the weight loss was observed to be more as the concentration of the acid was increased.

Analysis involving mass or weights can generally be subjected to a lot of inaccuracy especially as the weight of the subjects have very minute figures hence settlement of dust or other particles in air could as well alter the weights significantly. Nevertheless this approach was utilized in the hope to explore the kinetics behind the reactions that would take place when E-glass fibre is exposed to 1.5M malonic acid and 3M Glyoxylic acid.

Figure 21a to 21d exhibit how the weight of the fibres changes in relation to the duration of exposure to malonic and glyoxylic acids.

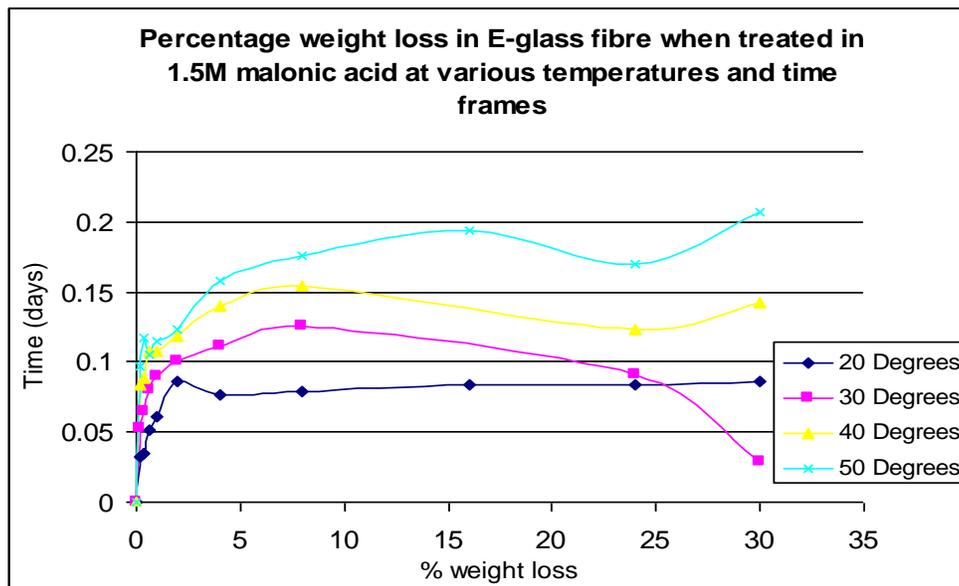


Figure 21a: Percentage weight change in fibres pre-treated in 1.5M malonic acid for various time periods

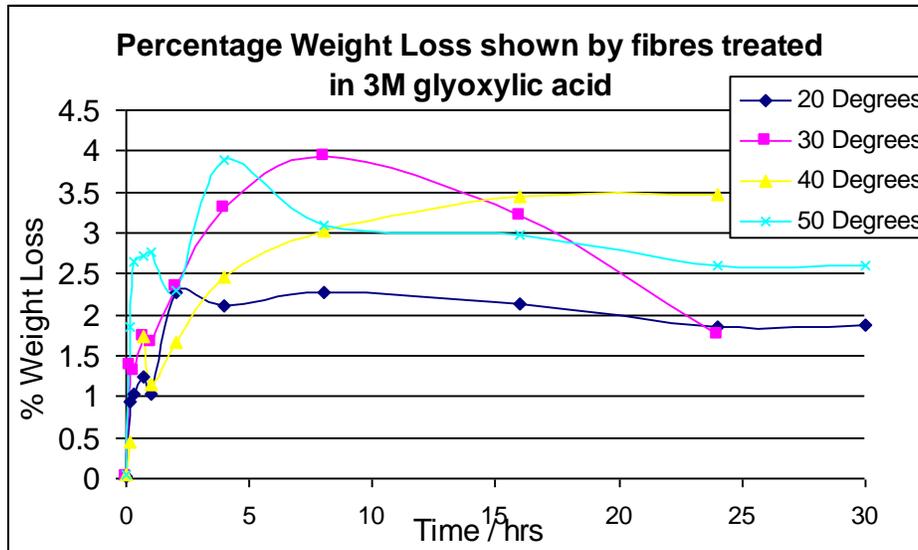


Figure 21b: Percentage weight change in fibres pre-treated in 3M glyoxylic acid for various time periods

Observing the weight losses having been the aim of this experiment, in the plots that follow in this section, the weight changes observed for the three longest time frames have been excluded for both acids as the weights appeared to have increased for these time frames. Jones (1995) associated the binding of anions to the cations on the surface of the glass matrix as the reason for the strength retention and the lower cation count in the residual solution at the higher concentrations for perchloric acid. This presumption was put forth under the implication brought for perchloric acid by Jones (1995). Based on the findings of the present research, a similar line of reasoning has been assumed for both malonic acid as well as glyoxylic acid for these time frames.

It is interesting to note the vast difference in the percentage scale between these two acids. The maximum weight loss reaches only about 4% for glyoxylic acid while that for malonic exceeded 20%. For malonic acid, the weight loss of fibres gradually appears to

increase with time for all temperatures, however as expected the rate of reaction appears faster at the beginning. In addition, the role of the temperature is apparent as the weight loss appears more at the higher temperatures for each of the observed time frames

A similar observation can be made for glyoxylic acid, with a rapid weight loss initially followed by a rather steady loss, while an increase in temperature showed an increase in the rate of weight loss.

In order to understand these trends and the reason behind them, it should be viewed from a 'Chemical Kinetics' perspective. The University of Waterloo (n.d., p.1 of 4) defines chemical kinetics as the study of chemical reactions in relation to the rates, variables, intermediates as well as arrangement of the atoms involved. LaFaro and Cooper (n.d., p.1 of 4) also explains chemical kinetics as a topic illustrating the connection between chemistry and mathematics through the interpretation of experiments in terms of mathematical models. How chemical reactions takes place at molecular level could be fully understood through combination of the experimental data with these models (LaFaro and Cooper, n.d., p.1 of 4). These models are chemical equations for the rates at which the reactants are consumed or the rates which the products would be formed. In the present study, the change in weight of one of the reactants, namely the glass fibre was observed with time and used to predict the behaviour. Atkins (1986, p.693) described a reactant following the first order rate law to obey the differential equation (2).

$$-d[A]/dt = k[A] \tag{2}$$

*Where A = reactant, t = time*

$$[A] = [A]_0 e^{-kt} \quad (3)$$

Where  $[A]_0$  = initial concentration of A,  $t$  = time of exposure,  $k$  = rate constant

$$\ln ([A]/[A]_0) = -kt \quad (4)$$

Where  $[A]_0$  = initial concentration of A,  $t$  = time of exposure,  $k$  = rate constant

Equation (2) is referred as the first order rate law as the rate is proportional to the first power of the reactant, in other words a rate which is proportional to one of the reactants (LaFaro and Cooper, n.d., p.1 of 4). Integration of this differential equation gives equation (3) which has been utilized in this section of the research in an attempt to obtain the order of the desired reaction. Figure 22a and 22b shows the first order plots or the figures obtained by the values generated using equation (3) on the weight loss data achieved against time. The value of the constant  $k$ , was fixed at 0.05 in both plots.

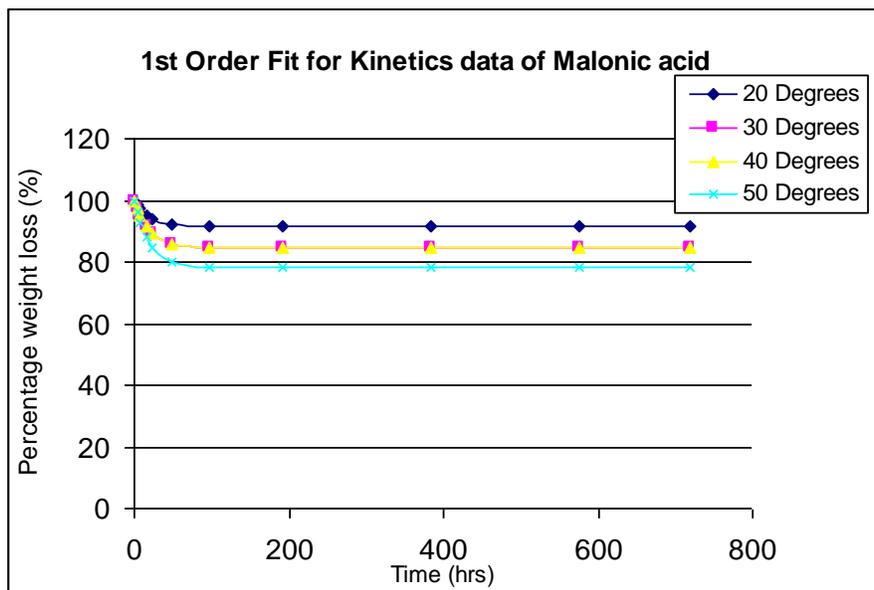


Figure 22a: Weight loss against time using equation (3) for kinetic data achieved when treated with malonic acid

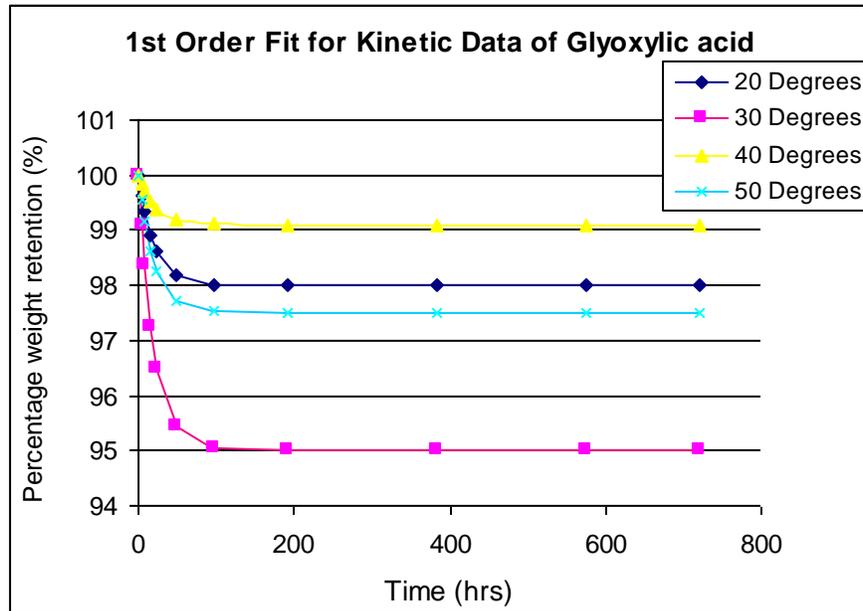


Figure 22b: Weight loss against time using equation (3) for kinetic data achieved when treated with glyoxylic acid

Based on the results, corrosion reaction of malonic acid is possible to follow the first order mechanism and therefore expect the rate of corrosion to have a proportional relationship with the concentration of glass fibre.

In addition, plots were also generated using equation (5) where  $1/[\text{weight}]$  at time  $t$  was plotted against time for obtain the figures 22c and 22d. According to Russell (1992, p 490) if a plot of  $1/[A]$  against time produces a straight line with a slope  $k$ , it denotes that the proposed reaction follows the second order mechanism.

$$1/[A]_t = kt + 1/[A]_0 \quad (5)$$

Where  $[A]_0$  = initial concentration of A,  $t$  = time of exposure,  $k$  = rate constant

(LaFaro and Cooper, n.d., p.1 of 4)

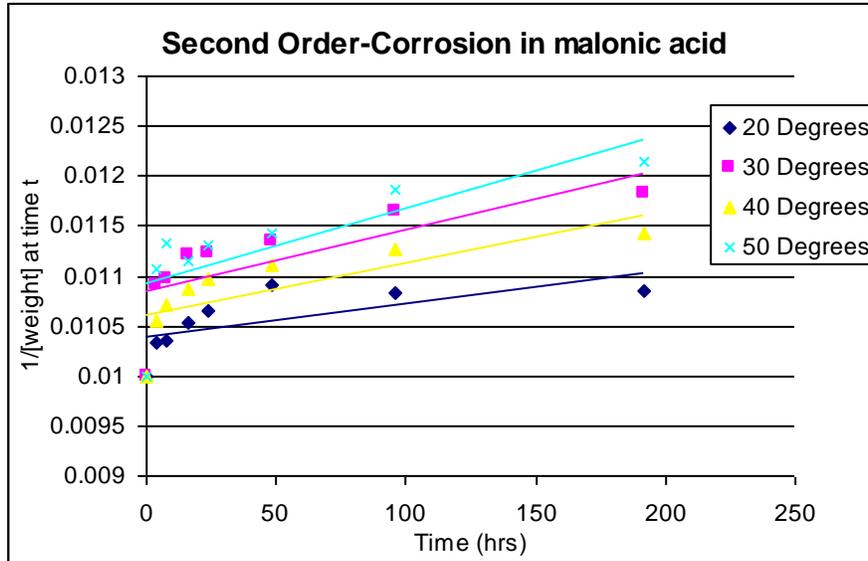


Figure 22c: Weight loss against time using equation (5) for kinetic data achieved when treated with malonic acid

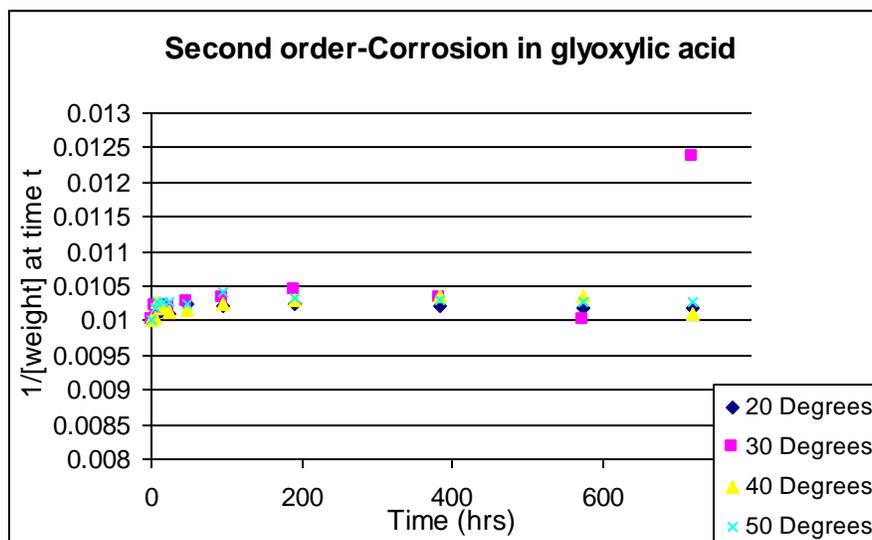


Figure 22d: Weight loss against time using equation (5) for kinetic data achieved when treated with glyoxylic acid

Figure 22c, shows that the reaction between malonic acid and glass fibre is possible to follow the second order second order mechanism emphasizing that the rate of this reaction is proportional to the square of the amount of glass fibre present (Russell 1992,

p.490) . However figure 22a, show illustrated the possibility of the same reaction following the first order mechanism. Hence the results of the present research failed to conclusively illustrate the kinetic mechanism behind the degradation of E-glass fibre by malonic acid.

On the other hand, when  $1/[\text{weight}]$  at time  $t$  was plotted against time for glyoxylic acid, figure 22d, is not clear enough to conclude the corrosion reaction to follow second order. This along with figure 22b demonstrates the possibility of the degradation between glyoxylic acid and glass fibre to follow the first order reaction mechanism stating that the rate of this reaction would be directly proportional to the concentration of the reactant, (Ramsden 1990, p. 268) in this case the amount of glass fibre.

It should be noted that this method of analysis is not often employed as the numerical values involved are extremely small and susceptible to large amount of error. This could have been the reason behind the failure to derive to a conclusion in this experiment. Analysing how the cations are leached from glass matrix could provide some insight to kinetics behind the reactions.

### ***3.4.2 Leaching of cations from fibres treated at 1.5M malonic acid at varying temperatures and time frames***

Figure 23a and 23b illustrates how the seven ions of concern, Ca, Al, B, Fe, K, Mg, and Na are leached out from glass matrix at temperatures 20 and 30 °C for various time

frames of exposure to 1.5M malonic acid (refer figure 56 and 57; Appendix I for similar leaching patterns at temperatures 40 and 50 °C).

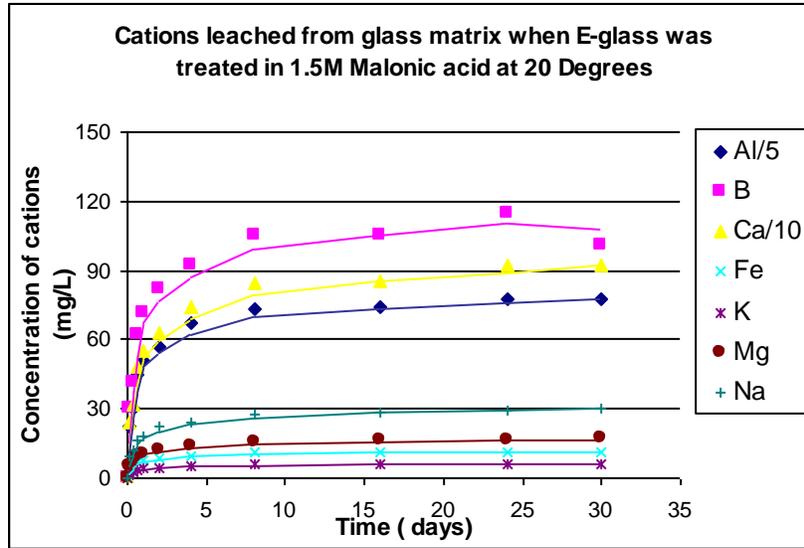


Figure 23a: Leaching of cation from glass matrix when E-glass was treated in 1.5M malonic acid at 20 °C for various time frames

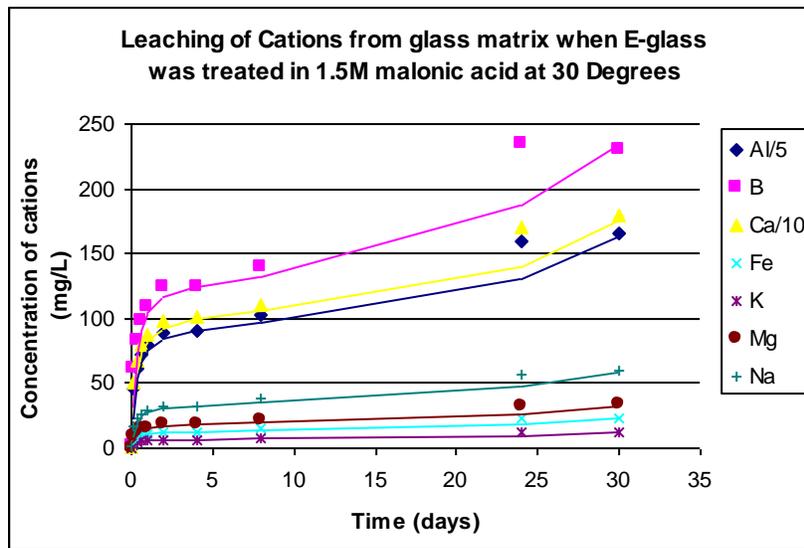


Figure 23b: Leaching of cation from glass matrix when E-glass was treated in 1.5M malonic acid at 30 °C for various time frames

It can be clearly seen from Figure 23a that at 20 °C all seven ions are leached very rapidly during the initial time frames of exposure until around 2 days is reached. This is followed by a slow and steady leaching of cations. The rate of leaching seems to slowly stagnate as the time duration was lengthened yet the leaching appeared to more or less continue within the analysed time frame for most cations. The patterns were similar for the rest of the temperature except for the enhancing effect of the temperature rise on leaching especially at the prolonged time frames.

The patterns were further explored by making plots for individual cations, which showed how the leaching of each ion behaved when E-glass was treated in 1.5M malonic acid at the four temperatures utilized in the present research. Figure 24a and 24b shows the patterns exhibited by boron and sodium (refer figures 58-62; Appendix J for the plots of Al, Ca, Mg, Fe and K).

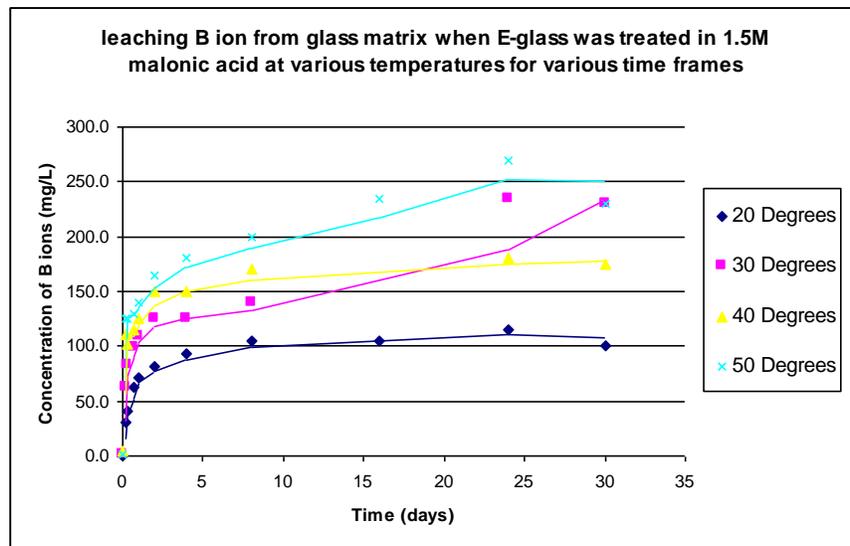


Figure 24a: Leaching of B from glass matrix when E-glass was treated in 1.5M malonic acid

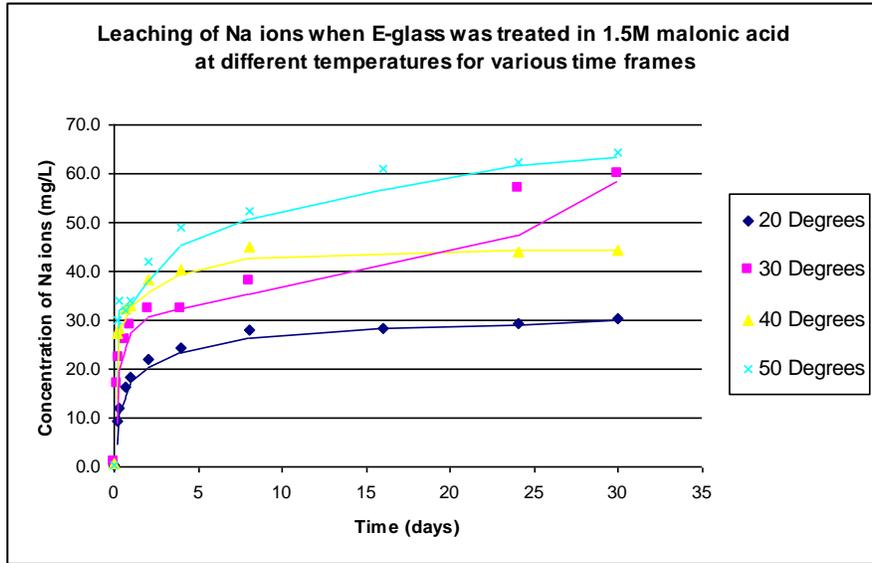


Figure 24b: Leaching of Na from glass matrix when E-glass was treated in 1.5M malonic acid

A pattern very similar to 20 °C can be seen for 40 °C and 50°C where a rapid rate of leaching can be observed during the initial time period until 24 hours, a gradual decrease in the rate of leaching can be observed subsequently. It should be noted that although the trends appear similar at these two temperatures the numerical values denoting the concentration of cations leached out were lower at 20 °C compared to 40 °C.

The plots of individual ions revealed an inconsistency in the trends of ion from 24 to 30 days at 20 °C where some ions appear to have stopped leaching, while others still continue to leach and yet others showing a significant decrease in leaching. This slight

variation could have arisen from mishandling in the dilution process of the residual solution.

At 30 °C, a rapid leaching is observed for the initial time frames similar to that observed at 20 and 40°C. This is however followed by a slightly slower but constant rate of leaching from 4 hours until 24 days after which the rate appears to increase for a second time. A quite similar pattern is exhibited at 50°C except that after 24 days leaching appears to decrease. The general observation made is that the leaching of all seven cations increase with increase in temperature for each time frame, except for 30 °C, where all seven ions can be seen to have overtaken the amounts leached at 40 °C within 16 to 24 days of exposure. This inconsistency could fall in the range of experimental error, which however on repeating could produce a better trend.

Comparing the percentage weight losses presented in figures 19a with the patterns of cations leached represented in figures 23a and 23b, it is certain that the cations were responsible for the weight loss for the shorter time frames up to about 16 days. Following this, the weight loss of fibres seems to have subsided, in fact a weight gain was observed although a steady amount of ions were unmistakably leached out.

Similar observation was made by Jones (1995) for the higher concentrations of perchloric acid and was linked to the binding of anions of the acid to the glass matrix. Similar reasoning has been proposed for the behaviour illustrated at the higher concentrations of malonic acid and glyoxylic acid. Although the present concentrations were not harsh for

either acid, the lengthened time of exposure could have initiated similar behaviour hence explaining the formed complexes that could have adhered to the glass surface accountable for the weight gain. As the bound complexes could inhibit the ion-exchange reaction, this hypothesis could further explain the stagnation in the rate and the amount of cations leached at the longer time frames. However this aspect needs to be further investigated before a conclusive explanation could be reached. Despite the reason behind the weight gain observed, it should be noted that weight changes are not ideal measurements to investigate the reaction and the mechanism behind the degradation process.

It should also be noted that Al, Ca and B carry the highest percentage mass in the E-glass fibre (Table 1), and that these are the ions that appear to have leached the most at all conditions utilized in the present research compared to the rest of the ions. This agrees with several of the previous findings such as that by Jones and Betz (2004), Kumosa and Qui (1997) and the postgraduate diploma research by the present researcher carried out the previous year (2005). To investigate this further the weight by weight percentages of all seven cations were calculated and presented in Tables 4 and 5 for two specific conditions namely 8 days exposure at 30°C and 40°C. A short time frame was selected as the weight loss appeared to be a direct correlation to the cations leached during these time periods.

*Table 4: Weight by weight percentages of ions leached out for 8 days exposure at 30 °C to 1.5M malonic acid*

Cation	Concentration (mg/L)	Mass leached to solution (mg)	Weight loss in fibres (mg)	w/w % of ions
Al	510	25.5	125.5	20.32
B	140	7	125.5	5.58
Ca	1100	55	125.5	43.82
Fe	15	0.75	125.5	0.60
K	7.5	0.375	125.5	0.30
Mg	21	1.05	125.5	0.84
Na	38	1.9	125.5	1.51

*Table 5: Weight by weight percentages of ions leached out for 8 days exposure at 40 °C to 1.5M malonic acid*

Cation	Concentration (mg/L)	Mass leached to solution (mg)	Weight loss in fibres (mg)	w/w % of ions
Al	610	30.5	140.55	21.70
B	170	8.5	140.55	6.05
Ca	1400	70	140.55	49.80
Fe	22	1.1	140.55	0.78
K	8.8	0.44	140.55	0.31
Mg	25.5	1.275	140.55	0.91
Na	45	2.25	140.55	1.60

However it should be noted that these are only rough values giving only an approximation as it is clear that the percentage weights do not add up to a 100. Nevertheless these estimations provide a better understanding of the contribution of each ion to the weight loss observed. It can be understood unmistakably that Ca ion is responsible for about half of the weight loss of glass fibre observed. Closely following Ca

contributing to about 20% percent is Al ion followed by B. Although a large percentage of B has been found to have leached from the matrix (Jones and Betz, 2003), its contribution to the weight loss is not very significant. The rest of the ions appear to play a lesser degree of a role in weight loss of fibres.

Whilst weight loss has been regarded as a measurement highly subjected to large amounts of error, the results achieved for the present analysis was fairly successful. The trends exhibited by weight loss coincided with the respective points for the leaching of cations for the shorter time frames making a correlation between the two clear. Although further work needs to be carried out to test the hypothesis put forth for the observations during the prolonged time frames. Once proven, this hypothesis could confirm weight loss of the glass fibre treated in 1.5M malonic acid as a consequence of the loss of cations from its matrix which in turn is responsible for decreasing the tensile strength of the fibres (exhibited in figure 10). Nevertheless with the present findings the weight loss in glass fibres can be concluded to be the direct consequence of loss of cations from the glass matrix by the corrosive medium over time.

#### ***3.4.3 Leaching of cations from fibres treated at 3M glyoxylic acid at varying temperatures and time frames***

Figure 25a and 25b exhibit how Ca, Al, B, Fe, K, Mg, and Na are leached out from glass matrix at temperatures 20 and 40 °C for various time frames of exposure to 3M glyoxylic

acid (refer figures 63 and 64; Appendix K for similar leaching patterns at temperatures 30 and 50 °C).

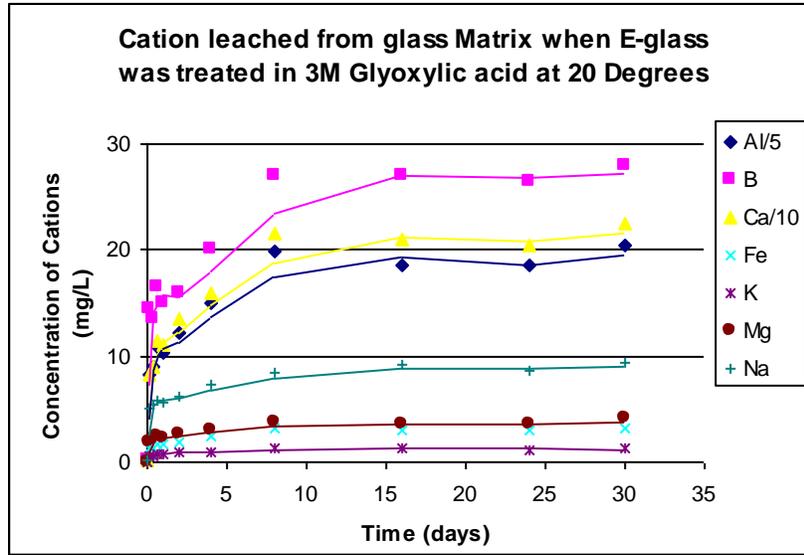


Figure 25a: Leaching of cation from glass matrix when E-glass was treated in 3M glyoxylic acid at 20 °C for various time frames

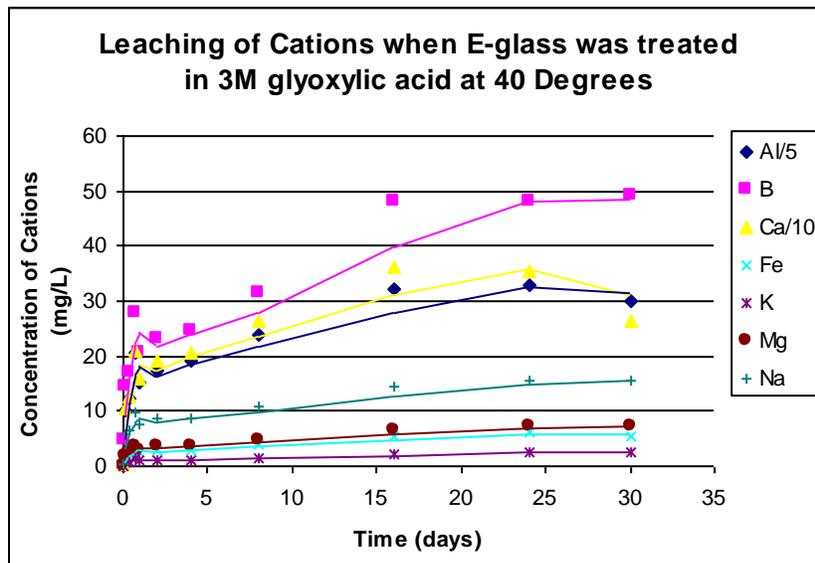


Figure 25b: Leaching of cation from glass matrix when E-glass was treated in 3M glyoxylic acid at 40 °C for various time frames

One of the initial observations that can be made is the difference in scale for these plots when compared to the respective plots for malonic acid. It is apparent that minimal amount of leaching has taken place when the corrosive medium was 3M glyoxylic acid. Another difference in these plots is that following the rapid leaching that was observed initially the cations appears to leach out of glass matrix at a fairly high rate until about 24 days. From this point on a reduction in the rate of leaching can be understood, in other words, the rate appears to be slowing gradually with time of exposure. Plots were made to analyse closely the behaviour of each individual ion. Figure 26a and 26b show the leaching exhibited by B and Na respectively (refer Appendix L for leaching patterns of Al, Ca, K, Mg and Fe)

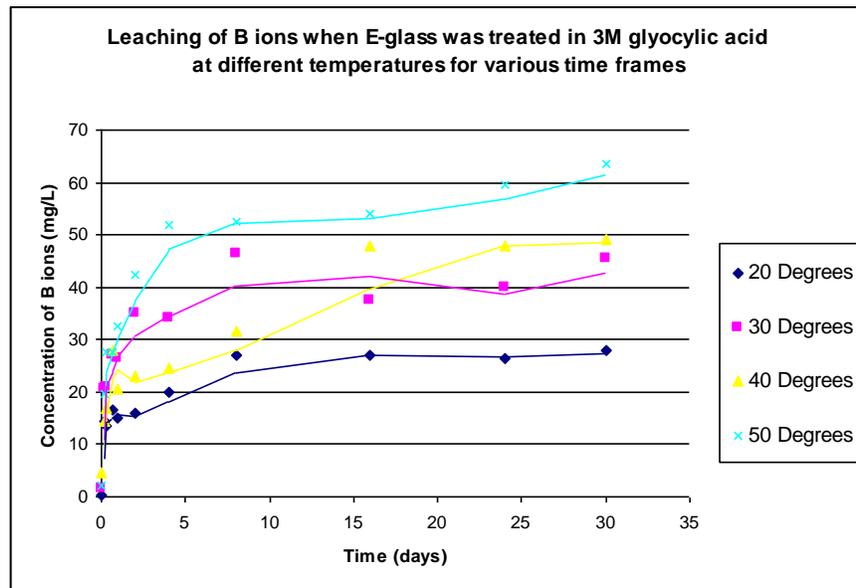
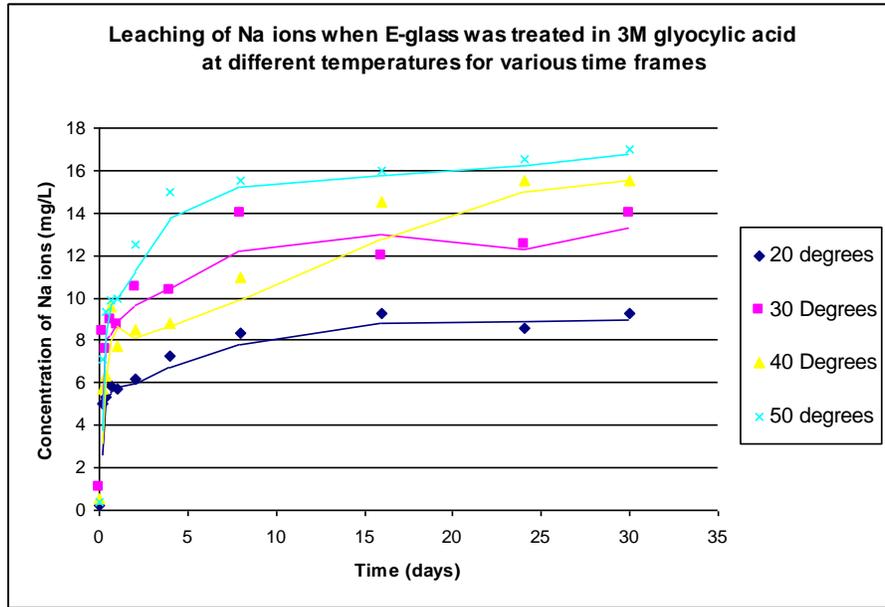


Figure 26a: Leaching of B from glass matrix when E-glass was treated in 3M glyoxylic acid



*Figure 26b:* Leaching of Na from glass matrix when E-glass was treated in 3M glyoxylic acid

In these figures the leaching appears to be extremely slow although clearly taking place even at the longest time frame. As a general trend the raise temperature can be seen to have enhanced the leaching of all seven except at the earlier time frames for 40 °C and 30 °C (appendix K) where they appear to contradict with the laws of kinetics (Lister and Renshaw (1990, p. 171). In addition, a depression in the concentration of ions leached can be observed at 24 days, which is especially apparent in the leaching patterns of Ca, Al and B, although to a lesser extent in the others. The difference observed in Ca and Al is difficult to explain as they along with B are usually found to leach in highest amounts. Although care was taken to ensure the production of accurate and reliable data, a point necessary to note here is that the concentrations achieved by cation analysis for 30 °C and

40 °C appear to be deviated compared to the fairly clean lines was achieved for the other temperatures.

The general trend observed in figures 11a and 11b along with appendix E (under the study of the glyoxylic acid in section 3.2) cannot be dismissed where the leaching of cations were clearly elevated at the higher temperature 35°C compared to 20°C. Hence these unexpected variations in the present results does not follow the general trend and is difficult to explain consequently require re-analysis either by repeating the cation analysis or repeating the experiment all together which could eliminate the inconsistency.

Comparing the pattern in weight change exhibited by glyoxylic acid (figure 19b) with the leaching of cations, it can be observed that the trend more or less coincides with each other at all four temperature for the shorter time frames up to somewhere between 8 days and 16 days. A steady flow of cations in to the solution is clearly visible from the figure 25a and 25b which however contradicts with the weight losses exhibited in figure 19b. Similar inconsistency was observed with malonic acid where the cations are presumed to have formed some form of complex that adhered to glass surface despite weight loss expected by the continuation of leaching. As this hypothesis was proposed for perchloric acid at higher temperatures, without doubt it needs to be investigated before it could be concluded.

To analyse the contribution of ions individually to the weight loss of fibres, percentage weight loss by each ion was calculated and presented in tables 6 and 7, where again two specific conditions were utilized.

*Table 6: Weight by weight percentages of ions leached out for 8 days exposure at 30 °C to 3M glyoxylic acid*

Cation	Concentration (mg/L)	Mass leached to solution (mg)	Weight loss in fibres (mg)	w/w % of ions
Al	170	8.5	39.45	21.55
B	45.6	2.28	39.45	5.78
Ca	380	19	39.45	48.16
Fe	5.35	0.2675	39.45	0.68
K	2.6	0.13	39.45	0.33
Mg	6.6	0.33	39.45	0.84
Na	14	0.7	39.45	1.77

*Table 7: Weight by weight percentages of ions leached out for 8 days exposure at 30 °C to 3M glyoxylic acid*

Cation	Concentration (mg/L)	Mass leached to solution (mg)	Weight loss in fibres (mg)	w/w % of ions
Al	140	7	29.85	23.45
B	31.5	1.575	29.85	5.28
Ca	270	13.5	29.85	45.23
Fe	3.95	0.1975	29.85	0.66
K	1.45	0.0725	29.85	0.24
Mg	4.85	0.2425	29.85	0.81
Na	10.35	0.5175	29.85	1.73

It can be concluded with confidence that about half of the weight loss is due to the leaching of Ca ions from the glass matrix in the case of glyoxylic acid similar to malonic acid. Al ions resemble about 20% of the weight loss while B closely follows, the rest of the ions have almost insignificant weight by weight percentages hence insignificant contribution to the weight loss compared to Ca, Al and B. This pattern in leaching of Ca and Al has been observed several times by various researchers carried out for a variety of acid media (Jones and Betz, 2004 and Kumosa and Qui 1997). This is not surprising accounting for the large percentage of Ca, Al in the composition of glass displayed in Table.1. The extremely large amount of leaching observed in B (which is the next highest component in glass) came about unexpectedly in the postgraduate diploma research by the present researcher when the acid under analysis was malonic acid. However the kinetic approach on the degradation of E-glass fibre has not been investigated. Although the figures in the table are rough estimates, the contribution of these ions to the weight loss is unmistakable.

As it was brought to notice previously weight measurements of such minute numerical values have a high probability of being subjected to large amount of inaccuracy hence decreasing the reliability of the results which might in the end prove the repetition of this analysis to be yet another failure. However a comparison between the patterns of weight change when E-glass was treated in 3M glyoxylic at different temperatures with the corresponding trends exhibited by the leaching of cations provided successful enough data for a conclusion. Although a few points at the longer time frames failed to match a direct correlation between the two is very clear. The loss of mass observed in E-glass

fibre specimens is the consequence of loss of cations by the corrosion for both acids to a period of time. However it should be noted here that the kinetic approach with the assessment based on weight change is not an ideal measurement to analyse the reaction and the mechanism behind it.

## **4. Conclusion**

The research consisted of four different objectives. Firstly the corrosive effect of malonic acid was explored in terms of tensile strength retention while that of glyoxylic acid was analysed through strength retention along with loss of cations. Next the passivation shown by 5M malonic acid (if any) was examined through pre-treatment in this acid for 10, 20 and 30 days followed by post-treatment in 1M HCl, 3M HCl, and saturated oxalic acid. Analysis was carried through measurements of mechanical strength retention. Lastly the kinetics behind the degradation of glass fibre exposed to malonic acid and glyoxylic acid was investigated through weight losses.

### ***4.1 Analysing the Corrosive effect of malonic acid***

When exposed to malonic acid, the strength decreased rapidly during the initial time period followed by a steady decline. This decline in the mechanical strength was unmistakable even for the longer time frames of exposure in the corroding medium. The kinetics of a chemical reaction in a solution is significantly affected by the motion of the molecules (D.W. Oxtoby and N.H. Nachtrieb, 1990, p.662). This is visible by the enhancing effect temperature had on the degradation both in terms of strength loss as well as leaching of cations. The ion exchange reaction proposed by Jones and Chandler (1984b) is suggested to be a mechanism governed by diffusion (Jones and Chandler 1984b). Hart (2001, p. 42) Explains that diffusion in liquids is a slow process hence the time of exposure has a significant effect on the strength loss of the fibres.

#### *4.2 Analysing the Corrosive effect of glyoxylic acid*

Jones and Chandler (1985b) considered glyoxylic acid to have a less deteriorative effect which was accentuated by the present research as 70% or more of the strength retained in glass fibres treated in this acid at all the conditions employed. On analysing the effect of glyoxylic acid concentration on glass fibre, a minima in strength retention was observed at 2M acid concentration similar to the trends observed in HCl, malonic, mesoxalic, as well as oxalic acid (Jones and Betz and 2003 and Jones and Chandler 1986). Leaching of cations showed a direct correlation to strength retention. The ions found in the residual solution revealed most leaching to have occurred at around the same concentration although not exact. These observations could be justified as follows; at the lower concentration extremes the ion exchange reaction responsible in the leaching of ions would be very slow owing to the low concentration  $H^+$  ions, on the other hand at the higher concentration extreme, anions of the acid could bind to certain cations at the glass surface inhibiting the rate of this reaction (Jones and Chandler, 1985).

Further investigation of the percentages of individual ions revealed that Ca and Al which make up about 35% of the glass fibre to have leached only minimally. Kumosa (2001) associated the strength loss to the loss of these ions hence explaining the large amount of strength retained in the fibres. B which is believed to exist in the silica network and which is regarded to have a stabilizing effect (Kumosa and Qui, 1997) was observed to have leached to unlikely high extremes similar to that observed with malonic acid recently (by the present researcher). Although the structure of glyoxylic acid is slightly

different from mesoxilic acid, glyoxylic acid could form stable complexes with B. This is likely to be the case for high amounts of B especially as complex formation is believed to be particularly favourable with trivalent ions owing to their favourable orientation with the acid group. Furthermore the results unmistakably showed the role of temperature explaining enhanced rate of degradation while the effect of prolonged exposure provided inconclusive results to establish a clear correlation.

#### ***4.3 Analysing the Passivating effect of malonic acid***

One characteristic of malonic acid was that it produced severe corrosion around 1.5 M concentrations while about 100% strength retention was observed with 4M. 10 days pre-treatment in 5M malonic followed by the treatment in 1 and 3M HCl, illustrated a severe initial strength loss followed by a slow and steady strength loss beyond 8 days. 70% strength retention was observed within 8 days of exposure to 1M HCl while strength retention was 40% with 3M HCl. Increasing the pre-treatment time to 20 and 30 days presented a striking improvement showing 70% of strength retention throughout the time periods except when pre-treated for 20 days, treated in 3M HCl and was exposed for over 8 days. In comparison to the study of Jones and Betz (2004) which featured 20-40% strength retention within a short time frame in 3M HCl, the immense amount of strength retention (60-70%) prior to pre-treatment should be noted with enthusiasm.

Post treatment in oxalic acid which has been regarded to produce severe corrosion generated slight resistance to any form of passivation induced by 10 days pre-treatment in

5M Malonic acid. However an immense amount of strength retention; 60% and about 80% has been illustrated by prolonging the pre-treatment time period to 20 and 30 days respectively. The passivation induced through prolonged pre-treatment in 5M malonic acid clearly inhibits the attack of this corrosive acid through out the 4 days time period of investigation. Hence the scope of the beneficial effects that could be induced through malonic acid is unmistakable consequently demanding future work on this topic.

#### ***4.4 Analysing the Kinetics involved in the corrosion process of E-glass fibre in malonic acid and glyoxylic acid***

Weight changes, although usually subjected to a large amount of inaccuracy, is believed to show the rate of reaction hence was followed in the present research in an attempt to better understand the corrosion of E-glass exposed to malonic as well as glyoxylic acid. Maximum weight loss reached 4% in glyoxylic acid while that for malonic acid exceeded 20%.

Ironing out some inconsistency, the general trend was that the glass fibres lost weight in both acids for a period of time followed by an evident weight gain. Weight losses for both acids illustrated the possibility of the degradation process following the first order mechanism; however the results also showed the likelihood of the same reaction with malonic acid to also follow the second order mechanism. Hence, the present findings failed to conclude the mechanism behind the degradation of E-glass fibres by malonic acid however, suggesting the degradation by glyoxylic acid to follow the first order.

Corresponding leached cations result revealed a rapid loss of cations followed by a much gradual and steady loss at the longer time frames. In other words, cation loss coincided with the respective points of weight loss for the shorter time frames making a clear correlation between the two. The weight gain could be explained in terms of binding of anions to certain cations on the glass surface, accounting for the hindrance in the loss of cations at the longer time frames. Although binding of anions has been presumed to be the cause, such circumstances have been observed at higher acid concentrations (Jones, 1995) and further investigation is necessary before it could be concluded.

Both weight loss and cation loss appeared to be enhanced by the increasing temperature although the reaction at 30°C surfaced as most severe. Percentage weight by weight approximations showed; about 50% of the weight loss to have caused by the loss of Ca, while about 20% was due to Al. B was responsible in only about 6% of the weight loss, where as the rest of the cations appeared to have almost insignificant roles in the weight loss.

This research revealed some insight on the reactions and mechanisms behind the degradation process of E-glass fibre exposed to malonic as well as glyoxylic acid. The study further exposed valuable information about the passivation introduced by malonic acid and possible passivation that could be introduced by glyoxylic acid. The passivation effect is likely to be a doorway for the future studies that could ultimately lead to aid in preventing the corrosion of E-glass fibre.

## **5. Future Work**

E-glass has been used around the globe for the past two decades as a reinforcing material especially in the form of GRP. As failure has been attributed to GRP it becomes vital to study the behaviour of E-glass fibre under mechanical and chemical stress in order to understand the mechanisms by which it loses its strength. This could help in understanding the causes of its failure and ultimately help in creating an improved GRP.

One of the areas in this research was to analyze the effect of glyoxylic acid. Due to the inconsistencies, the present results failed to show the effect time of exposure has on the corrosion process. Further work needs to be carried out utilizing closer time frames similar to that carried out for malonic acid in order to better understand the effect of glyoxylic acid.

The passivation produced by malonic acid was unmistakable in the present research, yet further work needs to focus on studying duration of the hindrance produced and the conditions for which it could be effective along with the limitations it could have.

Furthermore E-glass fibre appears to have retained about 100% of the strength when treated in 4M glyoxylic acid when exposed to 35 days. The possibility of passivation by glyoxylic acid is an aspect that too needs to be investigated as it could produce similar valuable and useful findings for the future.

In the present research, the kinetic approach showed the evidence of weight gain for the longer time frames. Although binding of anions has been proposed in this research, this aspect needs to be explored closely to understand and validate the reason behind the weight gain.

Another area that needs focus is the degradation of the plastic resin that is being used in the production of GRP. This could produce a clear picture of the acids that could be produced and the percentages of these acids that could be formed in order to make the results of the present research as well as future researches on organic acid more meaningful. Further studies can be focused on these acids in an attempt to understand their effects on the fibre degradation.

Boron which resides in the glass matrix with covalent bonds being leached out of the glass is a very new phenomenon. Studies could be conducted focusing on the leaching of B in terms of ions (if any) that could be facilitating its leaching as well as concentrating on the mechanism behind the leaching of B. Furthermore the effects of losing B from the glass fibre matrix in terms of tensile strength can be analysed.

The distribution of ions in the E-glass matrix seems to have an effect upon the leaching of ions. As this concept has not been completely understood or fully explored, exploring the effect of distribution of individual ions in the glass matrix on leaching of these ions could provide information that could assist in understanding corrosion behaviour.

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## Appendix - A

### LLOYD MACHINE SET – UP

FOR ANALYSIS OF 200mm GLASS SAMPLES: Parameters for use without computer.

LOCAL CONTROL → for operation with panel

LOAD RANGE → 0 – **1000N** – **Accept**

EXTENSION RANGE → **Automatic** – **Accept**

CROSSHEAD SPEED → **2.00mm/min** – **Accept**

**DISPLAY OPTIONS** / ACCEPT OPTIONS

COMPRESSION / **TENSION**

EXTENSION IN % / **EXTENSION IN mm**

UPPER MOVEMENT LIMIT – **Accept**

LOWER CROSSHEAD LIMIT – **Accept**

**MANUAL RETURN** / AUTOMATIC RETURN

MANUAL ZERO / **AUTOMATIC ZERO**

BREAK DETECT OFF / **BREAK DETECT ON**

BREAK MANUAL / **BREAK AUTO**

FOLLOW LOAD AND EXTENSION / **HOLD PEAK**

HOLD PEAK / **HOLD EXTENSION AT BREAK**

JOG SPEED – **Accept**

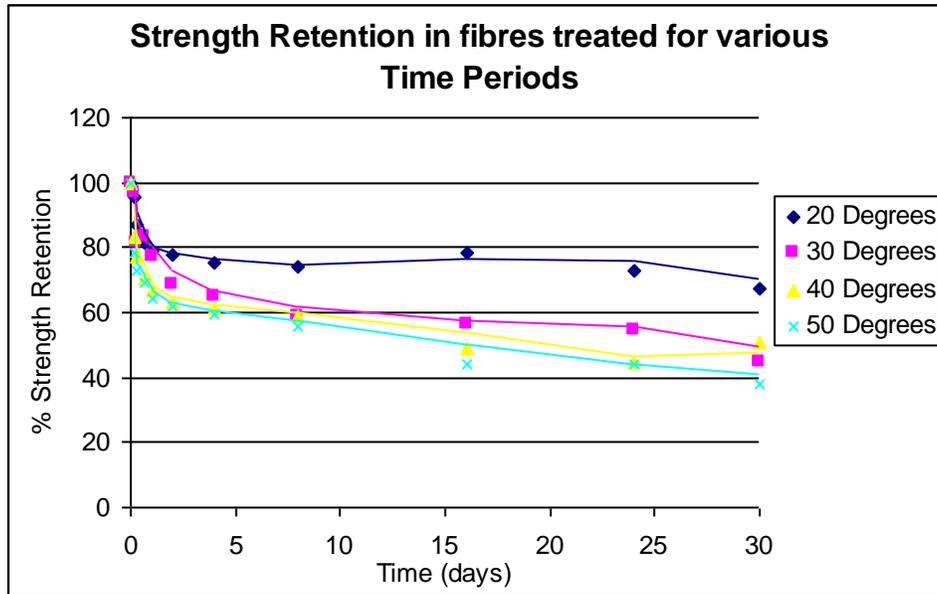
REMOTE EXTENSION / **INTERNAL EXTENSION**

GOTO COMPUTER CONTROL

NB: **Bolds** refer to option used.

Source: Lloyd Log Book (located in Bldg 305, room 006). Noted down by Frank Pachioli

## Appendix - B



*Figure 26:* Tensile Strength Retention in Fibres treated in 1M mlonic acid for various temperatures and time frames

### Appendix - C

Cation	Concentration (mg/L)	Mass in 50ml solution	Mass of ion in 0.8g fibre (mg)	Relative wt (%) Cation leached
Al	744.5	37.225	63	59.09
B	202.8	10.14	10.6	95.66
Ca	1540.13	77.0065	136.6	56.37
Fe	22.97	1.1485	2.16	53.17
K	8.87	0.4435	7.04	6.30
Mg	56.87	2.8435	8.56	33.22
Na	52.63	2.6315	6.08	43.28

*Table 8:* Percentage comparison of relative amounts of each cation leached at 50% strength retention for 1M malonic acid.

## Appendix - D

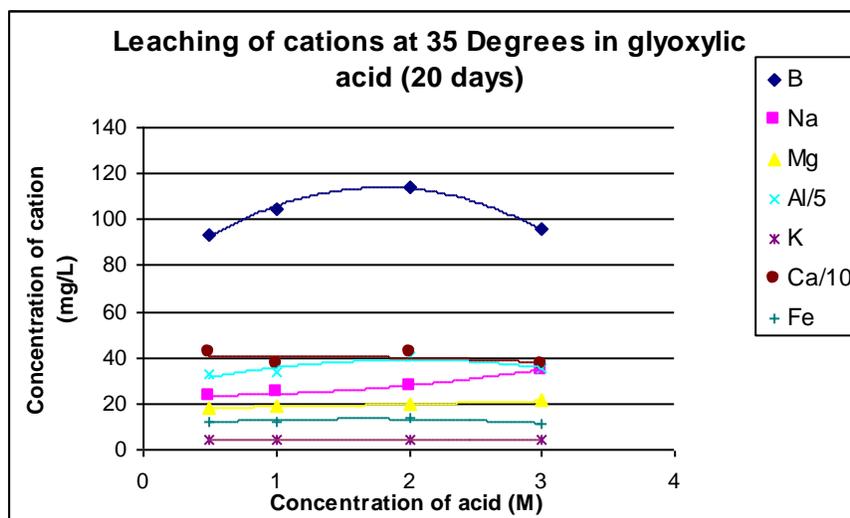


Figure 27: Leaching of cations at 35 °C for 20 days when treated in glyoxylic acid

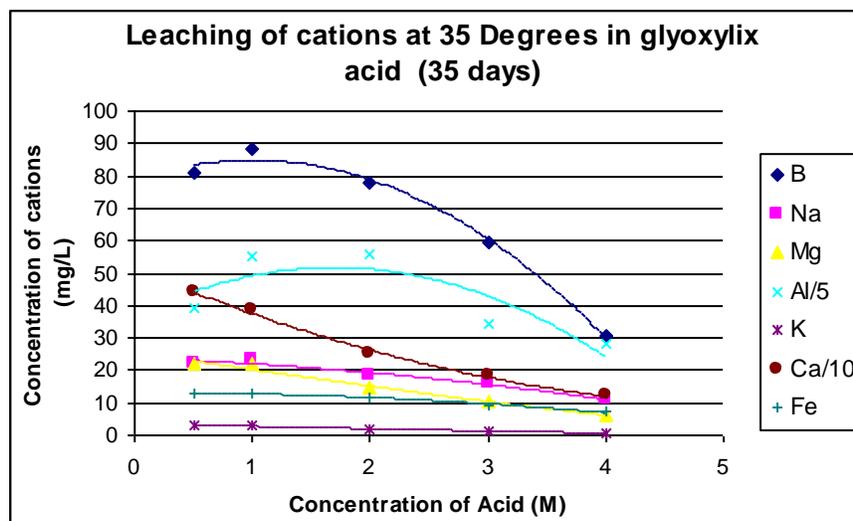


Figure 28: Leaching of cations at 35 °C for 35 days when treated in glyoxylic acid

## Appendix - E

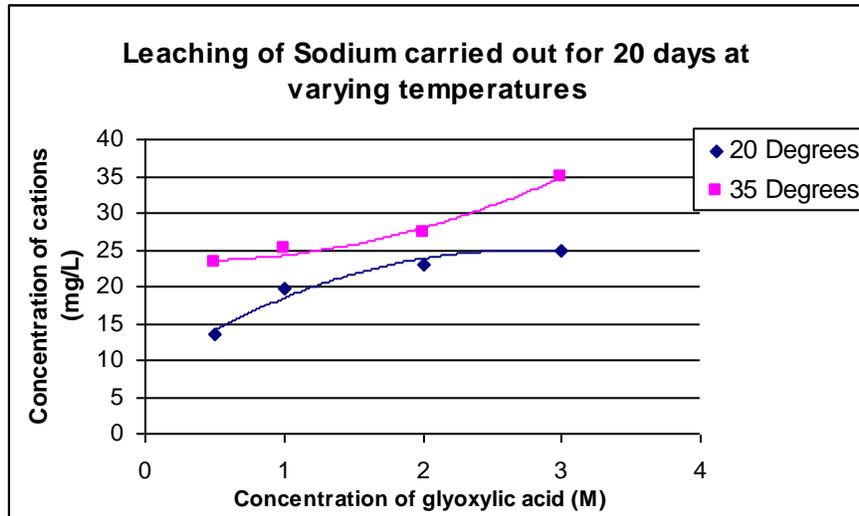


Figure 29: Leaching of Na at 20 °C and 35 °C for 20 days in glyoxylic acid

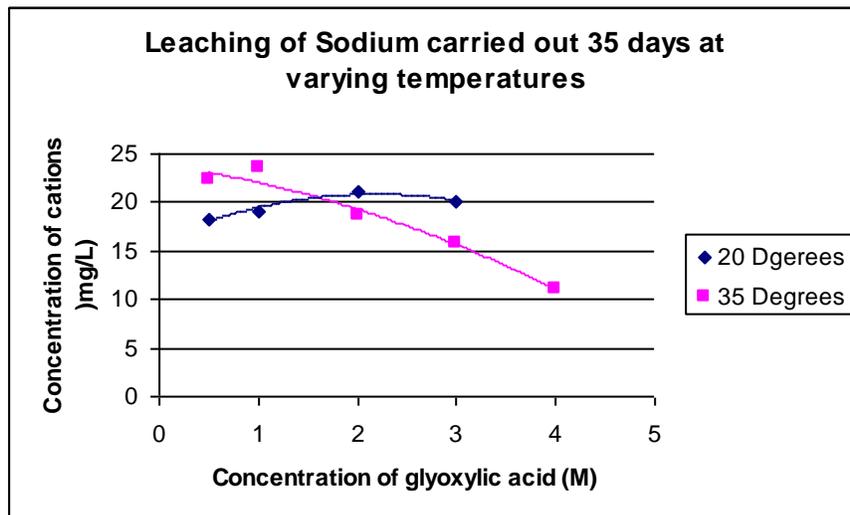


Figure 30: Leaching of Na at 20 °C and 35 °C for 35 days in glyoxylic acid

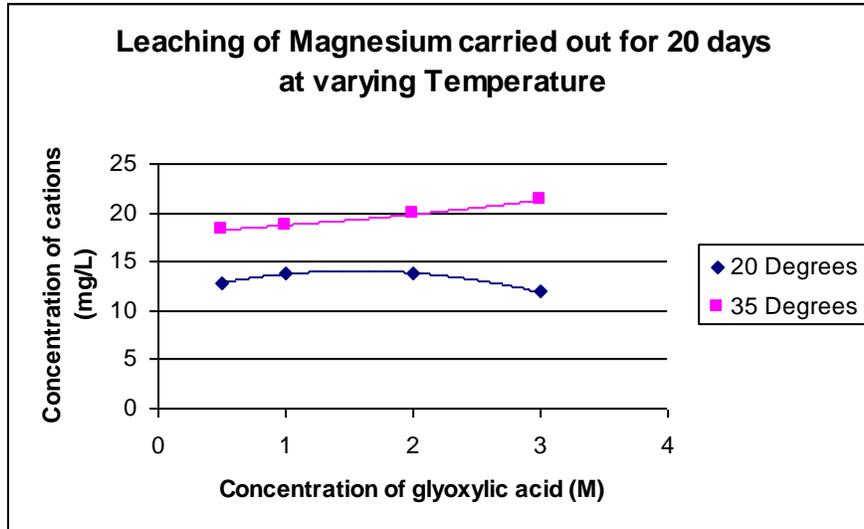


Figure 31: Leaching of Mg at 20 °C and 35 °C for 20 days in glyoxylic acid

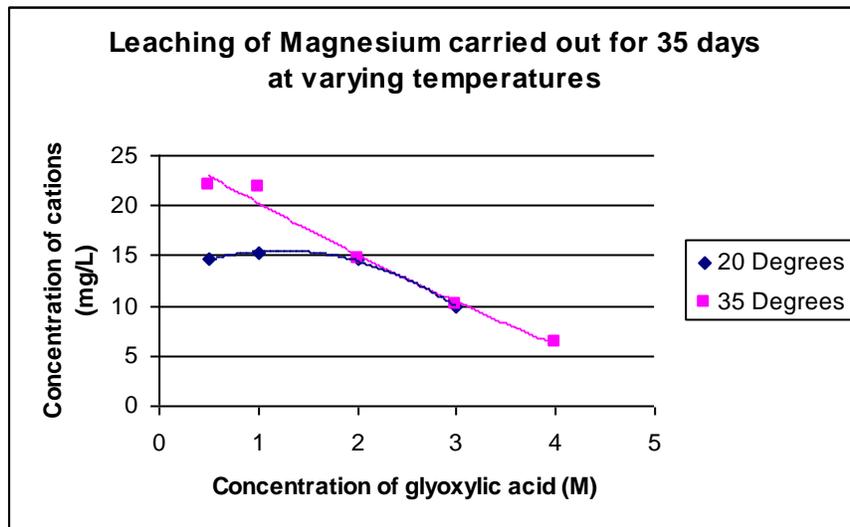


Figure 32: Leaching of Mg at 20 °C and 35 °C for 35 days in glyoxylic acid

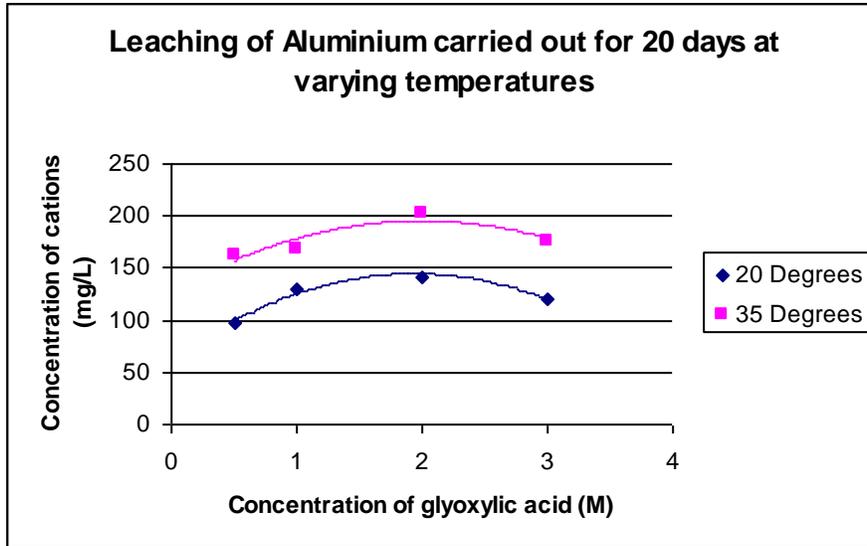


Figure 33: Leaching of Al at 20 °C and 35 °C for 20 days in glyoxylic acid

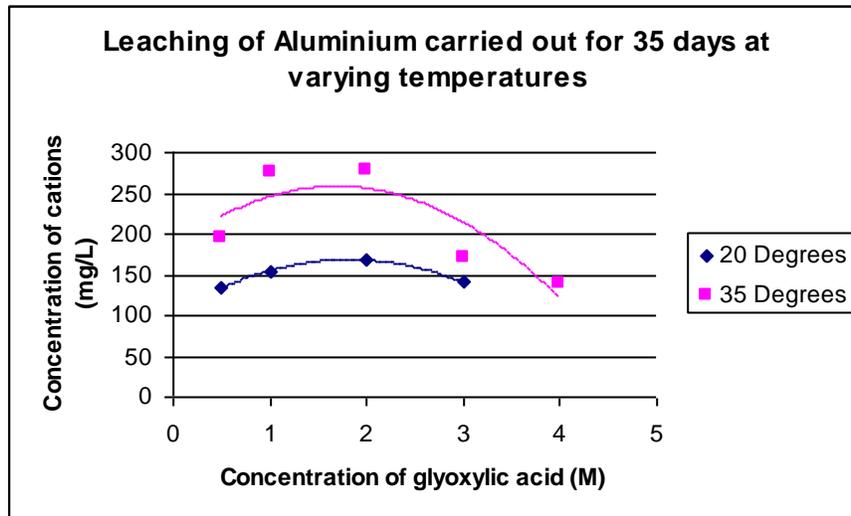


Figure 34: Leaching of Al at 20 °C and 35 °C for 35 days in glyoxylic acid

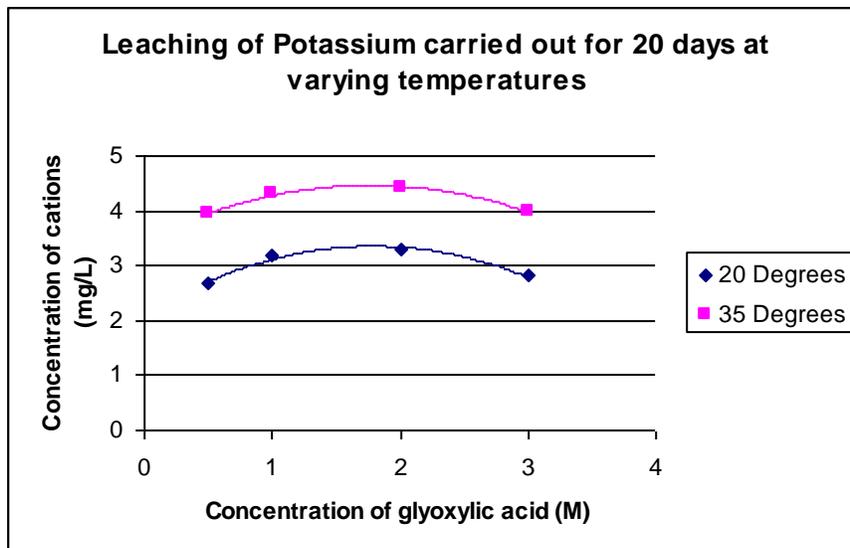


Figure 35: Leaching of K at 20 °C and 35 °C for 20 days in glyoxylic acid

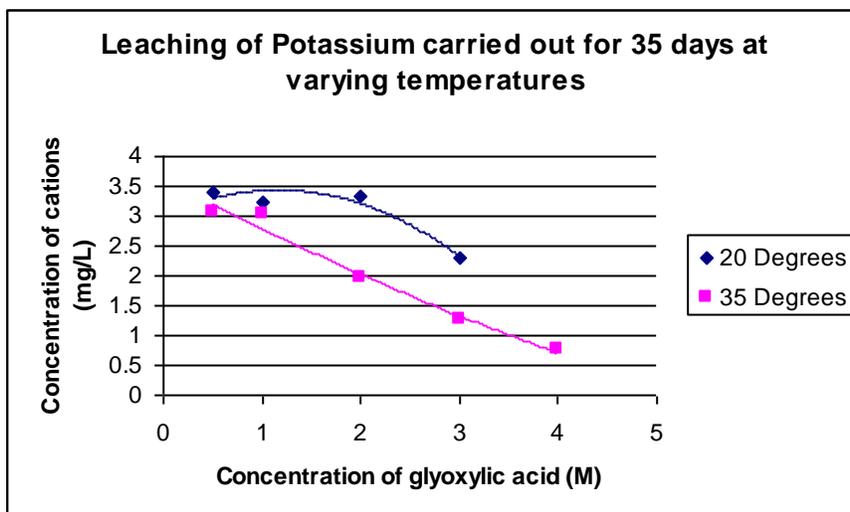


Figure 36: Leaching of K at 20 °C and 35 °C for 35 days in glyoxylic acid

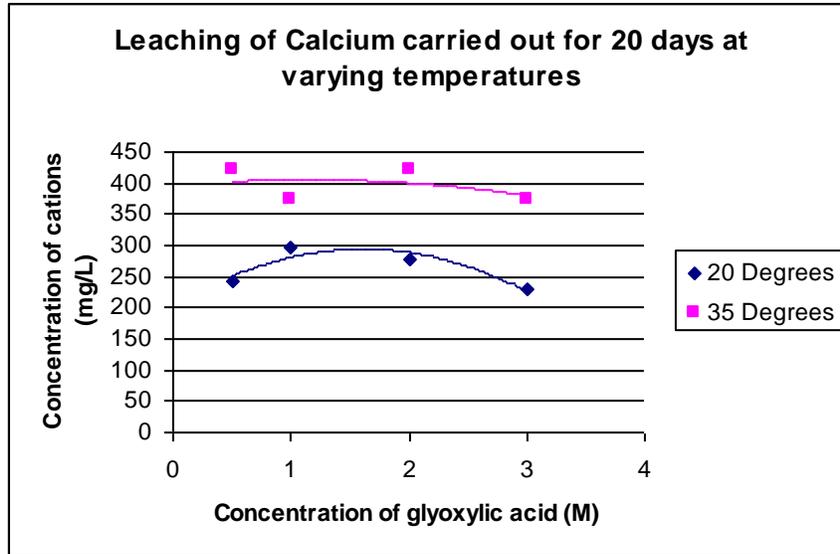


Figure 37: Leaching of Ca at 20 °C and 35 °C for 20 days in glyoxylic acid

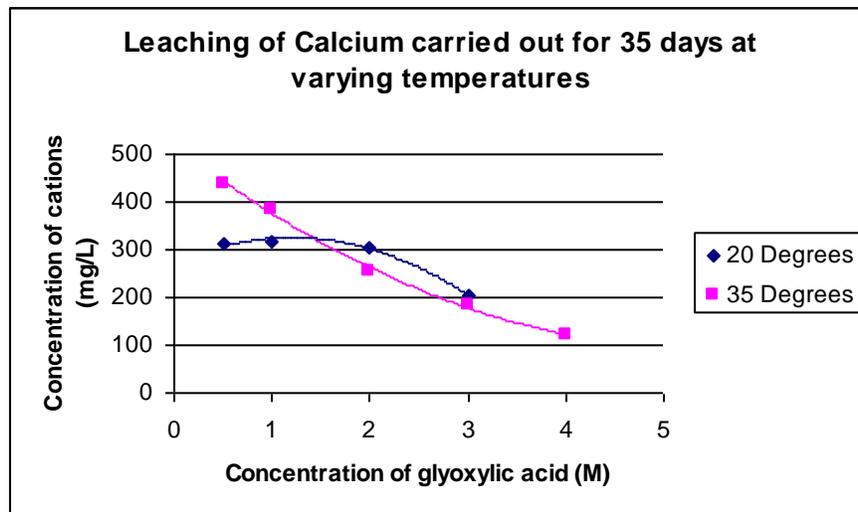


Figure 38: Leaching of Ca at 20 °C and 35 °C for 35 days in glyoxylic acid

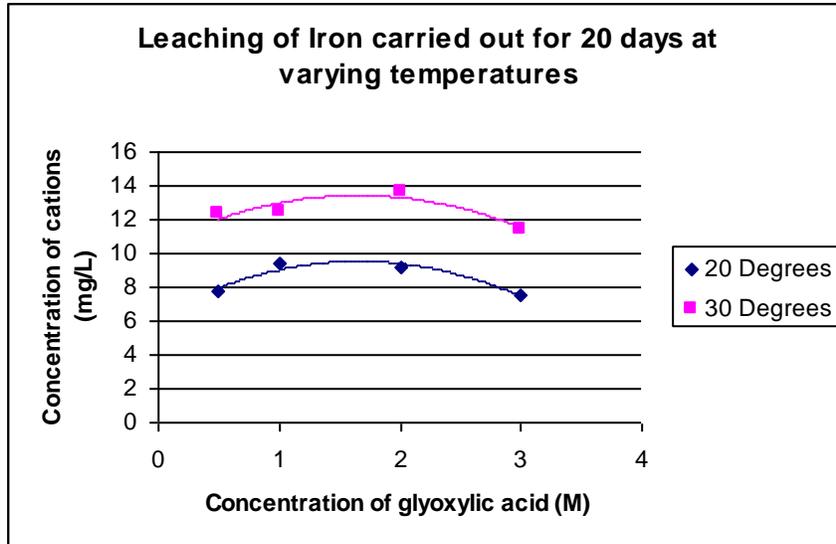


Figure 39: Leaching of Fe at 20 °C and 35 °C for 20 days in glyoxylic acid

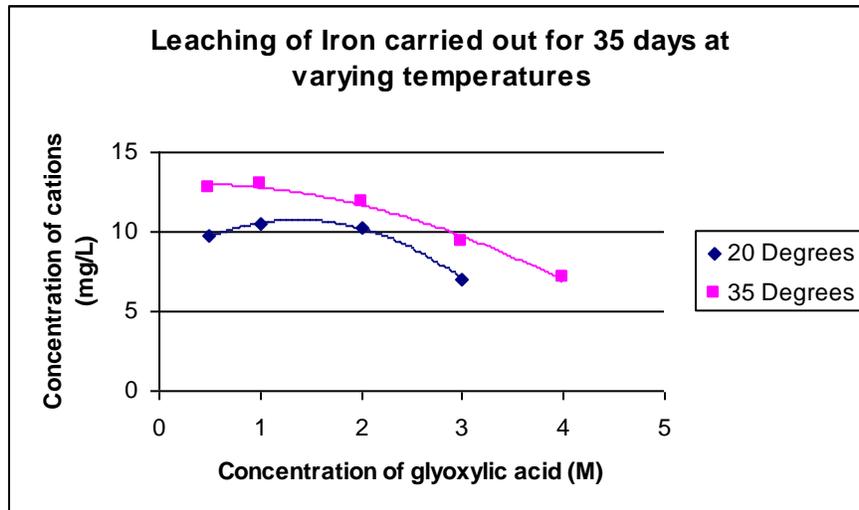


Figure 40: Leaching of Fe at 20 °C and 35 °C for 35 days in glyoxylic acid

## Appendix - F

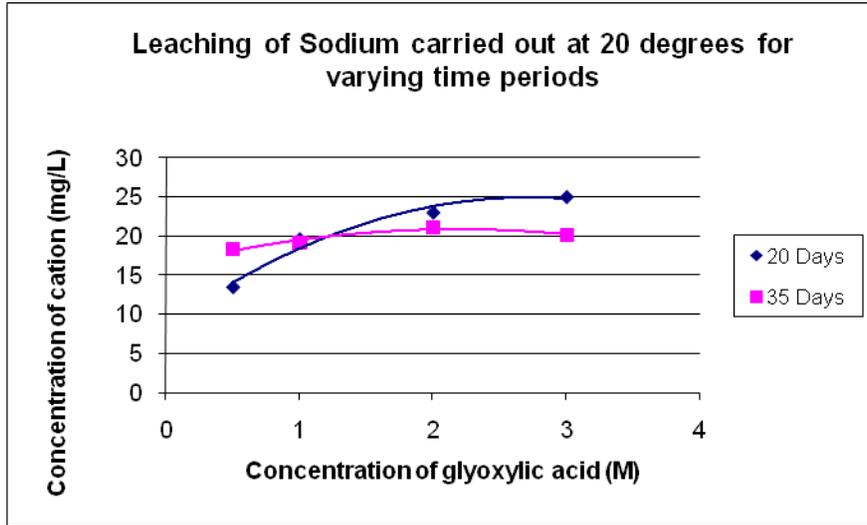


Figure 41: Leaching of Na at 20 °C for 20 and 35 days in glyoxylic acid

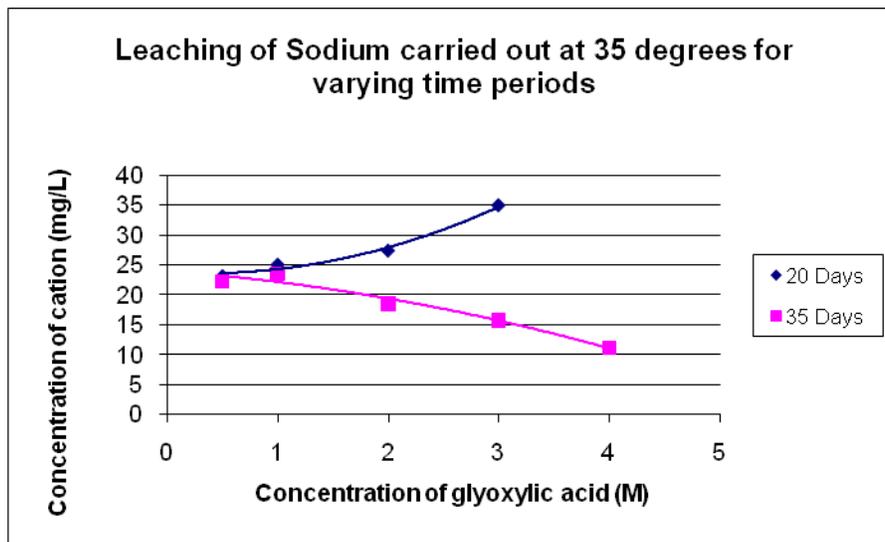


Figure 42: Leaching of Na at 35 °C for 20 and 35 days in glyoxylic acid

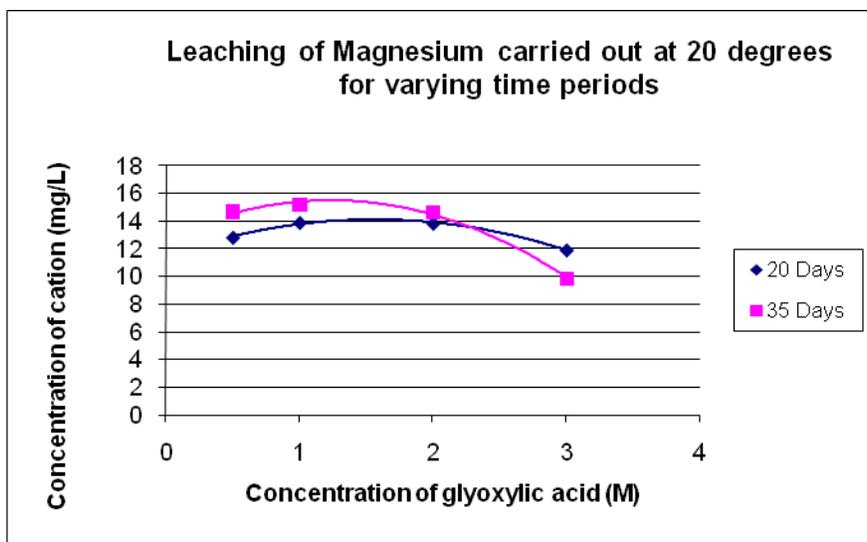


Figure 43: Leaching of Mg at 20 °C for 20 and 35 days in glyoxylic acid

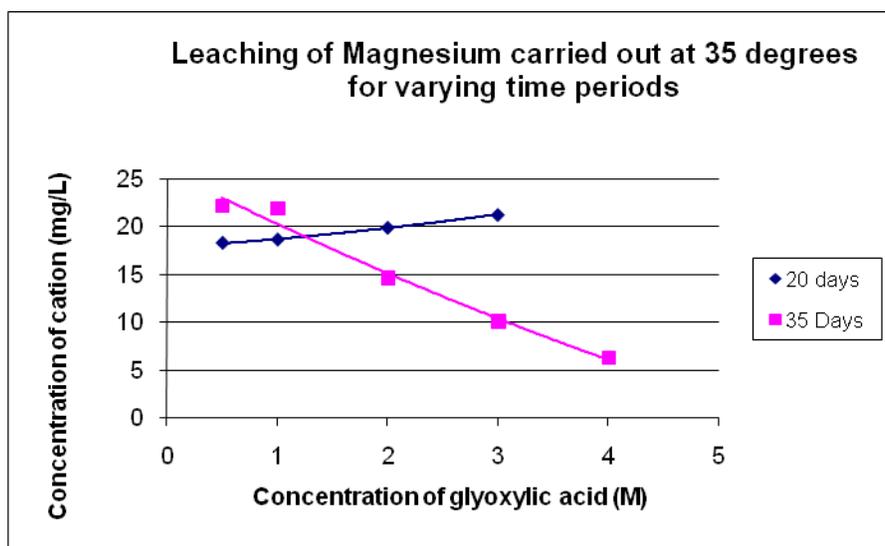


Figure 44: Leaching of Mg at 35 °C for 20 and 35 days in glyoxylic acid

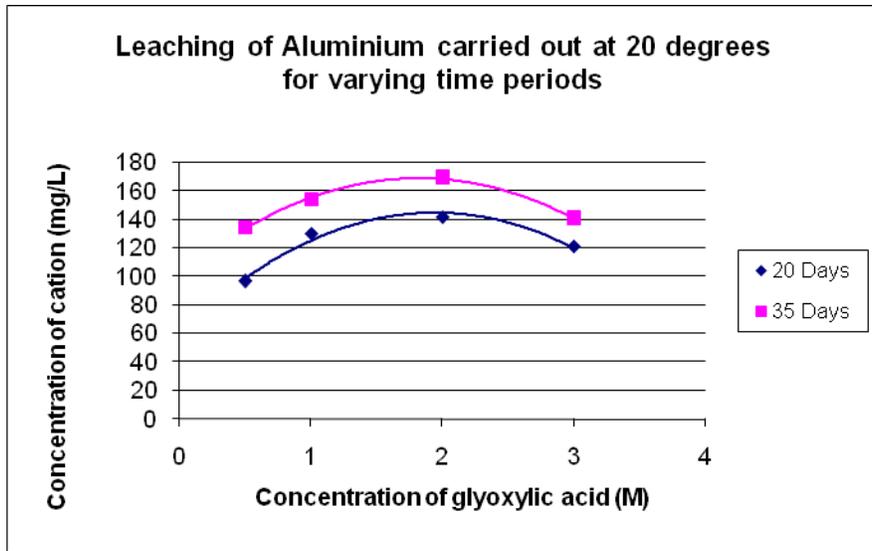


Figure 45: Leaching of Al at 20 °C for 20 and 35 days in glyoxylic acid

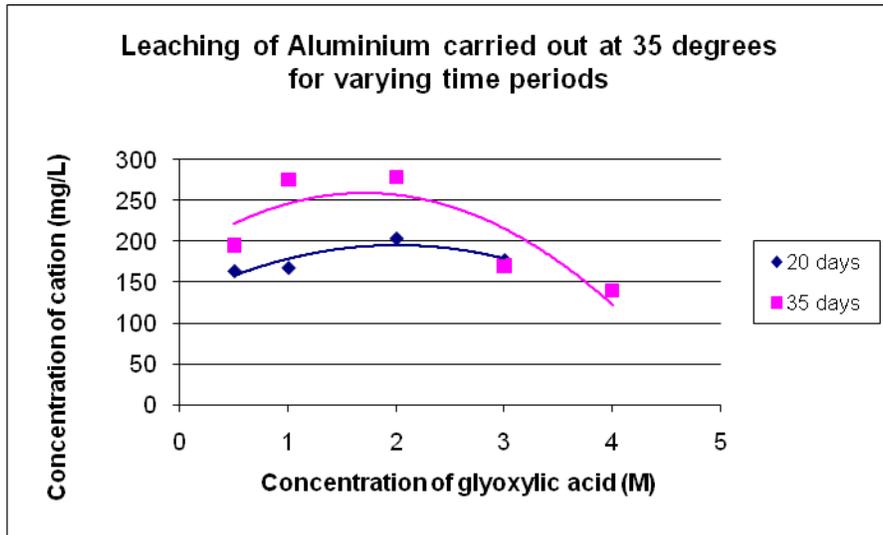


Figure 46: Leaching of Al at 35 °C for 20 and 35 days in glyoxylic acid

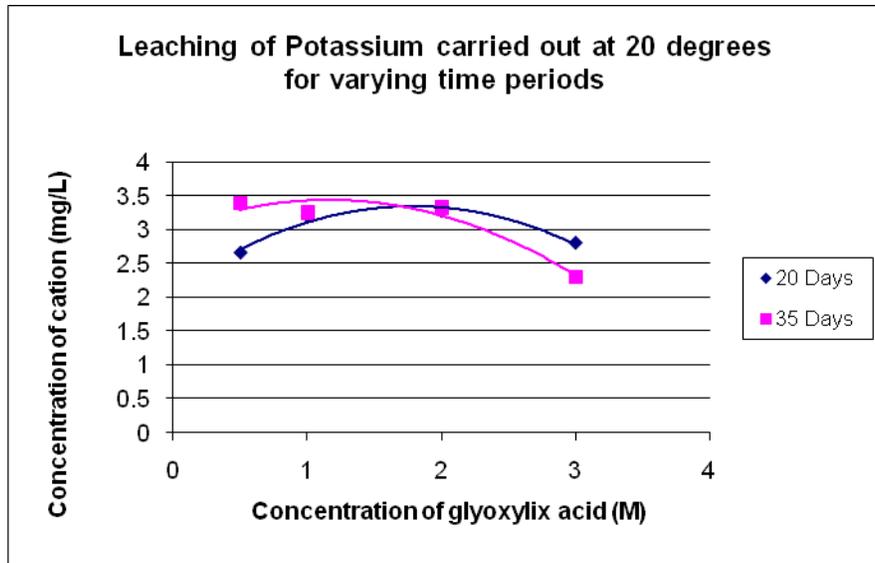


Figure 47: Leaching of K at 20 °C for 20 and 35 days in glyoxylic acid

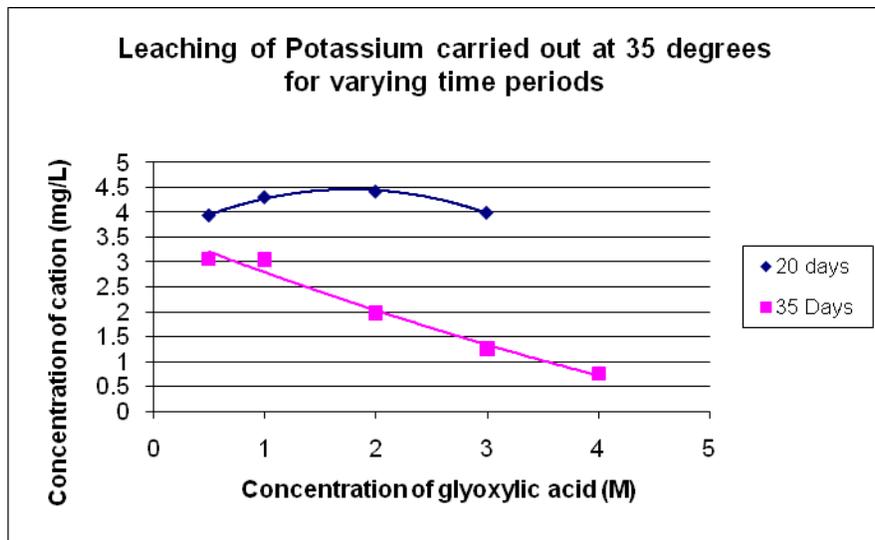


Figure 48: Leaching of K at 35 °C for 20 and 35 days in glyoxylic acid

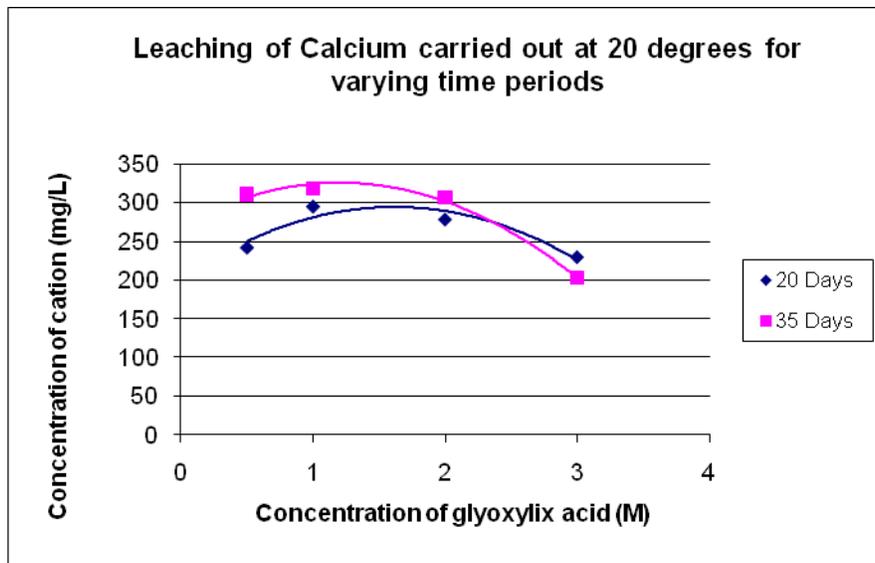


Figure 49: Leaching of Ca at 20 °C for 20 and 35 days in glyoxylic acid

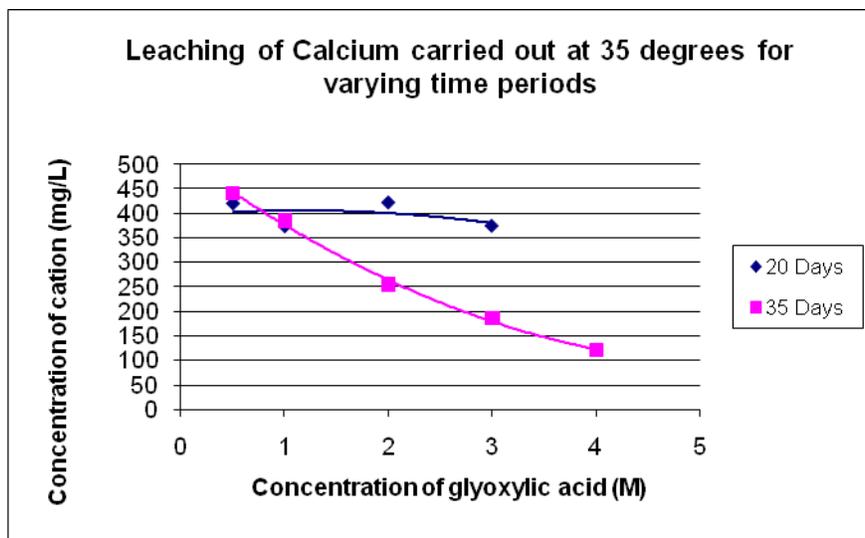


Figure 50: Leaching of Ca at 35 °C for 20 and 35 days in glyoxylic acid

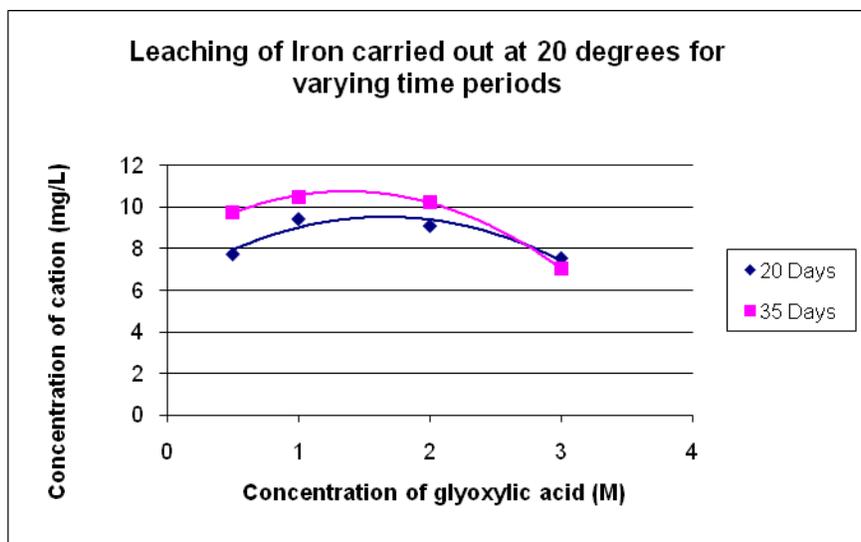


Figure 51: Leaching of Fe at 20 °C for 20 and 35 days in glyoxylic acid

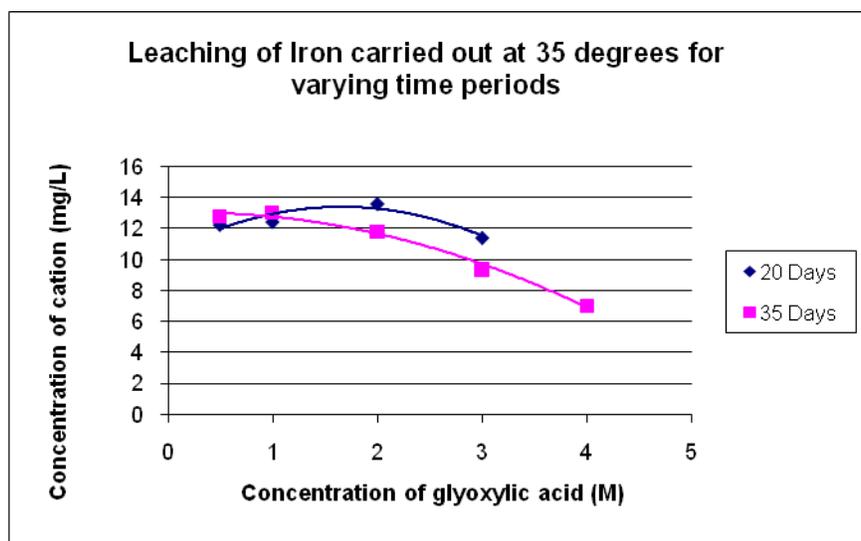


Figure 52: Leaching of Fe at 35 °C for 20 and 35 days in glyoxylic acid

### Appendix - G

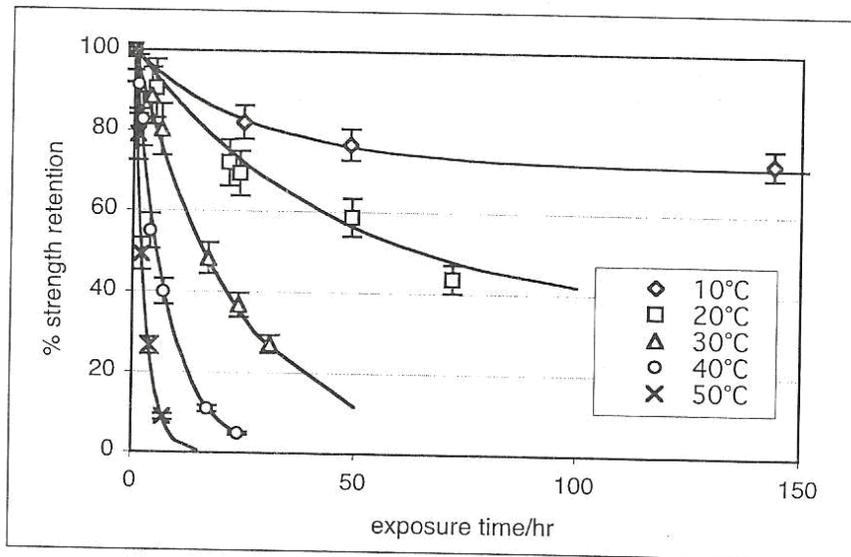


Figure 53: Corrosion of E-glass fibre in 3M HCl at varying temperatures (Jones and Betz, 2002)

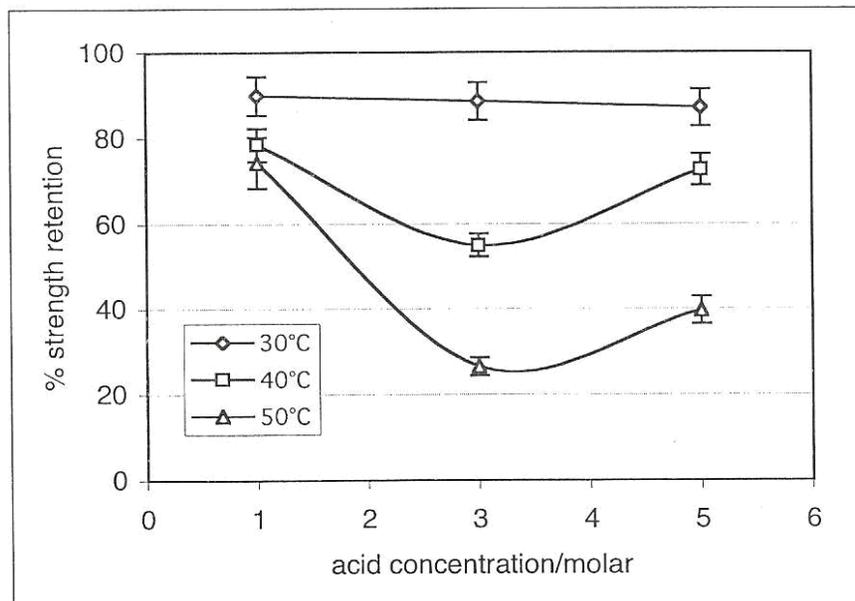


Figure 54: Effect of concentration and temperature on strength retention of E-glass fibre after 4 hours of exposure (Jones and Betz, 2002)

## Appendix - H

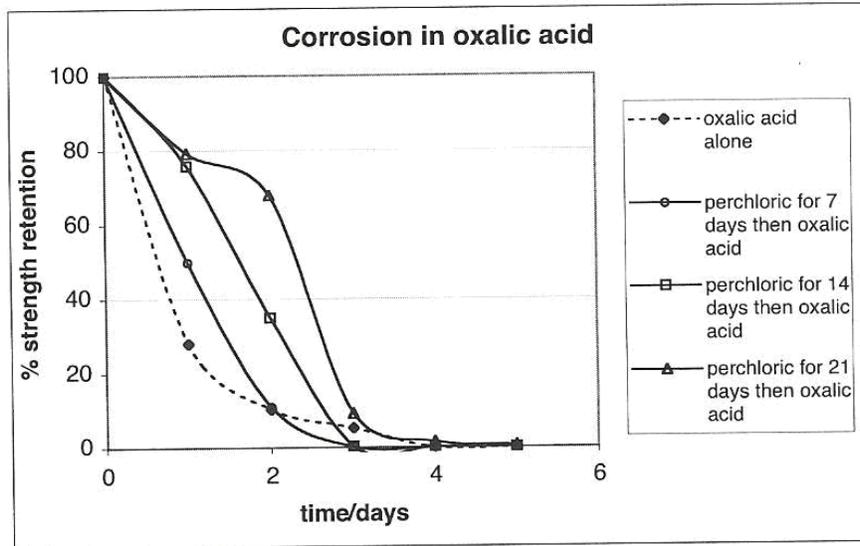


Figure 55: corrosion in hydrochloric acid before (solid) and after (open) treatment with perchloric acid ( Jones and Brunt, 2005)

## Appendix - I

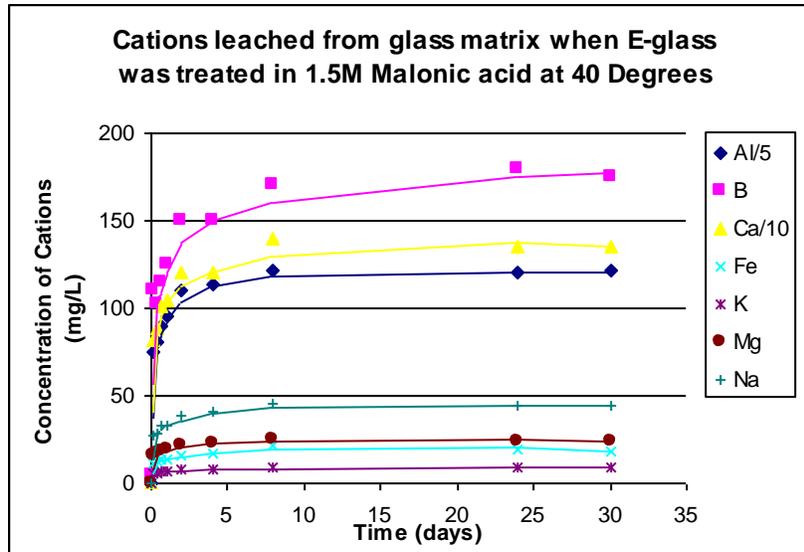


Figure 56: Leaching of cation from glass matrix when E-glass was treated in 1.5M malonic acid at 40 °C for various time frames

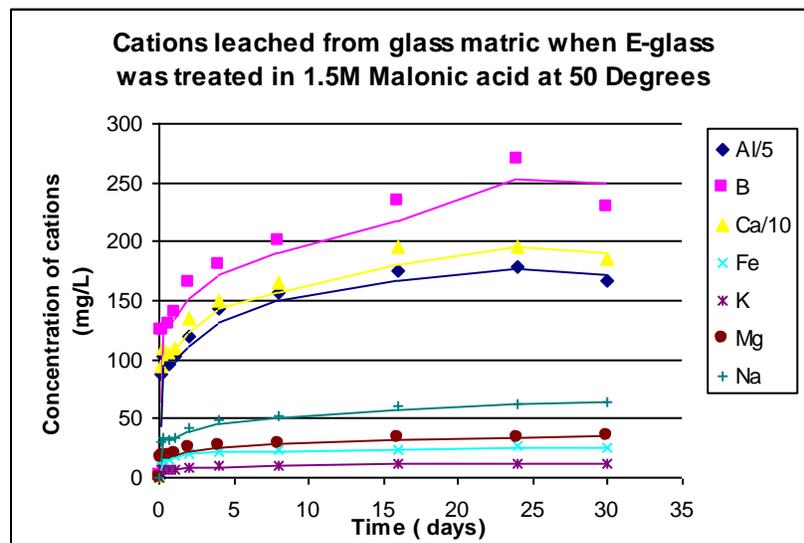


Figure 57: Leaching of cation from glass matrix when E-glass was treated in 1.5M malonic acid at 50 °C for various time frames

## Appendix - J

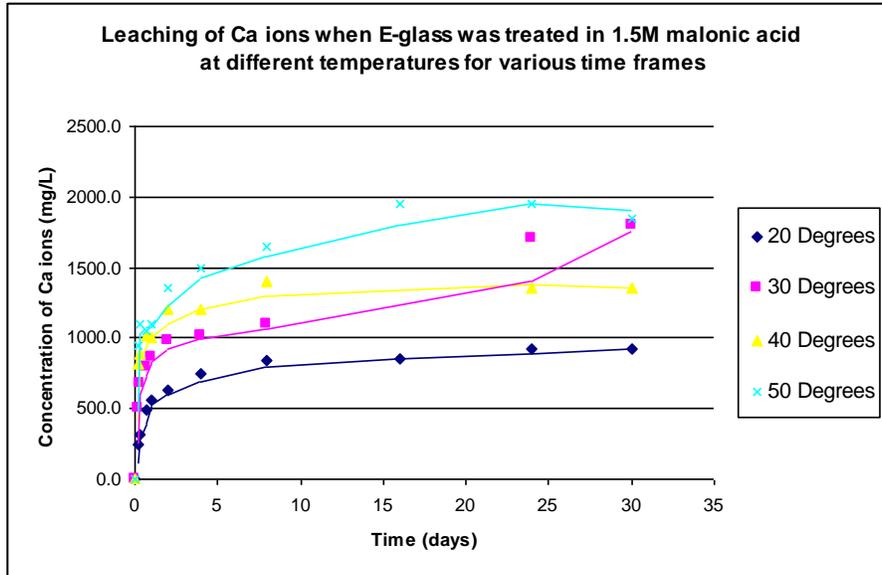


Figure 58: Leaching of Ca from glass matrix when E-glass was treated in 1.5M malonic acid

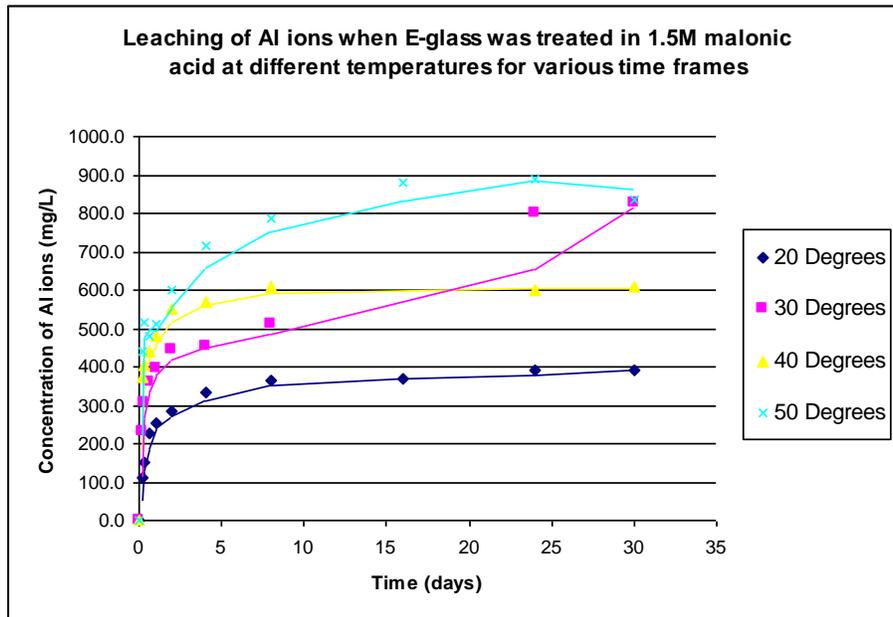


Figure 59: Leaching of Al from glass matrix when E-glass was treated in 1.5M malonic acid

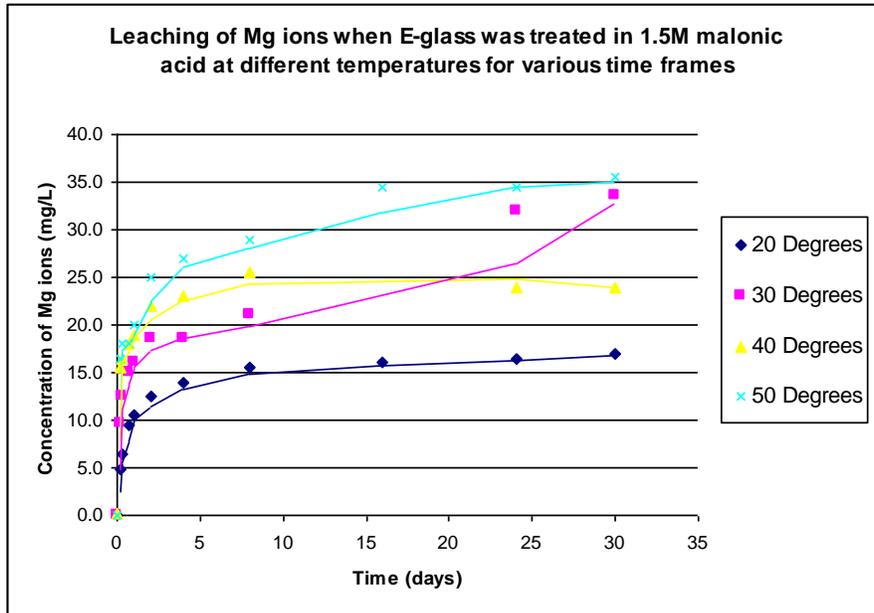


Figure 60: Leaching of Mg from glass matrix when E-glass was treated in 1.5M malonic acid

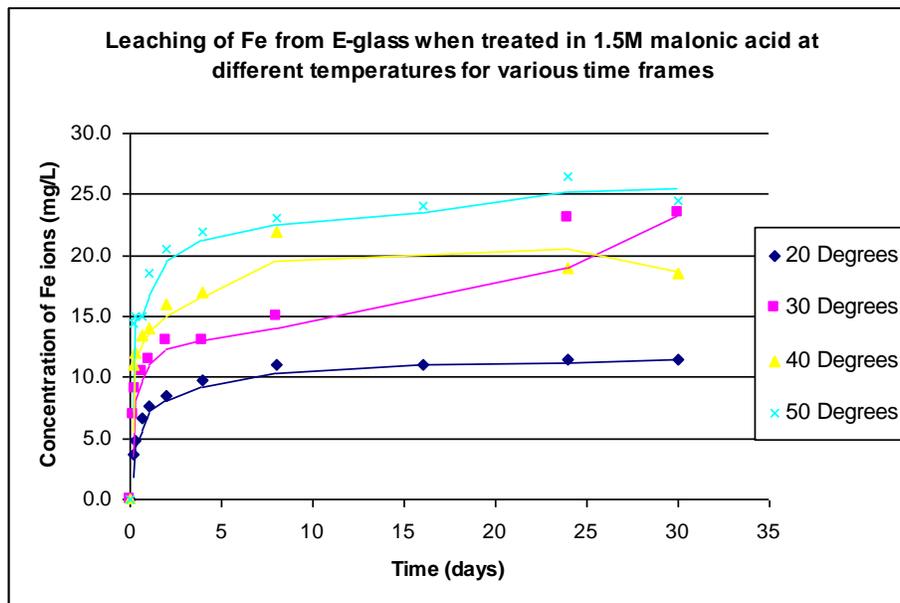


Figure 61: Leaching of Fe from glass matrix when E-glass was treated in 1.5M malonic acid

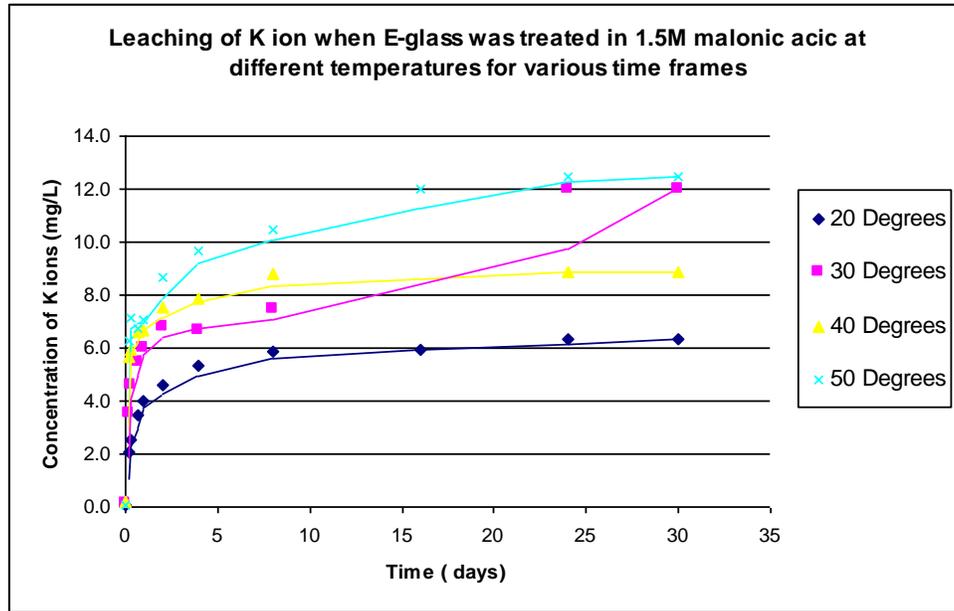


Figure 62: Leaching of K from glass matrix when E-glass was treated in 1.5M malonic acid

## Appendix - K

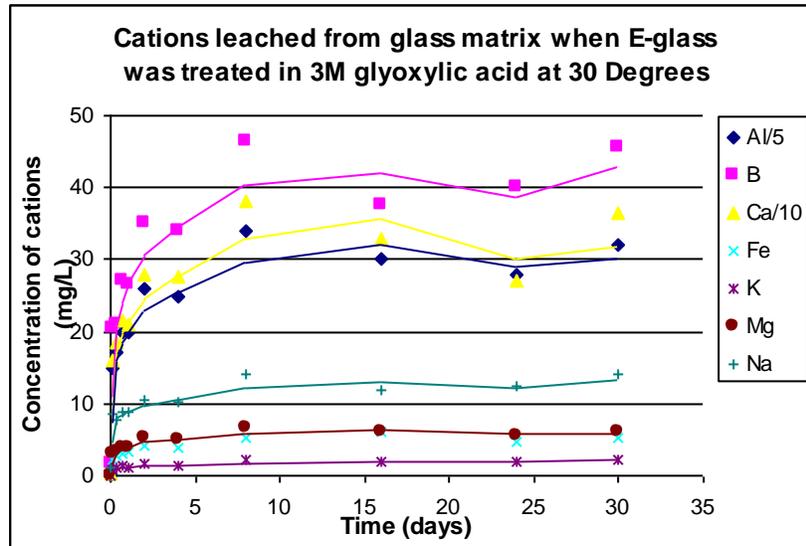


Figure 63: Leaching of cation from glass matrix when E-glass was treated in 3M glyoxylic acid at 30 °C for various time frames

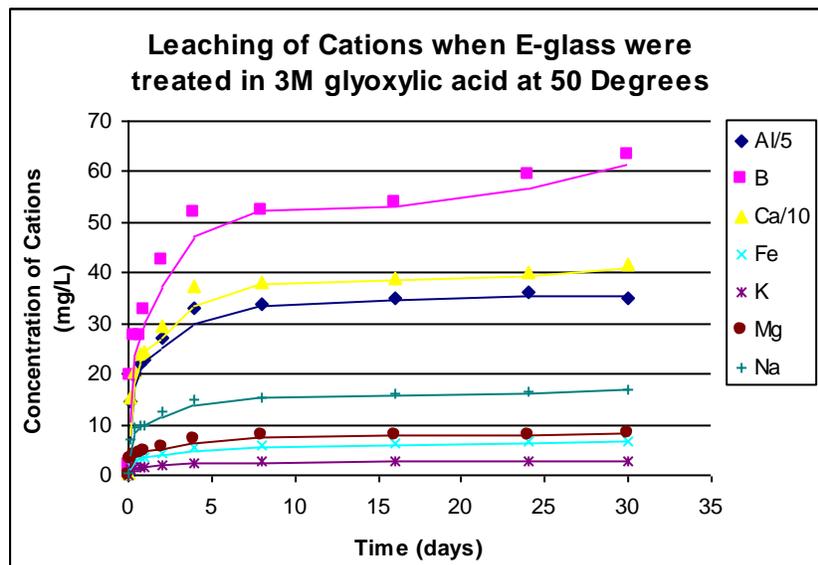


Figure 64: Leaching of cation from glass matrix when E-glass was treated in 3M glyoxylic acid at 50 °C for various time frames

## Appendix - L

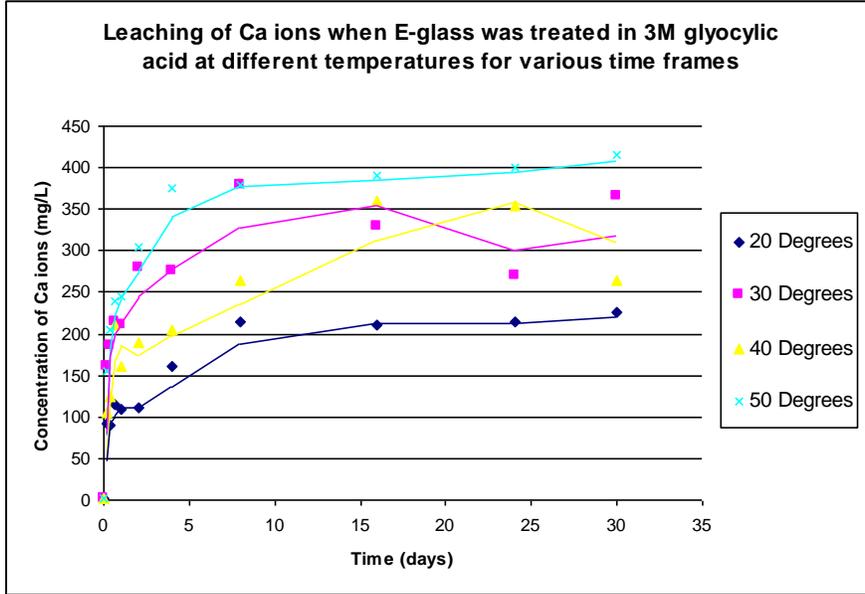


Figure 65: Leaching of Ca from glass matrix when E-glass was treated in 3M glyoxylic acid

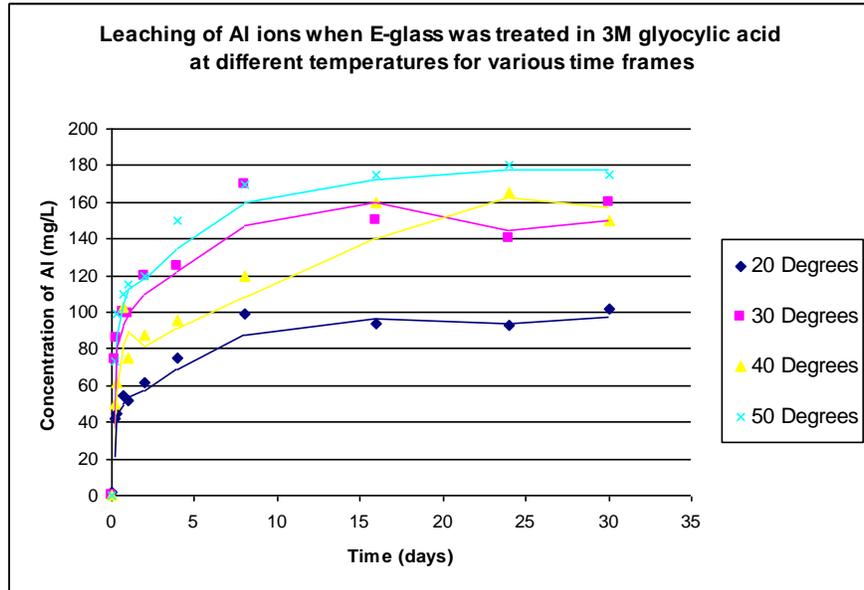


Figure 66: Leaching of Al from glass matrix when E-glass was treated in 3M glyoxylic acid

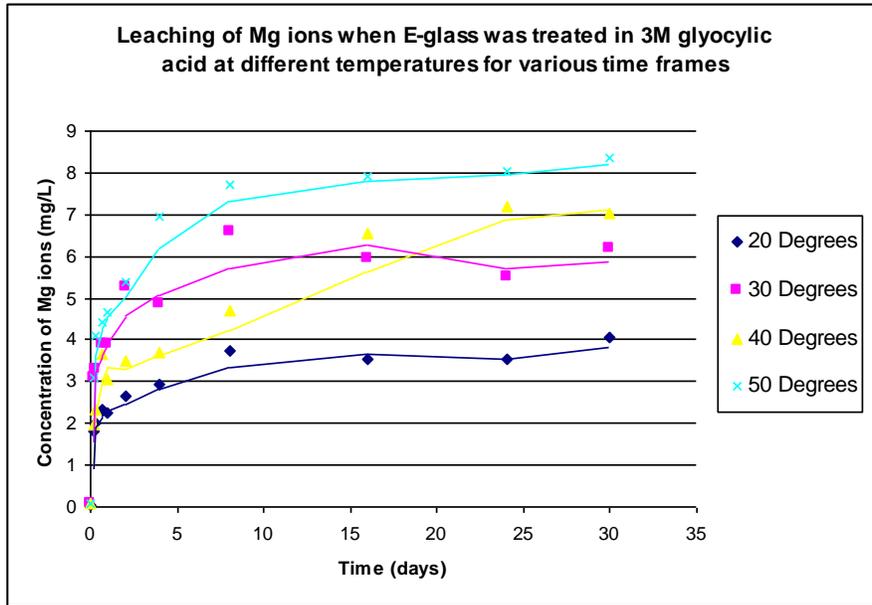


Figure 67: Leaching of Mg from glass matrix when E-glass was treated in 3M glyoxylic acid

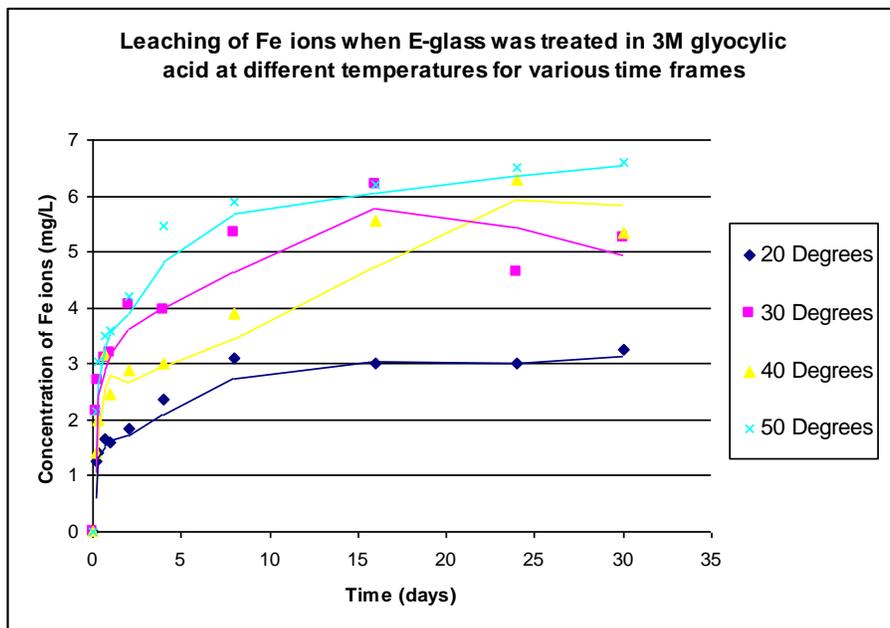
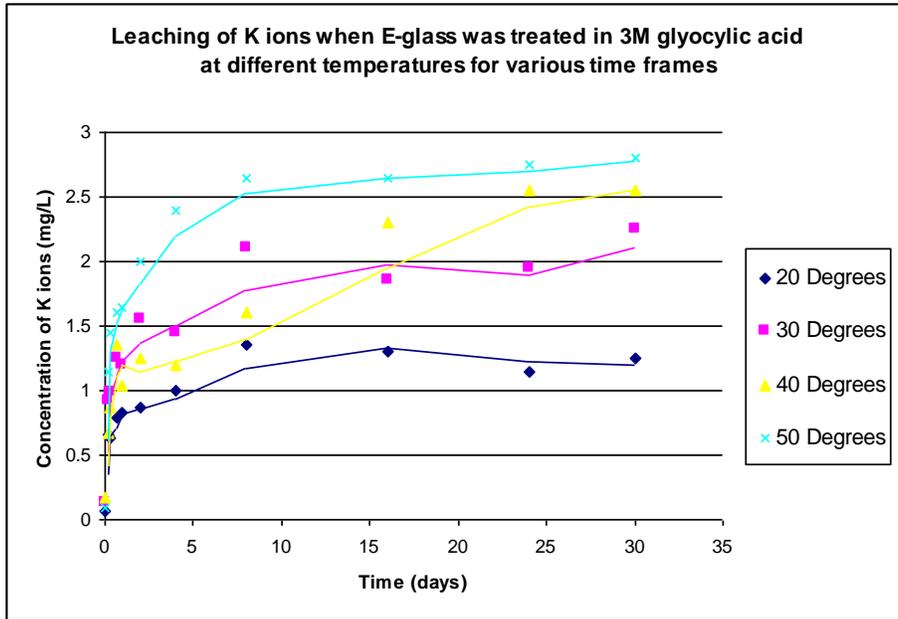


Figure 68: Leaching of Fe from glass matrix when E-glass was treated in 3M glyoxylic acid



*Figure 69:* Leaching of K from glass matrix when E-glass was treated in 3M glyoxylic acid