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AYDINLATMANIN E-CAMI ELYAFININ

MUKAVEMETİ ÜZERİNE ETKİLERİ

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THE EFFECT OF ILLUMINATION ON THE STRENGTH OF
E-GLASS FIBRE

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SUMMARY

The purpose of this study was to examine the effect of incident illumination on the stress corrosion of fibres immersed in aqueous sulphuric acid. Failure times of three types of Silenka E-glass fibres have been studied under load and immersed in a solution of 1M sulphuric acid under various illuminations. Also the iron(III) extraction has been done from three kinds of fibres.

The polymer size is not involved in the mechanism and has been shown to involve the formation of ferric iron complex. The rate of extraction iron(III) from glass, under u.v. light and blacked-out conditions, confirmed the involvement of Fe(III) in the mechanism.

Results have shown that failure times of each kind of fibres are dependent on the incident light. The data has been analysed by using Weibull statistics. It is clear that the failure probabilities of fibres under ultra violet radiation are higher than blacked-out condition. Also the results of extraction from each kind of fibres have shown that the amount of leached iron(III) under u.v.light is more than blacked-out condition.

ÖZET : AYDINLATMANIN E-CAMI ELYAFININ MUKAVEMETİ ÜZERİNE ETKİLERİ

E-camı elyafı, kalsiyum-alümina-borosilikat camından üretilen ve plastik takviye malzemesi olarak kullanılan endüstriyel bir üründür. İkinci dünya savaşı sonrası yıllarda plastik üretimindeki artışa paralel olarak cam elyafı, başta A.B.D. olmak üzere pek çok ülkede üretilmeye başlanmıştır. Ülkemizde ise bir Şişe Cam Fabrikaları A.Ş. kuruluşu olan Cam Elyaf San. A.Ş. tarafından 1974 yılından beri üretilmektedir.

E-camı, yapısal olarak alkali komponentler içermediğinden elektriksel iletkenliği diğer camlara göre oldukça düşük olması nedeniyle (electrical glass) olarak tanınmaktadır. E-camı, yapısında büyük oranda bor ve alumina bulunması nedeniyle kimyasal dayanımı ve elyaf olarak çekilme özelliği oldukça yüksektir. Refrakteri özel olarak seçilmiş fırında eritilen cam, platin-rodyum alaşımından yapılmış nozüller içeren ve elektrik ile ısıtılabilen plakadan (bushing) akıtılarak, elyaf sarma makinasında (winding machine) elyaf olarak üretilmektedir.

E-camı elyafının plastik ile kullanımı değişik proseslere göre olmaktadır. İlk başlarda polyeşter ve epoksi reçinelerde normal sıcaklıkta kullanılmaktaydı.

Daha sonra sıcak kalıplama komponentleri SMC, sheet molding compound, BMC, bulk molding compound, pultrüzyon gibi ürünlerde kullanılmaya başlanmıştır. Termo-plastiklerin gelişmesiyle; polyamid, polypropilen, polyetilen, naylon gibi pek çok plastikte takviye malzemesi olarak kullanılmaktadır. Günümüzde fabrika donanımlarında, alt yapı borularında, endüstriyel depolama tankı yapımı gibi pek çok alanda kullanım alanı bulmaktadır.

Camlarda "static fatigue" yük altında ortam şartlarında rutubetin etkisi ile oluşan mukavemet kayıpları Charles tarafından incelenmiştir. Metcalfe, E-camı elyafına değişik kimyasal çözeltilerin etkisini "stress corrosion" derinlemesine incelemiştir. Bu mekanizma genel olarak iyon değişimi olarak açıklanmaktadır. Yapıdaki özellikle alkali ve toprak alkali iyonlar asit protonu ile yer değiştirerek çözeltiliye geçmektedir. Elektron mikroskobu ile yapılan çalışmalar bu iyon transferi sonucu yüzeyde oluşan mikro çatlakları göstermektedir.

Cam elyafı ve plastiklerden yapılan kompozit malzemeler üzerine yapılan çalışmalar, özellikle asidik şartlar altında, takviye olarak kullanılan elyafın daha çok etkilenecek mukavemet kaybına neden olduğunu ortaya koymaktadır. Bu çalışmada, hammaddeden safsızlık olarak

gelen ve E-camı içerisinde %0.3-0.5 arası bulunan demir iyonlarının özellikle ultra-viole ışıklardan etkilenerek demir(iii) şeklinde asidik çözeltiye geçmeleri sırasında, yapıyı bozarak alumina ve kalsiyum gibi komponentlerin uzaklaşmasını kolaylaştırarak, mukavemet kaybına neden olup olmadığı araştırılmıştır. Birinci aşamada üç çeşit elyafın ultra-viyole ve karanlıkta 1M sülfirik asit içerisinde kopma zamanları bilgisayar kullanılarak tespit edilmiştir. Ultra-viole ışın kaynağı olarak ortalama dalga boyu 256 nm olan floresan lamba kullanılmıştır. Radyasyondan etkilenmemek için sistem kapalı olup, iki adet lamba üst kapağa yerleştirilmiştir. Filament (tek bir elyaf) lerin çapları 632 nm dalga boylu He-Ne laser kullanılarak bulunmuştur. Bulunan elyaf çapları, % uzamanın hesaplanmasında kullanılmıştır. Filamentlerin kopma sürelerini kısaltmak için belli bir % uzamayı verecek camdan yapılmış ağırlıklar uygulanmıştır. Literatürde E-camı elyafı için % uzama 2.5-4 arası verilmektedir. Bu çalışmada %-uzama 0.3-0.4 arasında tutulmaya çalışılmıştır. Çapı ölçülen filamentler aralarındaki mesafe 5'er cm olacak şekilde bir ucundan cam çubuğa diğer ucundan ise cam ağırlığın asılacağı lastik banta yapıştırılmıştır. Daha sonra içi su ile doldurulmuş stres korozyon tankı içindeki 1M sülfirik asit çözeltisi ile dolu 1 litrelik beher içerisine cam ağırlık ve filament çözelti içine batacak şekilde tel

çubuga asılmıştır. Tel çubugun diğer ucunda "magnetic switch" mıknatıslı devre açıp-kapama sistemi bulunmaktadır. Filamentin çözelti içine asılma ve kopma zamanları bilgisayar tarafından tespit edilerek ne kadar sürede koptuğu kesin olarak bulunmuştur. Ultra-viyole ve karanlık denemeleri için iki ayrı tank bulunup her birinde 16 adet filamentin izlenmesi mümkün olmaktadır.

İlk olarak 084 M19 kodlu direkt sarma rovinginden alınan 28 filamentin kopma zamanları ultra-viyole ışınları altında ve 31 filamentinki ise karanlıkta bulunmuştur. Bu filamentlerin ortalama elyaf çapları 14.3-14.5 mikron arası, % ortalama uzama 0.322-0.335 arası, ortalama kopma süreleri u.v. ışınları için 38550 saniye ve karanlıkta ise 121960 saniye olarak bulunmuştur. İkinci olarak yalnızca γ -propil üçhidroksi silan ile kaplı elyaflar kullanılarak 30'ar filament u.v. ışınları ve karanlıkta kopma zamanları bulunmuştur. Filamentlerin elyaf çapları 14.8-14.9 mikron, ortalama % uzama 0.321-0.348 ve ortalama kopma süreleri ise u.v. ışınları için 73450 s ve karanlıkta ise 146140 s olarak bulunmuştur. Üçüncü olarak yüzeyi kaplamasız elyaflardan alınan 29 adet filamentin kopma zamanı u.v. ışınları altında ve 31 adet ise karanlıkta bulunmuştur. Ortalama elyaf çapları 15.2-15.4 mikron, ortalama % uzama 0.347-0.348, ortalama kopma süresi ise u.v. ışınları için 46200

saniye ve karanlıkta ise 145990 s olarak bulunmuştur. Dördüncü olarak korozyon çözeltisine ağırlık olarak %0.5 oranında demir(iii) sülfat ilave edilerek yüzeyi kaplamasız elyafların kopma süreleri bulunmuştur. Bu çalışmanın amacı kopma süresini etkilediği düşünülen demir(iii)'ün elyaftan ekstrakte olacak miktarı azaltarak kopma süresini uzatıp uzatmadığı idi. 29 adet filamentin kopma zamanları u.v. ışınları altında, 30 filamentin ise karanlıkta bulunmuştur. Ortalama elyaf çapı 15.3-15.4 mikron, ortalama %uzama 0.361-0.371, ortalama kopma süreleri ise u.v. için 74710 saniye ve karanlıkta 167860 saniye olarak bulunmuştur.

Sonuçlar Weibull istatistigi kullanılarak yorumlanmıştır. Kopma zamanları kopma ihtimallerine göre grafiğe çizildiğinde üssel bir eğri vermektedir. Bu metod uygulanarak lineerleştirme yapılmıştır. Weibull parametreleri yani lineer doğruların eğimleri tüm denemelerde birbirine oldukça yakın bulunmuştur. Bu sonuç kopma mekanizmasının hem u.v. ışınları altında hemde karanlıkta aynı olduğunu göstermektedir. Ayrıca karakteristik kopma zamanları ki $\ln \ln(1/(1-P))=0$ olduğu durumdaki zamanı ifade etmektedir, u.v. ışınları altında ve karanlıkta tüm deneylerde oldukça farklı bulunmuştur. Buna göre, u.v. ışınlarının kopma süresini kısaltarak elyafların mukavemetini etkilediği söylenebilir.

Mukavemet azalmasının camda safsızlık olarak bulunan demir(iii)'ten gelip gelmediğini araştırmak için yapılan kopma süresi deneyleri ortamda demir(iii) iyonları bulunması durumunda sürenin açık bir şekilde uzadığını göstermektedir. Ayrıca yapılan ekstraksiyon deneylerinde u.v. ışınları altında daha fazla demir(iii)'ün ekstrakte olduğunu göstermektedir. Ekstraksiyonda solvent olarak yine 1M sülfirik asit kullanılmış ve Fe(iii) miktarı u.v. spektroskopisi kullanılarak bulunmuştur. Deneyler ağız açık 100 cc lik beherlerde 50 cc solvent içine 1 gram elyaf konularak kopma süresi deneylerinde olduğu gibi aynı şartlarda yapılmıştır. Tüm elyaflardan demir(iii) ekstraksiyonu iki durumdada aynı mekanizmaya göre yürümektedir. Ekstrakte edilen Fe(iii) miktarı, mg/g elyaf, $w=t/(a*b*t)$ şeklinde verilmektedir. Bu ifadede t ekstraksiyon zamanı saat olarak, a ve b ise sabitlerdir. En kötü durumda korelasyon katsayısı 0.98 olacaktır şekilde katsayılar bulunmuştur. Ayrıca bu çalışmada kullanılan silan kaplı elyafın ve Cam Elyaf San. A.Ş. den temin edilen elyaf yüzeylerine asidik çözeltinin etkisini görmek için elektron mikroskopunda yüzey fotoğrafları çekilmiştir. Silenka-Hollanda'dan sağlanan silan kaplı elyafların yüzeylerinde spiral çatlakların olduğu görülmesine rağmen diğer elyaflarda herhangi bir şey görülmemiştir. Bu sonuç, alümina ve bor gibi kimyasal dayanımı artırıcı Komponentleri daha fazla içeren elyafların daha az korozyona uğradığını göstermektedir.

CHAPTER 1: INTRODUCTION AND LITERATURE SURVEY

1.1. INTRODUCTION

Continuous filament glass fibres were introduced as a reinforcement for plastic materials some 30 or so years ago. Many different types of glass are available which can be converted into usable fibres; however, for commercial reasons only a few basic compositions are used. E-glass is a very low alkali content borosilicate glass which provides good electrical and mechanical properties, coupled with good chemical resistance. Compositions of some of the glasses likely to be encountered are shown in Table 1.1 [1].

All glass fibres must be sized ie. coated with a polymeric finish, when produced. This finish determines the processability of the fibres and prevents inter-fibre abrasion. It also helps to hold the filaments together during processing into twisted yarns and fabrics. A typical size will contain four different components: i. a coupling agent to promote bonding of the resin matrix to the fibre -usually an organo silane; ii. a film forming polymer to act as a size-often a polyvinyl acetate emulsion; iii. a lubricant-usually a fatty acid amide; iv. other materials such as anti-static additives to give

particular properties to fibres. In the formation of discontinuous or continuous glass fibre mat and woven rovings additional polymeric binders are used.

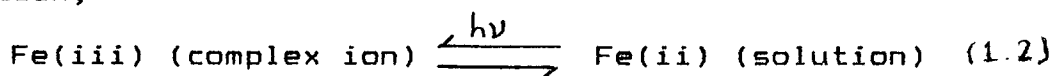
E-glass fibre reinforced plastics are increasingly being used in industrial applications in which the composite material is in contact with corrosive environments. Until now much work has been done in order to examine the stress corrosion of the glass reinforcement and their GRP (Glass Reinforced Plastic). The most interesting thing is that the glass fibres which are in the composite materials are effected by environmental conditions more than matrix polymers.

It was observed by Sheard [2] during extensive study of the acidic stress corrosion failure of single glass filaments that the failure apparently occurred more rapidly during daytime experiments. More recently, it was confirmed that a u.v. source of 256 nm accelerated the failure [3]. However, the mechanism was not clear because the fibres chosen for the study were coated with a commercial polymeric size. In this study the role of the polymer coating has been explored by comparing the stress corrosion failure times for uncoated (so-called water sized) filaments, silane sized and commercially sized glass fibres. The fibres were obtained from the same manufactures and have the same nominal bulk compositions.

Iron is the most commonly found impurity in E-glass. Chandler et al [4] studied the corrosion of fibres in different solutions and observed presence of the Fe(iii) in corrodent solution. Iron is present in alkali silicate glasses as Fe(iii) and Fe(ii) but according to the equilibrium, concentration heavily favours Fe(iii) in this case. In low soda glasses of which E-glass is typical Fe(iii) is considered to be tetrahedral co-ordination within a bridging oxygen network. The leaching process in aqueous sulphuric acid will therefore lead to the presence of Fe(iii) ions in solution. The equilibrium between ferric and ferrous in the solution can be written as below,



Also the dissolution of ferric iron from the complex into solution as ferrous can be shown by the following equation;



encouraging more Fe(iii) to be leached out of the glass, making the removal of calcium and aluminium ions easier and hence accelerating the stress corrosion.

A technique for the testing of single glass fibres for stress corrosion in the controlled aqueous environment has been developed by Sheard [2]. He found

that stress corrosion was affected not only by the applied stress and the acid concentration but also on the nature of the illumination employed during the experiments.

The purpose for the present study is to examine the effect of incident illumination on the stress corrosion of three types of E-glass fibres immersed in 1M aqueous sulphuric acid and its Fe(iii) solution by examining the failure times of the fibres and the amount of extracted Fe(iii) in acid solution and to consider the contribution of any of the polymeric size normally present on the glass fibre surface.

1.2. STRUCTURE OF E-GLASS FIBRE

E-glass is a calcium alumina-borosilicate glass containing less than 1% alkali oxides. It is now almost universally used for the reinforcement of plastics. This was chosen for its low electrical conductivity and for its excellent resistance to water. Although E-glass was originally developed for electrical applications, this is now only a small proportional of the total market, it has become standard for most uses [5].

Generally raw materials for glass making can be considered under three headings; 1. Network formers:

Silica, boric oxide and alumina 2. Network modifiers: Calcium oxide, barium oxide, sodium oxide and potassium oxide 3. Intermediate oxides are : Magnesium oxide, beryllium oxide and titanium oxide.

The structure of silicate glasses is based on the fundamental unit of a silicon-oxygen tetrahedron in which a central silicon ion is surrounded by four oxygen ions. A continuous but irregular three-dimension spatial network is built up from these tetrahedron joined corner to corner via a common oxygen ion. Other oxide cations fit into holes in the structure and cause a number of broken linkages in the network which may itself be modified in a few places by the presence of small amounts of other network forming oxides [6]. The --Si-O-Si-- chemical bonds are strong and have significant covalent, character. This, together with the irregular structure, gives a mechanical behaviour similar to that of oxide crystals—that is plastic deformation is extremely limited and only occurs at very high stresses [7].

Silica, SiO_2 , in all its forms exists as a polymer $(\text{SiO}_2)_n$, it has no melting point but gradually softens as the temperature is raised to 2000°C , above which it begins to decompose. In its various crystalline forms it consists of rings of SiO_4 groups, the linking between

groups being achieved by sharing of O^{2-} ions between Si^{4+} ions.

Silica, in the form of quartz, consists of a continuous three-dimensional network of repeated rings containing 3 or 6 SiO_4 groups [8]. This basic group has a tetrahedral structure with the four oxygens at the corners and the silicon at the centre of the tetrahedron.

Silica is a perfectly viable material as glass fibres. Commercially, fused silica fibre is produced for optical purposes. Other commercial glasses based on silica are obtained by fusing a mixture of materials at temperatures ranging from $1300^{\circ}C$ to $1600^{\circ}C$. The silica network has been modified, its continuity interrupted and its structure made more irregular by the introduction of other oxides.

Alumina forms $(AlO_4)^-$ groups in glasses. At low concentration, $Al(III)$ ion will substitute for a Si^{4+} ion, i.e. an AlO_4 Tetrahedron can be formed which will join in the network formed by the SiO_4 tetrahedron, provided an additional cation is available and can be located in a nearby hole to preserve the electrical neutrality. The additional cation may be an alkali metal ion or even an alkaline earth ion "shared" between two adjacent AlO_4 tetrahedron [7].

Adding alumina to the glass will increase its durability because, as mentioned before, alkali or alkali earth ions are trapped by Al(III). Dillmore [9] has studied the effect of alumina additions to binary $\text{Li}_2\text{O}-\text{SiO}_2$ glasses. The first 2.5 % alumina addition has the greatest effect on decrease Si dissolution. On the other hand, alumina will cause to the increase of viscosity and decrease of melting temperature. We know that the high viscosity and low melting point are very important to make glass without crystallization.

Boric oxide can form two kinds of groups, $(\text{BO}_4)^-$ which require an ion with a single positive charge for electrical neutrality and (BO_3) groups which are electrically neutral. Depending on the availability of ions with positive charges, e.g. Ca(II), Ba(II), Na(I), etc. the introduction of B_2O_3 can give rise to BO_4 or BO_3 groups in the network or a mixture of both. For low alkali concentration boric oxide behaves like alumina, each BO_3 unit is linked to one BO_4 .

Boric oxide reduces viscosity without producing adverse changes in thermal expansion and durability [7]. Its effects depend on concentration and that of the alkali or alkali earth metals. At high alkali concentration, non-bridging oxygens are produced but vice versa 4-fold borons occur.

Modifier oxides like CaO , BaO , Na_2O , etc., break $-\text{Si}-\text{O}-\text{Si}-$ bonds and by doing so reduce the melting temperature of glass. These ions locate themselves in the holes of network. CaO inhibits mobility of alkali ions, hence increases resistivity and durability of glasses. It also causes the shortening of the working range because of the increase of viscosity.

Substitution of 10 mole % CaO for 10 mole % SiO_2 in a 20 mole % Na_2O , 80 mole % SiO_2 glass produces a remarkable improvement in glass durability. Clark et al [10] studied the surface chemical changes resulting from the CaO substitution using solution analysis. They found that both glasses, 20% Na_2O , 80% SiO_2 and 20% Na_2O , 10% CaO , 70% SiO_2 , develop alkali depleted layers as a result of preferential dissolution of sodium.

It has been observed that when $1/3$ CaO is replaced by MgO the melting temperature decreases 100°C and the viscosity increases. On the other hand, by using more than one alkali earth components the durability of glass can be improved.

1.3. STRENGTH OF GLASS FIBRE

Glasses are brittle materials and like other brittle materials there are a number of methods used to estimate

the strength of the interatomic binding forces. Orowan [11] estimated the theoretical strength of brittle materials by considering that the mechanical work done in stretching the bonds across a plane to cause failure equals the fracture surface energy of the new surfaces created. According to Orowan theory the theoretical fracture stress can be given by the following equation, $\sigma_m = (E \gamma / a_0)^{1/2}$ where E is the Young's modulus of the materials, a_0 is the interatomic distance and γ is the fracture surface energy. This quantity, the fracture surface energy, γ (units of joule/sq.meter) is very important in the study of brittle fracture. The energy of the newly-formed fracture surface arises because the forces acting on the surface atoms are primarily inward-acting forces of attraction from atoms in the interior. These atoms are subjected to forces which are practically the same in all directions. Until more recently γ could only be estimated, but now there are many methods by which it can be measured. Wiederhorn [12] has found that, for a commercial soda-lime-silica glass, the value is in the range 2-4 joule/sq.meter, according to the ambient conditions.

Thin filaments usually have a higher tensile strength than thick ones. Many factors contribute to this. One of the most important of these factors is the

process by which the thin filaments are produced. Because glass fibres are non-crystalline, crystal drawing and work hardening are not operative factors. The ratio of the strength of fine glass fibres to that of bulk glass is much greater than the corresponding ratio for other materials. For brittle materials, the measured fracture stresses are usually much less than the theoretical values. This is explained by the presence of submicroscopic flaws in the surface which concentrate the stress at the flaw tip. Griffith [13] demonstrated that for a given applied stress a flaw will extend and cause fracture only if its length exceeds a critical value. Such deep flaws would not be possible in a glass fibre. Most experimental work has shown that the tensile strength increases with a decrease in diameter. It is therefore the fashion to base a discussion of the strength of fibres on this observation; the results on Griffith [13], Smekal [14], Murgatroyd [15] all support this dependence of strength on diameter.

Adderregg [16] suggested that although the solubility of gases in glass decreases with rise in temperature, there would still be some gas dissolved in molten glass. Hence when the glass was pulled out into fine fibres the discontinuities would be pulled out into fine capillaries so that their effect on the strength of glass would be much less, especially as these capillaries

will tend to be near the centre of the fibre leaving the fibre with an undamaged surface.

Table 1-1 The weight % of glass compositions used in the fibre manufacture. Taken from ref.1.

Comp.	E-Glass	A-Glass	C-Glass	S-Glass	CemFIL
SiO_2	52-56	72	59-64	65	70
Al_2O_3	12-16	2.5	3.5-5.5	25	-
B_2O_3	8-13	0.5	6.5-7	-	-
ZrO_2	-	-	-	-	16
MgO	0-6	0.9	2.5-3.5	10	-
CaO	16-25	9	13-14.5	-	-
Na_2O	)	12.5	-	-	12
	) 1				
K_2O	)	1.5	-	-	tr
Fe_2O_3	0.3	0.5	0.1-0.3	tr	tr
F_2	0-1.5	-	-	-	-

Many workers have suggested that the origin of the flaws might be the orientation of molecules in the glass during the drawing process. Prebus and Michener [17], using an electron microscope, have found evidence which they interpreted as indicating ordered molecular structures of up to 10 nm in length.

Thomas [18] has also determined the effect of production conditions on the tensile strength of glass fibres. He found that fibre strength is independent of

diameter, a result which is at variance with that of previous workers. The fracture stress of a glass fibre is found to be constant provided the temperature of the molten glass from which the fibre is drawn is sufficiently high to permit a fibre of uniform diameter to be produced. The room temperature strength of glass fibres decreases on annealing at temperatures as low as 100°C , and the rate of decrease of strength increases with increase of annealing temperature. At an annealing temperature of below 300°C heating for at least 2 hours is required to reduce the tensile strength to a constant value.

Loewenstein [19] studied a single fibre of E-glass, A-glass and a high-strength glass using in the main a technique similar to Thomas. The strength of glass fibre, when measured at room temperature and under the not uncommon condition of 65-75% relative humidity, is a function of the glass composition, the diameter of the fibre and the temperature of the glass from which the fibre was drawn. The alkali-containing A-glass shows a very significant strength-diameter relationship, whereas the strength of fibres from the early alkali-free E-glass is almost independent of diameter. The composition of glasses are such as in Table 1-1.

Metcalfe and Schmitz [20] studied the effect of

specimen length on the strength of E-glass fibres and showed the apparent strength was less, the longer the fibre. The effect of area and size of surface flaws cause measured failure strengths for comparable specimens to be scattered over a wide range. Hence the results of any tests have to be analysed mathematically using flaw statistics, such as Wiebull statistics [21].

Another important factor in considering the strength of glass is the time over which the stress is applied. A high enough stress will cause immediate failure of the glass, but at lower stresses it is found that the glass fractures after some time. The lower the stress, the longer the time-to-failure. The effect is known as static fatigue and is affected by ambient conditions.

Since static fatigue is produced by a synergism between the applied stress and the environment it is now termed environmental stress corrosion. In the present study the environmental stress corrosion of E-glass fibres will be considered more closely.

1.4. STRESS CORROSION OF GLASS FIBRES

Glass fibre reinforced plastics are becoming increasingly used in applications in which the material is in contact with acidic environments, such as process

plant equipment, storage vessels and sewage pipes. In such applications, the material is subjected both to an aggressive environment and to applied stresses which together produce a synergistic effect that can lead to failure. Therefore it has become important to study the environmental stress corrosion of such materials [22,23]. Much work has been done on environmental stress corrosion of GRP and their glass reinforcement. It has been found that there is remarkable qualitative similarity between the behaviour of GRP and the glass reinforcement alone on the same concentration of aqueous sulphuric acid [24] leading to the conclusion that at least for composites with cut edges and no gel coat, strength loss in H_2SO_4 is principally due to attack on glass rather than degradation. The glass resin interface is important and a poor bond gives rise to capillary transport of the acidic environment. Chemical degradation of the interface can therefore affect the rate of stress corrosion. However, the crucial aspect is the introduction of a sharp crack promotes stress corrosion of the filaments.

Metcalf and Schmitz [25] have also shown that the rate of stress corrosion of GRP laminates is strongly dependent on the susceptibility of the glass fibre reinforcement to environmental attack. This is exemplified in work by Jones et al [26,27] where glass fibre reinforced epoxy laminate and single glass filament

exposed to the same environmental conditions failed in the same time period.

In stress corrosion it has been found that the dilute solutions of acid in the 1-4 molar range are more aggressive to E glass than the more concentrated solutions and this is found to be true at all temperatures in range 22-88 °C [24]. This has been interpreted in more than one way.

Collins [28] interprets minimum strength retention with acid concentration as being due to ionic association in concentrated solutions so that the maximum concentration of hydrogen ions occurs at 1-6 M.

Jones and Rock [29] could not confirm this hypothesis by calculating the hydrogen ion activity for a range of sulphuric acid solutions. However they observed that NaHSO_4 was as corrosive as H_2SO_4 and suggested that the mechanism was more complex. Chandler and Jones [4] have examined this further and proposed that iron complex formation plays a role.

Roberts [23] on the other hand prefers the interpretation that in concentrated solutions there are insufficient water molecules for solution of hydrogen ions, thus decreasing their reactivity at the glass surface. Either would explain why strong acid solutions

are less aggressive than weaker ones and point to hydrogen ions as being responsible for glass attack.

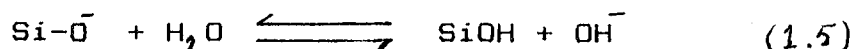
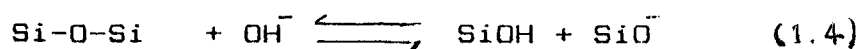
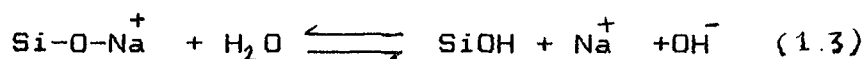
There has been much study on environmental stress corrosion. Charles [30] proposed a mechanism of dissolution in which the sodium ion diffusion in the glass is considered, the rate controlling step and the ultimate breakdown of the glass structure due to its reaction with hydroxyl ions at the crack tip. It was noted that since the temperature dependence of the corrosion of silicate in water vapour has similar activation energy to that required for sodium ion migration, alkali content causes low long-time strengths in inorganic glasses.

Charles and Hillig [31] investigated the stress corrosion phenomenon by examining the relationship between slow crack growth prior to catastrophic failure and changes in crack geometry due to stress corrosion. They concluded that this type of corrosion occurs due to a stress dependent chemical reaction between water and existing flaws which causes the flaws to grow large enough to create spontaneous crack propagation.

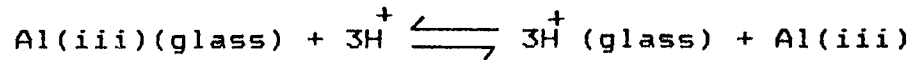
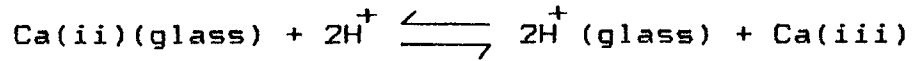
Stress corrosion is thought to be an ion exchange mechanism [30]. The original thinking on ion exchange theories assumed that hydrogen ions are associated with water molecules which then cause swelling of the glass surface [2].

Metcalfe et al [25,32] however, considered that ion exchange between hydrogen ions in solution and alkali ions in glass is the cause of strength loss. This ion extraction causes contraction of molar volume because the hydrogen ions are smaller than the extracted alkali ions, thus setting up tensile stresses in the surface. In E-glass, the diffusion of sodium ions is thought to be the rate controlling step and further hydrolysis by reaction with hydroxyl ions is considered to be responsible for fracture [30]. Further work on ion exchange mechanisms identified the major factor which are expected to influence the equilibrium reactions in the glass-acid system [33]. These are: i. activity of H^+ and metal cations in solution ii. preference of glass for high valence ions iii. preference of glass for ions with smaller hydrated volume iv. preference of glass for more strongly bound ions v. metal ions which become involved in anionic complex formation are more likely to be removed from the glass.

The ion exchange mechanisms are shown as follows:

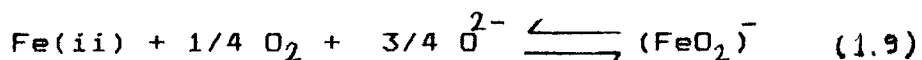
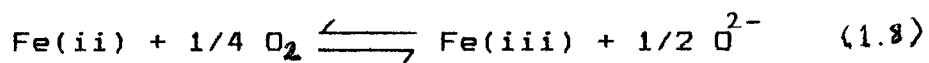


Particular reactions likely to govern corrosion of E-glass fibres according to Chandler et al [4] can also be given as below:

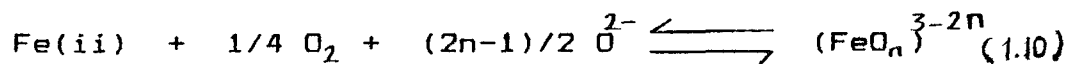


where a reaction from left to right leads to corrosion. Adding Al(iii) and Ca(ii) separately shows the former has the greater effect which may indicated slight favour of reaction.

Looking at the structure of silicate glasses shows us that oxygens can exist in three forms: bridging oxygens which link the silica tedrahedra, non-bridging oxygen which result from additions of network modifier such as calcium and free oxygen which are present in very small concentration and exist for very short times. Iron exist in glass in either of two valence states the proportions of which are dependent on the forms of oxygen and the amount of network modifier. The valence states can be represented by the equilibrium:



The general form of the equation involving oxidation of ferrous to ferric may be written as;



The value of n is likely to remain within the limits $1 < n < 4$.

It would be reasonable to suggest that this equilibrium tends towards the ferric concentration in E-glass since it contains a high amount of lime which increases the number of non-bridging and free oxygens and thus push the equilibrium towards the right.

Recent work by Kordas and Oel [34] examined the effect of radiation damage on iron silicate glasses. They studied the effects of beta and x-rays but it must be noted that these are of much higher energy than the ultra-violet radiation being considered in this work. However they found that irradiation causes changes in the physical and chemical properties of glasses, depending on the composition.

McKinnis [35] was able to apply Charles' theory to high strength glass fibres by calculating that Griffith flaws could be generated by a reaction between water and

the stressed bonds in a dispersed crystabolite phase at the fibre surface.

Douglas and Isard [36] demonstrated that the extraction of sodium ions from soda-lime glasses is diffusion controlled. Douglas proposed a model where silica dissolves at the leached layer solution interface and alkali ions diffuse across the leached layer into the water. This layer has been observed [37]. In Douglas' mechanism the rate of diffusion of alkali ions is initially proportional to square root of time, linear proportionality with time being established, it is assumed that silica and sodium ion diffusions are balanced. This theory accounts for the effect of pH and the stabilising effect of calcium oxide in soda-lime glasses [38]. The precipitation of calcium at the crack tip to stabilise the decomposition of the glass and limit sodium ion loss was also proposed by James and Healey [39].

The stability of the silica network in glass is strongly pH dependent. Mould [40] demonstrated that a high pH increases the strength by up to 20%. Study of the equilibria between glass and water by Fox [41] shows that the reactions are pH controlled. The calculated pH value correlates well with that found experimentally by Wiederhorn [42] and thus implies it is the dissolution of

the sodium which controls the pH at the crack tip.

Cockram [43] confirmed that the strength of E-glass depended on the pH of the solution in which it was immersed. Also Collins [44] observed that stress corrosion was most aggressive in glass reinforced laminates for acidic concentrations in the range 0.5 to 3M. On the other hand Kielland [45] calculated that neither the concentration nor activity of hydrogen ion was maximised within a range of acid concentration. Jones et al [46] calculated that stress corrosion of glass fibres by sulphuric acid could not be explained by simple ion exchange and there must be a mechanism change with acid concentration. They reasoned that another species in the acid could be involved in the process as well as the sulphate and hydroxonium ions. The corrosive nature of the bisulphate ion was proven on observation of cracks in glass fibres immersed in aqueous sodium bisulphate. Ernsberger [47] showed that non-bridging oxygen concentration in the structure affects the rate of proton transport into glass from an acidic environment. He concluded that the proton transport does not occur by an ion exchange mechanism, but probably occurs as part of an oxygenated species-molecular water.

Michalske and Frieman [48] found that the size and charge distribution of the attacking molecule is

critical. They proposed a three step process to represent the interaction between a strained bridging bond at a crack tip in silica with water from the environment. This molecule must be able to form a transitional state with the Si-O bond if, as Weyl suggested [49], the reaction with this bond causes the growth of subcritical flaws. Hence the attacking molecule must be polarised.

Another alternative theory to ion exchange was proposed by Griggs [50]. He suggested that water plasticises the glass by breaking the hydrogen bonds between neighbouring hydrolysed siloxane links.

The change in mechanism by Cockram [43] was observed by Jones and Chandler [51,52]. They proposed that a complexing reaction is responsible for this. As the anion concentration is increased there is a tendency for them to associate with ferric ions on the glass surface and so inhibit the leaching process. In other papers [53,54] they showed evidence that acid strength was not the most important factor in studying stress corrosion.

The various cracks which have been observed are attributable to different factors. Charles and Hilling [31] reported a core-sheath structure in fibres tested in super heated steam. This is attributed to the fibres swelling.

Bledzki et al [55] have observed radial, axial and spiral cracks in glass fibres immersed in sulphuric acids, but these were only present when completely dry. They correlated the type of crack with the penetration depth into the leached zone, and concluded that crack formation is due to water removal causing axial and circumferential contractive forces.

Another crack propagation hypothesis by Holloway et al [56,57] assumed that the mechanism is modified by a ductile region present ahead of the crack tip. There has been considerable study of the environmental stress corrosion of silicate glasses and although it is agreed that the rate of corrosion is affected by different environments, temperature and glass composition, no single theory of the mechanism of stress corrosion has yet taken precedence.

Some glassfibre strands which have different glass compositions were in water or water vapour examined and the results shown in Figure 1.1. When we look at this Figure it is easy to see that E-glass fibres show more strength loss than CemFIL.

At the other end of pH range, Metcalfe et al [32] drew attention to severe strength loss of E-glass fibres in strong acids and attributed this to ion exchange between hydrogen ions in solution and alkali metal ions in the glass which leads to contraction, and hence tensile stress, in the surface of the fibre. Recent results of strand strength tests after 16 hours exposure at room temperature to 1M H_2SO_4 for standard E-glass fibres and an experimental "alkali free" E-glass were;

Standard E-glass strand strength.....:63 MPa

Alkali free E-glass strand strength.....:941 MPa

which would tend to conform Metcalfe et al's hypothesis. The strength of different kinds of fibre-strands in 0.5 M H_2SO_4 at 80°C and 50°C are given in Figure 1.2. C-glass contains significant amount of alkali and should be more sensitive than E-glass.

Another most important thing for acid corrosion of glass fibres is pH of acid. The effect of this parameter on strength of fibre is being shown in Figure 1.3. E-glass fibre is more effected at pH 1. The least effect is around pH 7. It means that neutral solution effects on fibres less than acidic and alkaline solution.

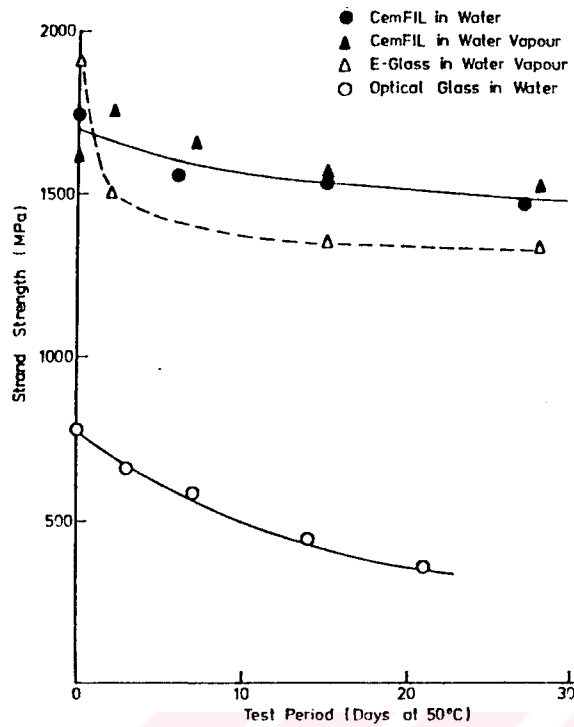


Figure 1-1: Strengths of glassfibre strands in water or water vapour at 50 °C. Taken from ref.1.

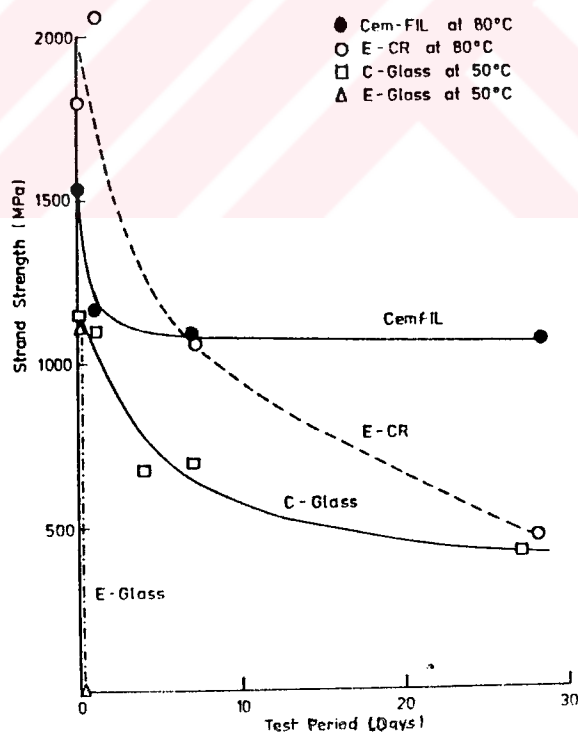


Figure 1-2: Strengths of glassfibre strands in 0.5 M sulphuric acid solution at 80 and 50°C (taken from ref.1).

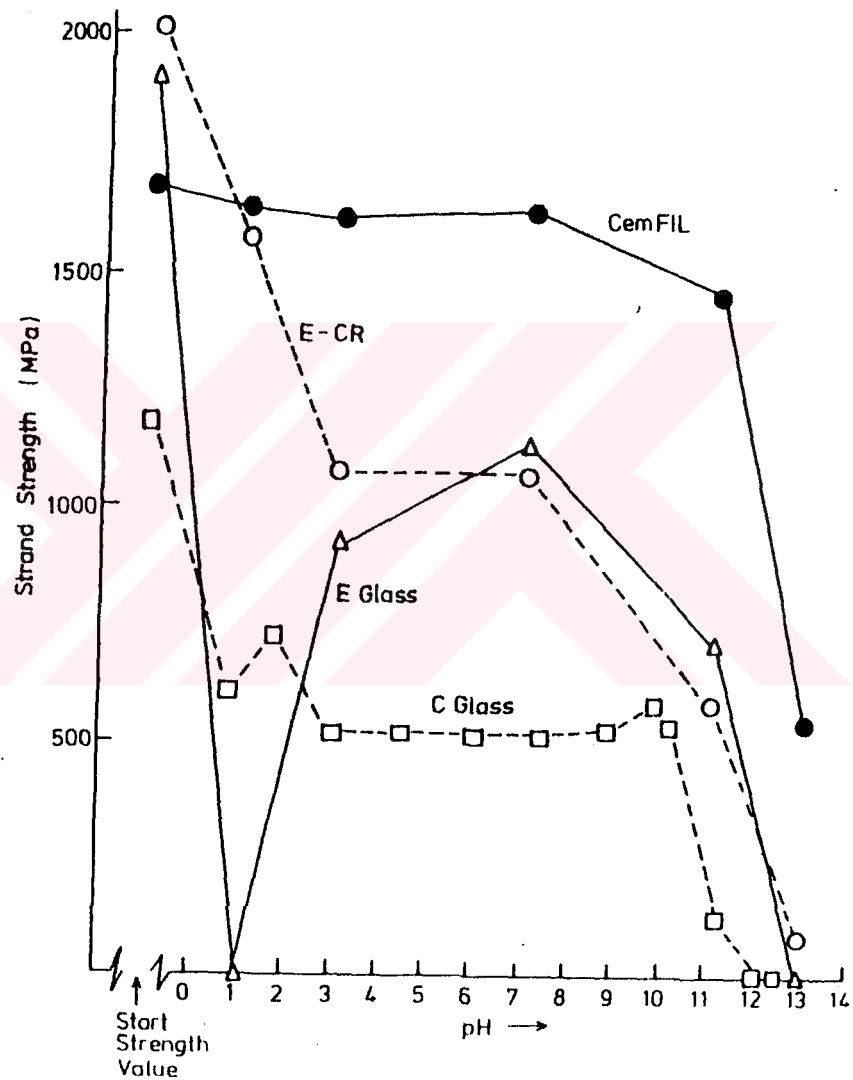


Figure 1-3: Strengths of glassfibre strands in solutions of different pH after immersion for 2 days at 80°C (taken from ref.1).

Scrimshaw [58] reported static fatigue results for E-glass strands in 2M sulphuric acid at room temperature and the trend line for these results has been plotted on Figure 1.4 which also shows trend lines for recent preliminary results for cemFIL and E-CR strands in 0.5M sulphuric acid.

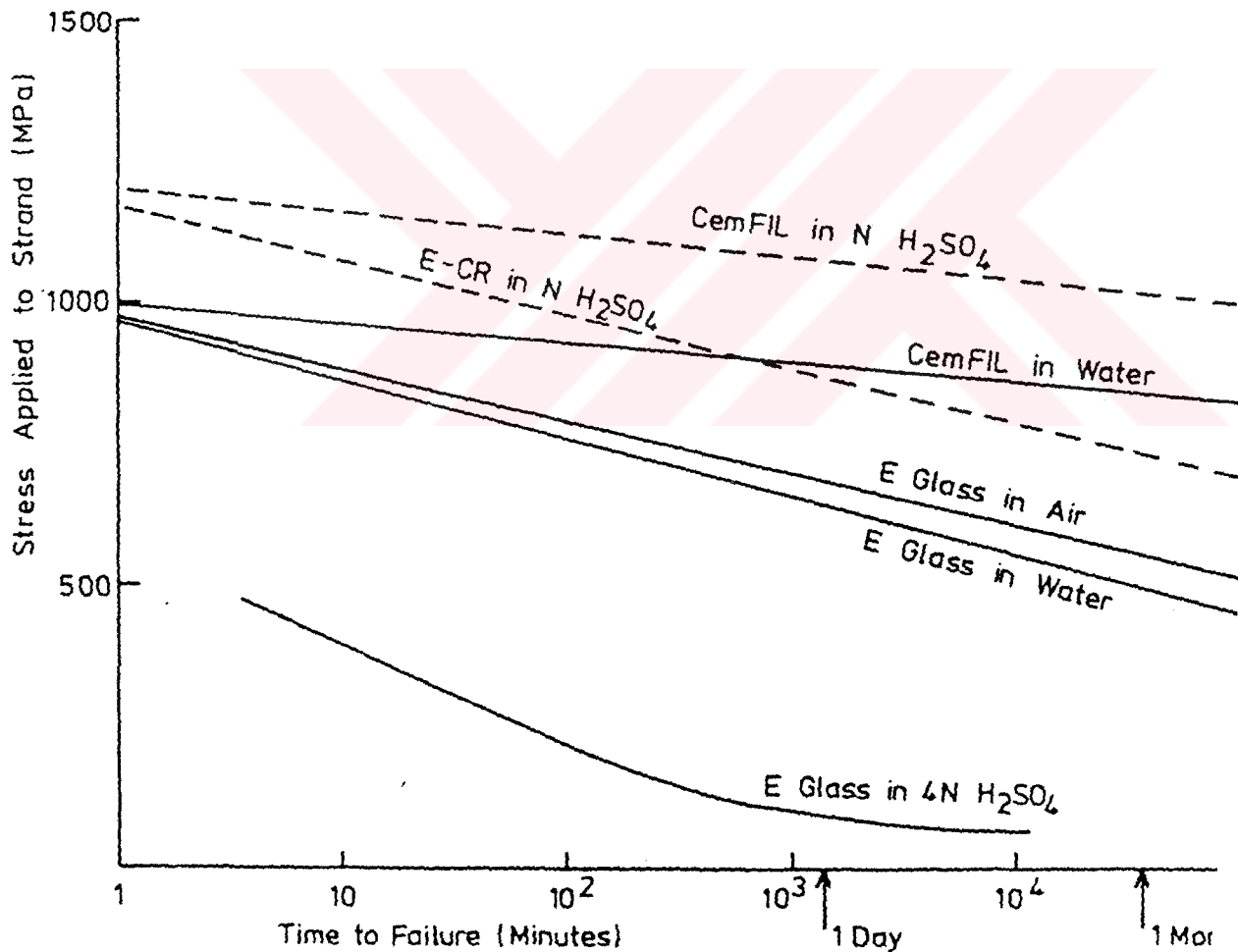


Figure 1.4: Static fatigue of strands in air, water and acid at room temperature. (Taken from ref.57.)

1.5. STRENGTH IMPROVEMENT OF GLASS FIBRES

Polymer coatings are effective in maintaining the strength of silica fibres, partly by reducing fatigue effects. It is clear that the effectiveness of surface compression coating depends on the thickness of the coating relative to the depth of the flaws present in the surface before the coating is applied. To obtain the maximum benefit, the most severe flaw should be completely enclosed within the coating [59].

Figure 1-5 shows the factor by which the strength is increased as a function of the surface compressive stress, S_c , and the ratio of the thickness of the coating, d , to the depth of the strength-controlling flaw, a_0 . S^0_f is the strength of the body in the absence of residual stress. S_c is assumed to be uniform through the layer thickness. S_f is the service stress of glass. Note that when d is less than a_0 , there is a limitation at the service strength of glass. If d is more than a_0 , the service strength goes up as shown in Figure 1-5.

In the manufacture of continuous filament glass fibres for the reinforcement of composites, great care is taken to protect the surface of the fibre from undue damage during both the production process and prior to incorporation in the composite. Before any mechanical

contact with other fibres or guide surfaces, the fibre is coated with a multi-component "size" [60] which serves to
i. protect filaments from abrasive damage by lubrication.

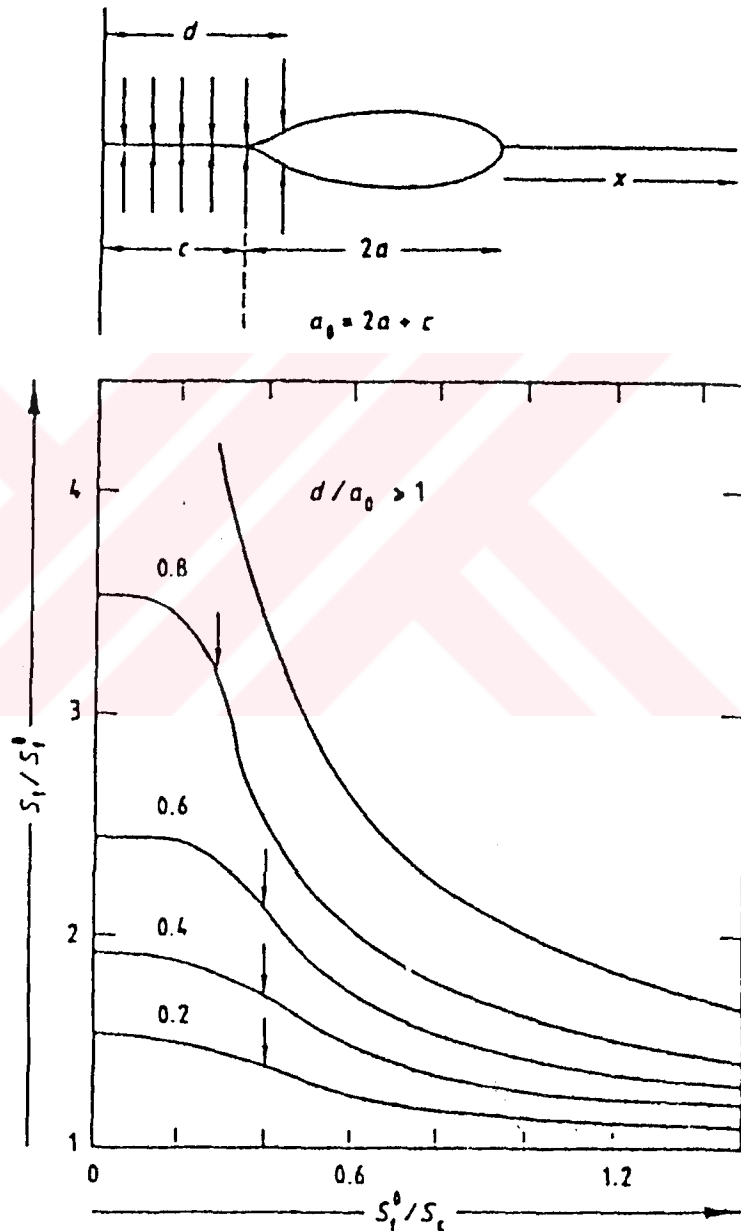


Figure 1-5: Strengthening due to surface compression in a semi-infinite plate in terms of the base strength of the material (taken from ref.59).

ii. bind individual filaments together into convenient bundles or "strands" for subsequent processing and use.

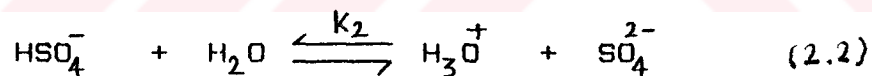
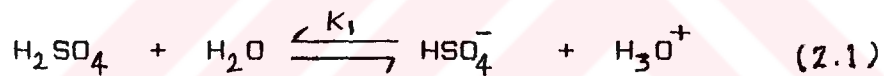
iii. improve adhesion between the glass fibres and resin matrices in the final composite. The pristine glass surface is extremely sensitive to abrasion and there is inevitably some reduction in strength from the absolutely untouched value of about 3.5 GPa to around 1.5 – 2 GPa [61]. However this still represents a relatively "perfect" glass surface which can be extremely sensitive to corrosive attack leading to roughening and strength loss-which would be quite undetected in low strength glass articles.

CHAPTER 2: EXPERIMENTAL DETAILS

2.1. MATERIALS

2.1.1. SOLUTIONS

In this study 1M sulphuric acid has been used as the corrosive environment. Jones and Rock [29] have studied the mechanism of stress corrosion of E-glass fibres in sulphuric acid. They found that 0.5M sulphuric acid has as corrosive effect as higher concentration. Sulphuric acid ionises according to equations;



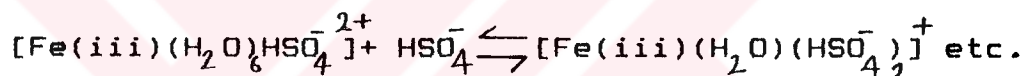
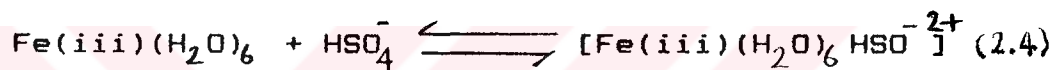
K_1 is very large and up to 14M sulphuric acid is completely dissociated. On the other hand K_2 has a value of 1.2×10^{-2} . The SO_4^{2-} concentration is at a maximum in 10M sulphuric acid. Thus the HSO_4^- , SO_4^{2-} , and H_3O^+ are in aqueous sulphuric acid solutions could all be involved in the stress corrosion of E-glass.

It is known that in sulphuric acid, ionisation leads to the presence of sulphate and bisulphate ions (HSO_4^-)

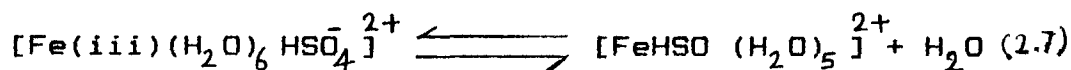
and $(\text{SO}_4)^{2-}$ and it is known that on the extraction of Fe(iii) from the glass into the solution complexes are formed with the dissociated ions forming. In an aqueous solution, iron normally solvated:



At this ionic strength, the formation of ion pairs and agglomerates must be considered which involve sulphate and bisulphate.



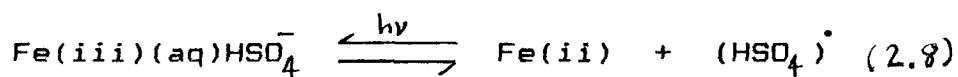
It is furthermore recognized that it is difficult to distinguish between a complex ion and an ion pair and the following rearrangement can be envisaged,



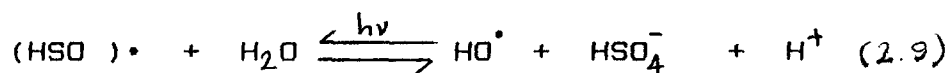
The formation of these complex ions may also explain the similar rates of stress corrosion of E-glass fibres in 1M sulphuric acid solution.

The ultra-violet absorption of Fe(iii) in aqueous

sulphuric acid solution occurs at 300 nm by a charge-transfer mechanism.



and



The presence of this free radical has been confirmed by Evans et al [62] however, SO_4^{2-} could be involved in similar charge transfer reactions but the net effect is considered to be much smaller.

Studies on the ionic concentration of sulphuric acid show that there is a linear relation between ionic activities and molar concentration of sulphuric acid. Also studies on the leaching of ions from glass have shown that the ion which is added into the solution reduces the rate of extraction from glasses. In order to check the corrosion effect of Fe(III) extraction from glass fibres, 0.5 w% iron(III) sulphate had been added into the 1M sulphuric acid aqueous solution.

2.1.2. GLASS FIBRE

Three types of glass fibre have been used in this study. One of them was Silenka commercial fibres called as 084 M19, the second was γ -aminopropyltriethoxy silane sized fibres described as 001 P61 and the third was water-sized fibres as 006 P61. The last two kinds of

fibres had not been converted to the roving for commercial manner. As mentioned before, E-glass fibres are being sized during production. Hence it is clear that the size, which is on the fibre protects the influence of the corrosive environment. Because of this reason we decided to use non-sized E-glass fibres with a nominal composition; SiO_2 :55.2, Al_2O_3 :14.8, B_2O_3 :7.3, CaO :18.7, MgO :3.3, Na_2O :0.3, K_2O :0.2, Fe_2O_3 :0.3.

2.2. STRESS CORROSION APPARATUS

The environmental stress corrosion of single glass fibres has been studied by using the apparatus that developed by Sheard [2]. This consisted of two corrosion tanks and each of them had sixteen terminals linked to a microcomputer such that each sample could be monitored individually. One of the tanks for testing single glass fibres under blacked-out condition is an open glass tank filled with water into which eight beakers can be placed. Each beaker contains the corrosive solution as 1M sulphuric acid. Other apparatus for testing fibres under ultra violet radiation consisted of a glass tank contained in an aluminium box, the lid of this box has two 256 nm fluorescent lamps mounted in it which can only emit radiation if the lid is properly aligned on the box, for safety reasons.

For accurate results of the failure times of stress corroded fibres it is important to minimise any bias due to local human activity. These influences were reduced by carrying out the experimental procedure in a special laboratory with blacked-out windows. To monitor and record the exact times-to-failure of each specimen, the suspended sample was connected via an interface to a Commodore PET Computer such that thirty-two samples could be monitored simultaneously and their status and breakages recorded directly by the computer.

The acid environment was held at constant concentration by simply regularly topping up the solution with distilled water, to replace that lost by evaporation. To maintain the environment at a constant temperature of 20 ± 2 °C a pump was installed to circulate water around the blacked-out tank. Although there was no system to adjust the temperature of the ultra-violet water bath, the temperature was monitored and found to be maintained over the same range as found for the blacked-out condition during the experiments.

The terminals consist of an arm which holds the specimen as in Figure 2.1. The arm has a reed switch attached to it, this transmits through an interface, to the computer which monitors the fibre breakages. The reed switch is in an "off" position when the fibre has broken,

because the weight put on the fibre to cause the stress has been removed and so the arm moves upwards breaking the circuit.



Figure 2-1a: Photograph of stress corrosion apparatus.

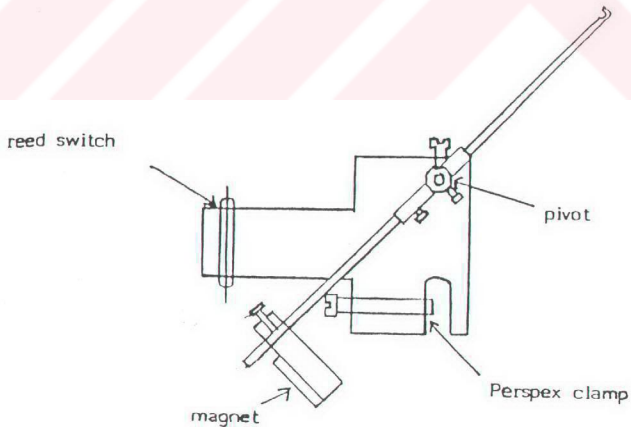


Figure 2-1b: Diagram of clamp of pivot assembly-failed fibre position.

2.3. EXPERIMENTAL PROCEDURE

2.3.1. THE WEIBULL MODEL IN LIFE TESTING

The stress corrosion of Silenka commercially sized, silane-sized and water sized fibres immersed in aqueous 1M sulphuric acid and 0.5 w% ferric iron sulphate-acidic solutions have been studied in differing illumination conditions. The failure times of the fibres in both solutions were estimated by using Weibull Statistics [21]. Although life testing of components during the period of useful life is generally based on the exponential model, it has been pointed out that the failure rate of a filament may not be constant throughout a period under investigation. In some instances the period of initial failure may be so long that the filament's main use is during this period, and in other instances the main purpose of life testing may be that of determining the time to wear-out failure rather than chance failure. In such cases the exponential model generally does not apply, and it is necessary to substitute a more general assumption for that of a constant failure rate. Weibull distribution adequately describes the failure times of filaments when their failure rate either increase or decrease with time. It has the parameters t_0 and w , its formula is given by following equation:

$$P=1-\exp(-t/t_0)^w \quad (2.10) \quad \text{where } P=n/(N+1)$$

P: probability of failure at time t

n: number of fibres failed at time t

N: total number of fibres tested

t_0 : characteristic failure time

w: Weibull shape parameter

t: failure time

This method is based on the fact that the reliability function of the Weibull distribution can be transformed into a linear function of $\ln t$ by means of a double-logarithmic transformation.

The above equation can be rewritten as below;

$$1-P=\exp(-t/t_0)^w \quad \text{Taking natural logarithm to base e,}$$

$$\ln(1-P)=(-t/t_0)^w \quad \ln[1/(1-P)]=w(-\ln t_0 + \ln t) \quad (2.11)$$

Taking logarithm to base e, $\ln \ln[1/(1-P)] = w(-\ln t_0 + \ln t)$

This equation is a linear of the form; $y=a+bx$

where $y=\ln \ln[1/(1-P)]$

$$a=-w \ln t_0$$

$$b=w$$

$$x=\ln t$$

The characteristic failure time is an indicator in order to compare the different stress corrosion results. It can be described as the time which corresponds to zero

on the $\ln \ln[1/(1-P)]$ axis. It is easy to calculate by using the equation of $a+bx=0$. In this equation a and b are known for each kind of line. The Weibull parameter indicates the shape of the distribution to the data has been fitted and is found from the gradient of the graph $\ln \ln[1/(1-P)]$ versus $\ln t$.

2.3.1. FIBRE DIAMETER MEASUREMENTS

The diameter of each filament has been measured accurately by using a laser beam from a He-Ne laser, (wavelength 632.8 nm and 1 mW) which was diffracted by the glass fibre specimen. When a beam of coherent light is incident upon an opaque fibre, diffraction produces a pattern of alternate light and dark fringes on a plane normal to the axis of fibre. If the fibre is transparent then interference between the reflected and refracted rays produces a similar pattern as diffraction.

Smithgall et al [63] demonstrated that the diameter is inversely proportional to the fringes period as shown by the following equation:

$$N = 2r/L [(\sin \theta_2 / 2 + (\mu^2 + 1 - 2\mu \cos \theta_2 / 2)^{1/2}) - (\sin \theta_1 / 2 + (\mu^2 + 1 - 2\mu \cos \theta_1 / 2)^{1/2})] \quad (2.12)$$

N : Number of fringes within the included angle $\theta_2 - \theta_1$

- μ : Refractive index of glass fibre
 L : Wavelength of laser radiation
 r : Fibre radius

The apparatus has been set up in Figure 2.2a,b. The screen to fibre distance was measured and the position of the sample adjusted to give the best diffraction pattern. The number of minima were counted over a measured distance and the diameter calculated by using a computer program which incorporates the above formula.

The effective diameter could be measured to an accuracy within a few percent range. Diameters determined by this method have been compared with those seen under Scanning Electron Microscope, and give good agreement .



Figure 2.2a: Photograph of optical bench.

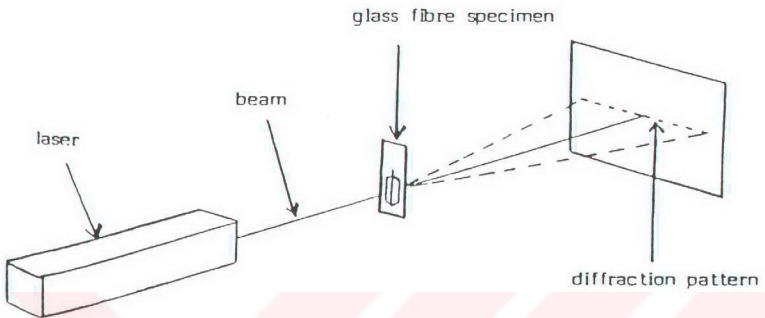


Figure 2-2b: Schematic diagram of laser set up.

2.3.3. PREPARATION OF THE SPECIMEN FOR TESTING

A single filament was removed from a tow of E-glass fibres and attached to a card as shown in Figure 2.3. After measuring the diameter each specimen was cut from the card frame and adhered at one end to a hooked glass rod, and at the other end to a rubber loop, using Evostick adhesive. The sample was then left for 24 hours for the glue to cure.

The stress corrosion test was carried out under a certain stress. The weights for the test were selected so

to produce a strain between 0.25 and 0.4%. As shown in Figure 2-3, the specimens were about 5 cm in length.

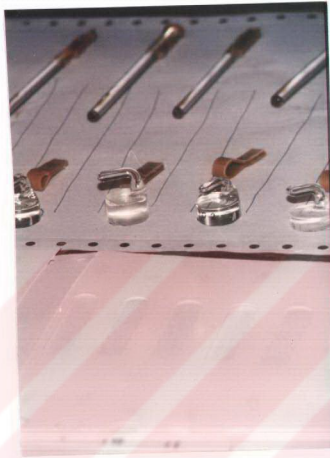


Figure 2-3a: Photograph of specimen preparation.

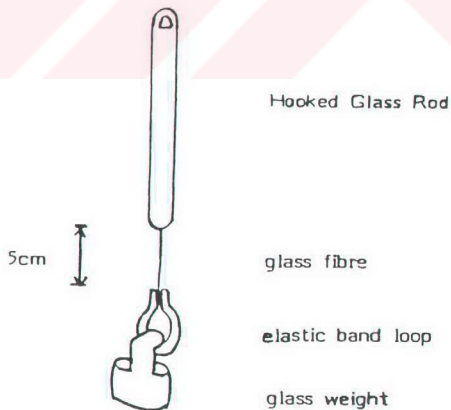


Figure 2-3b: Diagram of test specimen.

2.3.4. STRESS CORROSION TESTING

The computer program was then switched on and, after hanging the glass weight on the rubber loop, each fibre was lowered into the corrosion environment and hooked on to a pivoted sensor clamp which was suspended from the fibre, hooked through the rubber loop.

Much care must be taken in all these steps otherwise the fibres will be damaged and will break instantaneously. A magnetically operated reed switch at the end of each pivot connected it to the electric circuit when a fibre was suspended from the pivot. Hence the program could scan the fibres' status and record any breakages as the switch broke the circuit on fibre failure.

2.3.5. U.V. SPECTROMETER ANALYSIS

There are two main laws governing the absorption of electromagnetic radiation namely, Beer's law and Lambert's law: They apply to all forms of absorption spectroscopy. The former is concerned with the relationship of the absorption by the sample (called the absorbance) to the concentration of that sample in solution [64]. The latter law relates the absorbance to

the sample thickness, but they are usually combined such that:

$$I_2 = I_1 e^{-\alpha d} \quad (2.13)$$

where I_2 : the intensity of the transmitted radiation

I_1 : the intensity of the incident radiation

α : absorption coefficient

d : sample thickness (cell path length)

The above equation can be written as below,

$$I_2 = I_1 10^{-kd} \quad (2.14)$$

where k : extinction coefficient

$$k = \alpha / 2.303$$

Let's assume that α or k proportional with concentration.

From this conception the below equation can be given,

$$I_2 = I_1 10^{-\xi cd} \quad (2.15)$$

where c : concentration in mole/l

ξ : molar extinction coefficient

In general ξcd is called "optical density" and $D = \xi cd$

As a result we get $D = \log I_1 / I_2$ this final equation.

The absorption of iron(III) in silicate and borate glasses has been studied by using ultra-violet spectrometer [66]. It was determined that the spectra of solutions of ferric ammonium sulphate in 1M sulphuric acid gave two peaks at 304 and 228 nm, the molar extinction coefficients of which were calculated to be 2240 and 4550 respectively. On the other hand we have done some experiments with ferric sulphate in 1M

sulphuric acid solution. The spectra shown in Figure 2-4, confirmed the same molar extinction coefficient at the same wavelengths.

U.V. experiments to find out the extracted iron(iii) from E-glass fibres were carried out with 100cc beakers under the stress corrosion conditions. Each time 50cc 1M sulphuric acid and 1 g glass fibre were put into the beaker then replaced in the blacked-out water bath or ultra-violet box. Also it is well-known that the most important parameter for ion extraction from glasses is temperature. During the experiments the temperature was held constant at 20 °C.

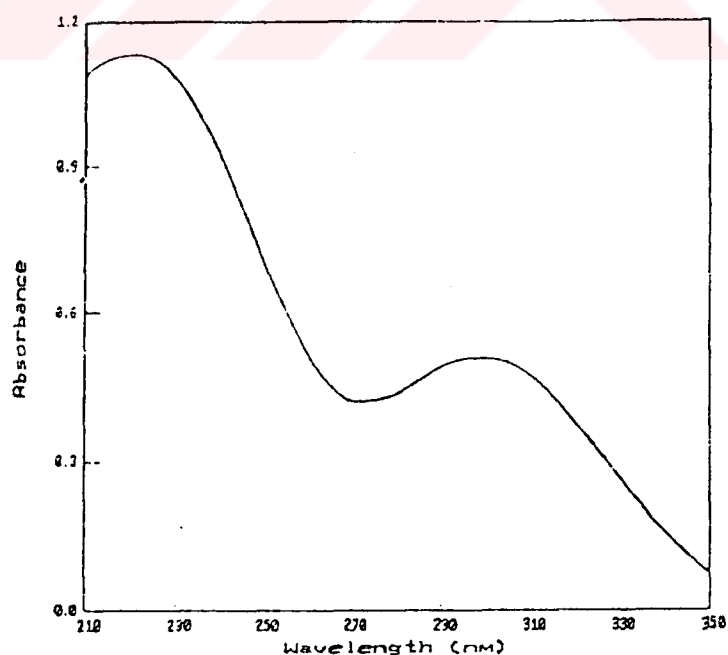


Figure 2-4a: The ultra-violet spectra for ferric sulphate in 1M sulphuric acid (2.28×10^{-4} mole/l Fe^{3+})

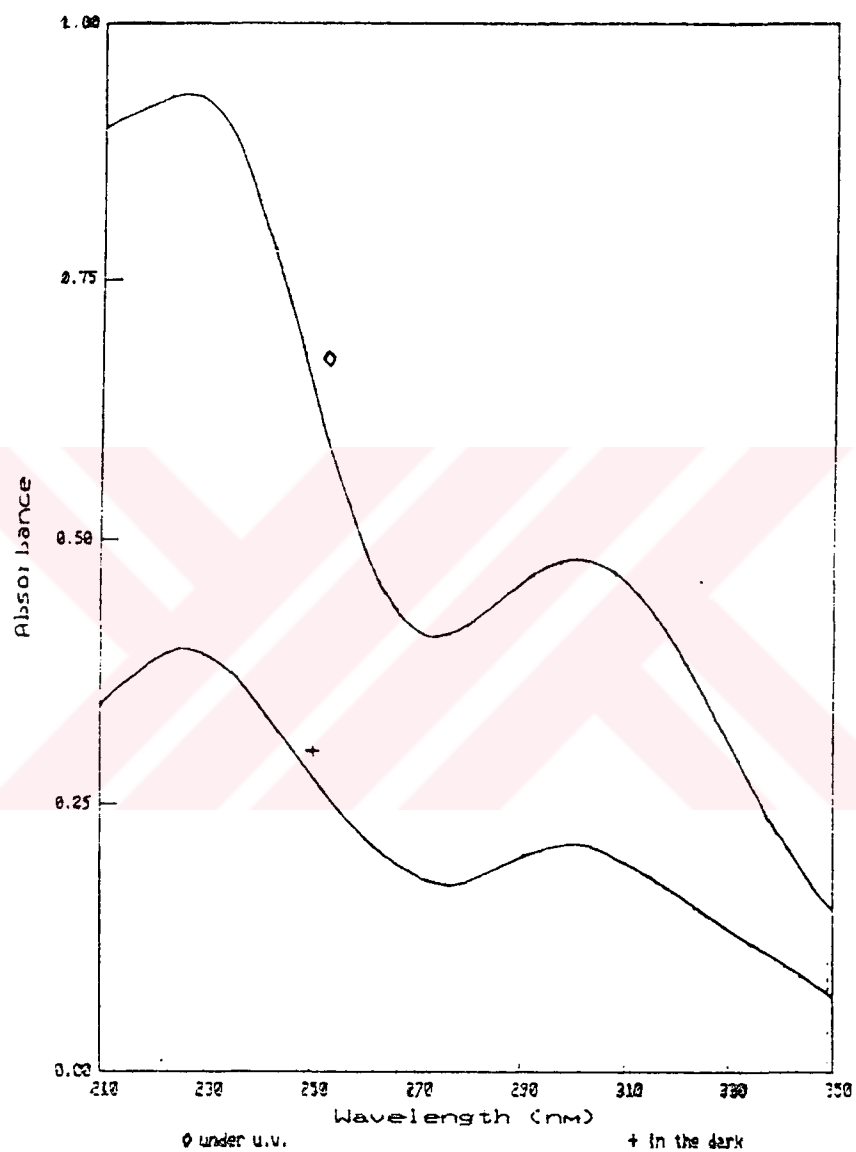


Figure 2.4b: The ultra-violet spectra of 1M sulphuric acid contacted water-sized fibres for 29 hours, (◊) under u.v. light (+) under blacked-out.

CHAPTER :3. RESULTS

3.1. ILLUMINATION EFFECTS ON THE STRESS CORROSION OF E-GLASS FIBRES

Firstly, commercially sized filaments taken from Silenka 084 M19 roving were used in order to examine the illumination effects on the strength. Thirty one under blacked-out and twenty-eight filaments under u.v. light have been tested as described before. The data according to these experiments is given in Table 1a,1b Appendix. The graphs which were plotted probability vs failure times of filaments for both of illuminations are shown in Figure 3-1. A summary sheet shown the average fibre diameter, μ , % strain and failure time is given in Table 3-1. As shown from this table fibre diameter and % strain are very close for blacked-out and u.v. light conditions because the strength of fibres is a function of these parameters. Therefore it was aimed to keep close together. In order to calculate % strain, the Young's modulus is approximately known for E-glass as 7300 kg/mm^2 and can be described $E = \text{stress} / \text{strain}$ where stress is force/area and strain is length difference/original length of filament. First of all, %-strain was estimated as 0.3 then force, F or the pyrex weight was calculated by

using above equation. After that one of the present pyrex weights near to the calculated value was taken for hanging under the tested filament and the % strain was calculated by considering this exact force. On the other hand the failure probability can be described as mentioned before $P_f = n/(N+1)$ where n , number of fibres failed at time t and N , total number of fibres tested. For example, in Table 1a Appendix, the first value of P_f is 0.406. How was it calculated? The failure time of this filament was found 34200 second and it failed 13th in the 31 filaments. As a result the probability of this fibre was calculated as $P_f = 13/(31+1) = 0.406$.

Table 3-1: The summary of total result of commercially sized fibres under u.v. light and blacked-out conditions (given table 1a, 1b Appendix).

Cond.	No test.	fibre dia., μ	Av.% strain	Failure times / 10^4 s
				min. max.
B.out	31	14.3	0.325	0.142 56.807
U.V.	28	14.5	0.322	0.090 13.731

Secondly, filaments coated with a silane coupling agent taken from the tow were used in each kind of experiment. Thirty filaments for blacked-out and thirty filaments for u.v. light were examined to find out of illumination effect on the strength of different kinds of

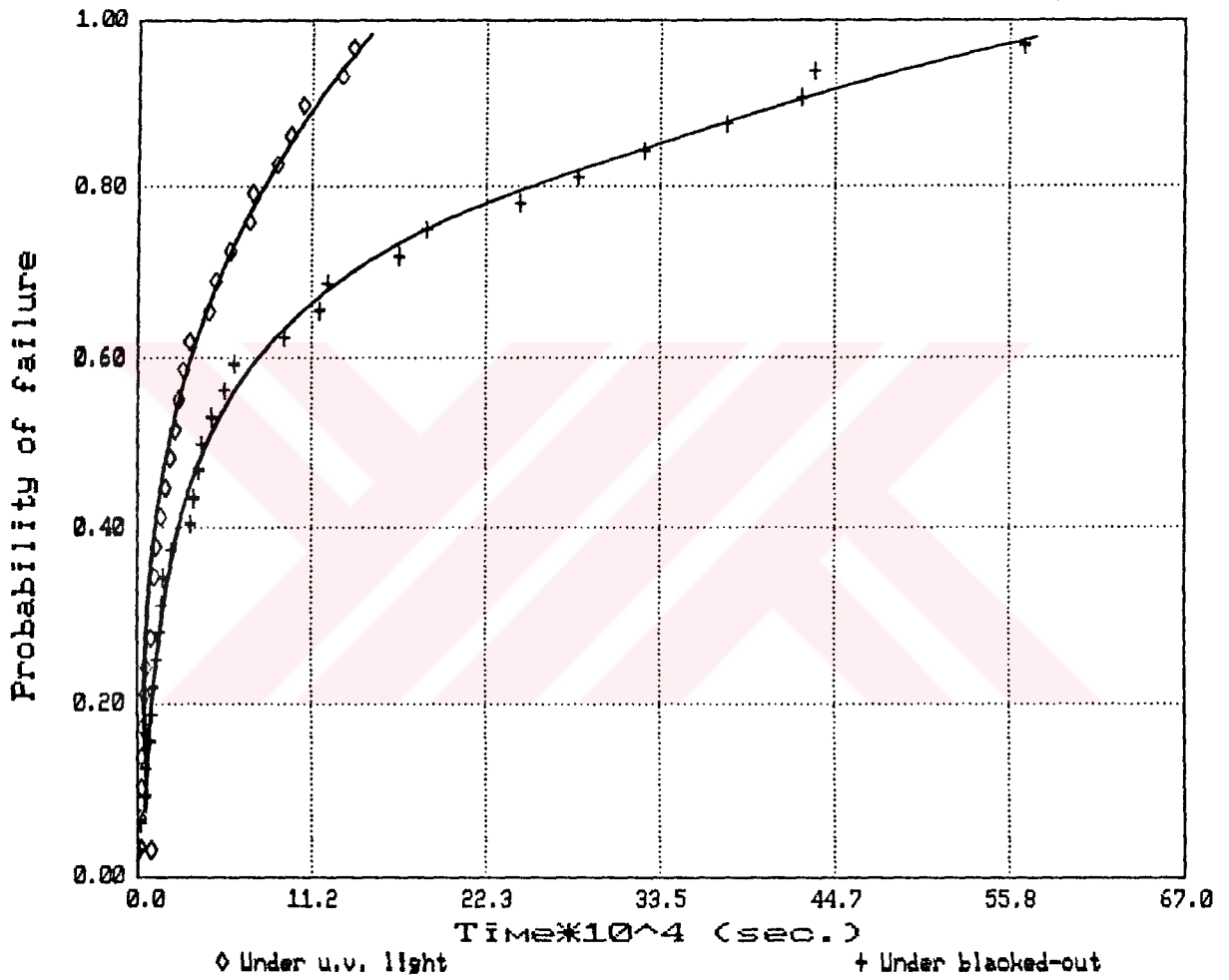


Figure 3.1: Failure times of single commercially sized E-glass filaments in 1M sulphuric acid under ultra-violet and blackout conditions.

fibres. Total experimental results are given in Table 2a,b Appendix. Graphs in which were plotted failure probability vs breakage time are shown in Figure 3.2. A summary of the total results given in Appendix for blacked-out and u.v. illuminations is shown in Table 3.2. Also in these experiments the average fibre diameter and % strain for blacked-out and u.v. illuminations were tried to keep close together because of their effects on strength of fibres. It can be seen in Figure 3.2 that curves of blacked-out and u.v. light are similar and confirm to exponential life time model.

Table 3.2: The summary of total result of silane sized fibres under u.v. light and blacked-out conditions (given Table 2a,2b Appendix).

Cond.	No test.	fibre dia. μ	Av. % strain	Failure times / 10^4 s	
				min.	max.
B.out	30	14.9	0.321	0.284	76.681
U.V.	30	14.8	0.348	0.196	37.325

Thirdly, filaments non-coated namely water sized were used in order to eliminate of the size effect on the illumination. Totally sixty fibres for blacked-out and u.v. light experiments have been examined. Complete data is given in Table 3a,3b Appendix. Graphs were plotted probability vs failure time are shown in Figure 3.3.

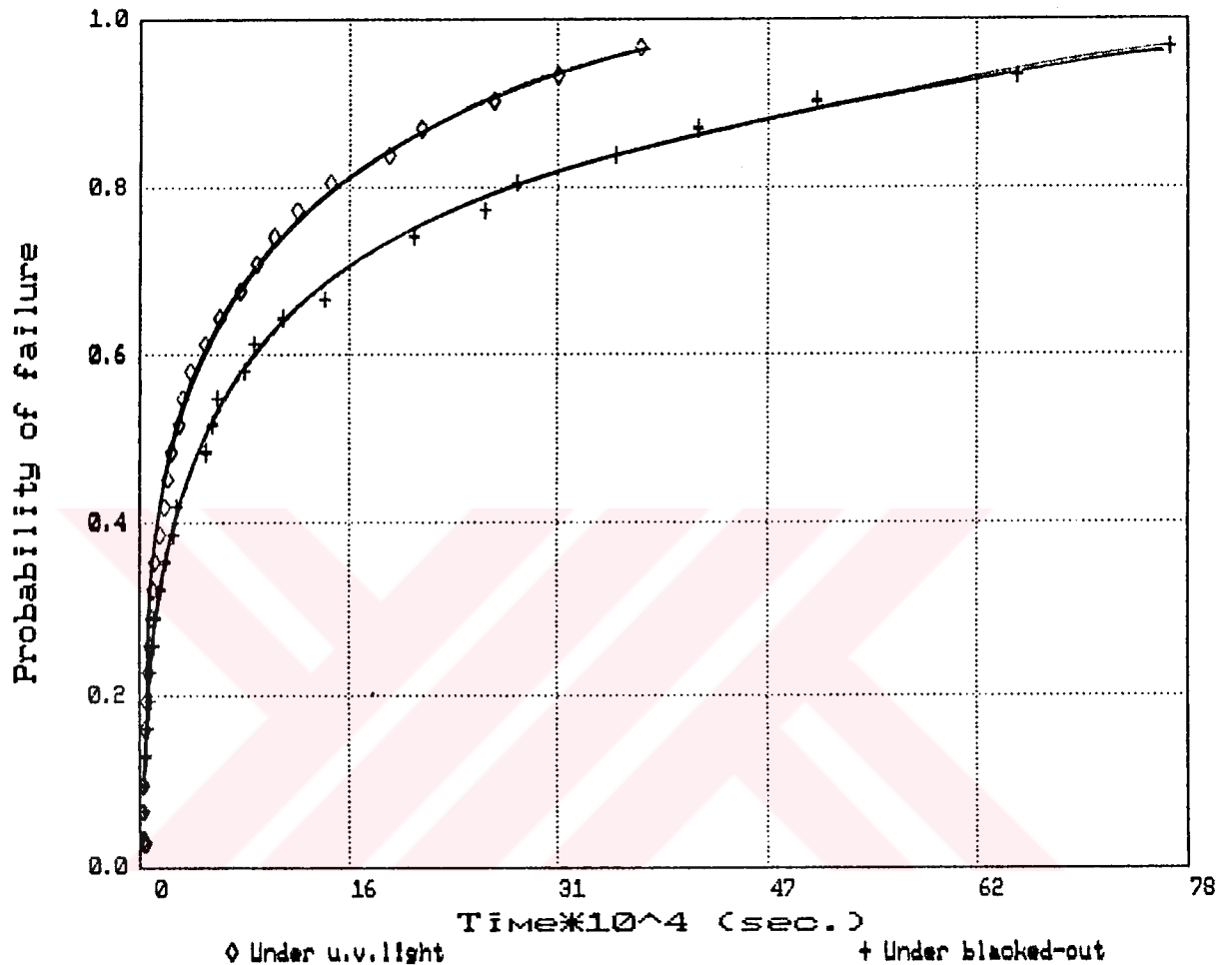


Figure 3.2: Failure times of single silane-sized glass filaments in 1M sulphuric acid under ultra-violet and blackout conditions

Average fibre diameters, % strains and failure times for blacked-out and u.v. illuminations were found as in Table 3.3. All things said before about commercially and silane sized fibres are valid for the water sized fibres. But the results showed that there was not any important effect of size on the stress corrosion mechanism.

Table 3.3.: The summary of total results of water-sized fibres under u.v. light and blacked-out conditions (given Table 3a,3b Appendix).

Cond.	No test.	fibre dia., μ	Av.% strain	Failure time / 10^4 s	
				min.	max.
B.out	29	15.2	0.348	0.230	68.010
U.V.	31	15.4	0.347	0.160	18.168

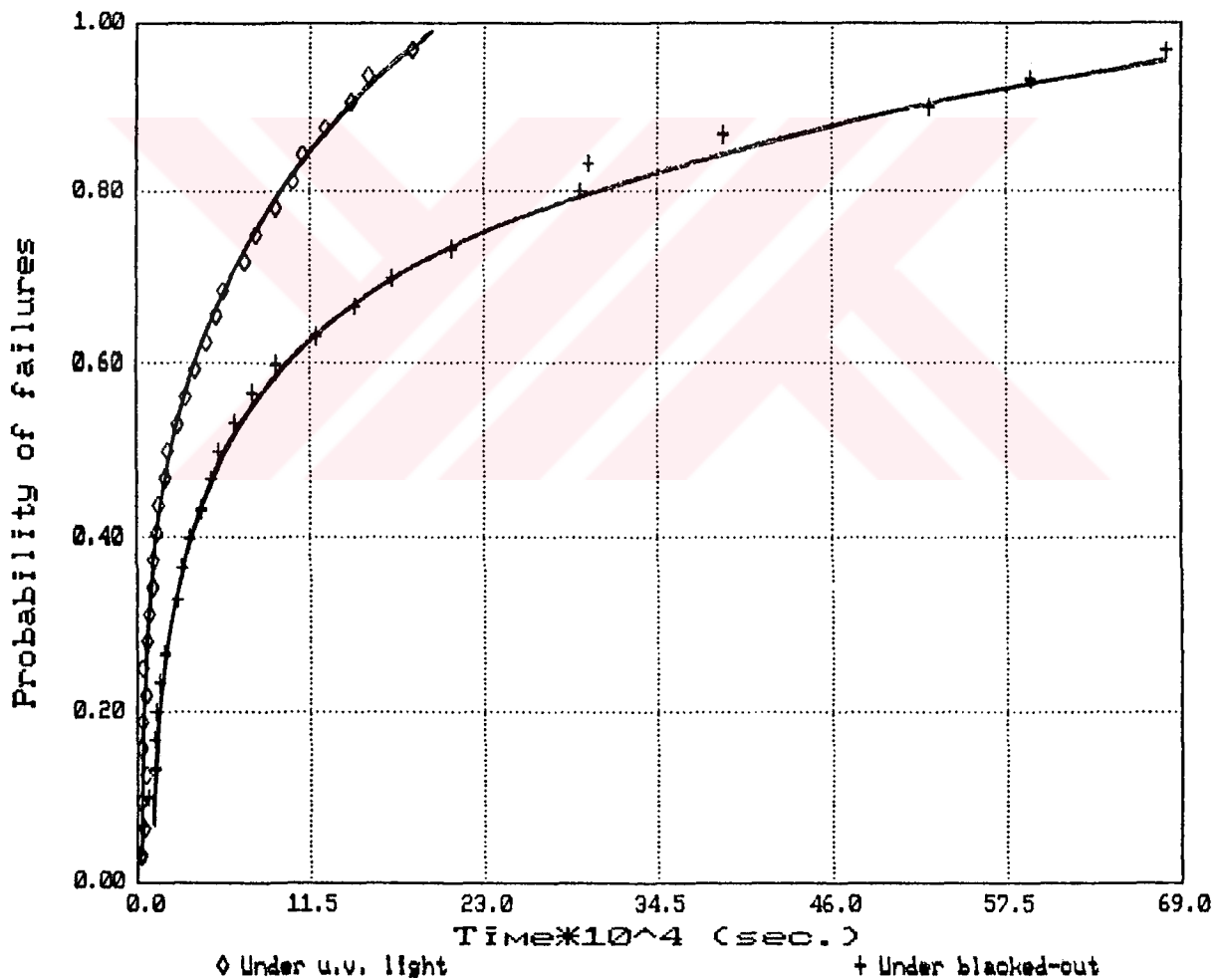


Figure 3.3: Failure times of single water-sized E-glass fibres in 1M sulphuric acid under u.v. light and blackout conditions.

It is well-known that any iron(iii) concentration in 1M sulphuric acid will decrease the rate of the fibre stress corrosion. The solution used in the stress corrosion experiments was the 0.5 weight % ferric iron sulphate in 1M sulphuric acid. According to the stress corrosion it can be made two considerations. Firstly, the corrosion effect of solution is limited by the complex formations between Fe(iii), bisulphate and sulphate ions. Secondly, the present of Fe(iii) in the leaching solution will be decreased the Fe(iii) ions transfer from fibres to the solution because of low concentration difference. Thirty filaments under blackout and twenty-nine filaments under ultra-violet condition have been tested. The data related to filaments is given in Table 4a and 4b Appendix. The same graphs were plotted for this data shown in Figure 3-4. Also a summary of total results can be seen in Table 3-4. The average fibre diameters for blacked-out and ultra-violet radiation were 15.3,15.4 micron respectively.

Table 3-4.: The summary of water-sized filaments data in 0.5 w% ferric iron sulphate/1M sulphuric acid solution.(Taken from Table 4a,4b Appendix)

Cond.	No test.	fibre dia., μ	Av.% strain	Failure time /10 ⁴ s	
				min.	max.
B.out	30	15.3	0.361	0.371	75.918
U.V.	29	15.4	0.359	0.162	30.255

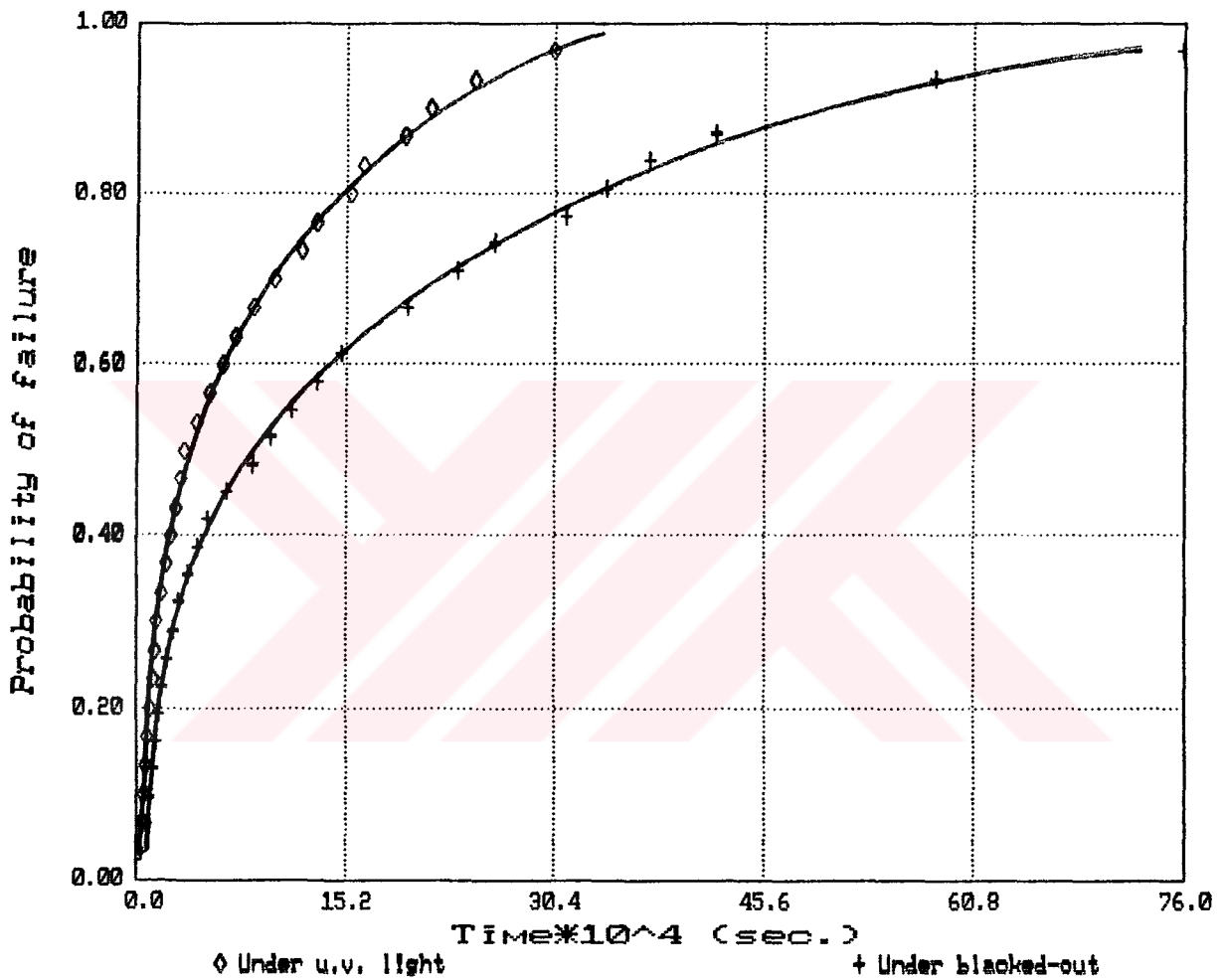


Figure 3.4: Failure times of single water-sized E-glass filaments in 0.5 w% ferric iron sulphate/1M sulphuric acid solution under u.v. light and blacked-out.

3.2. IRON(iii) EXTRACTION

First of all, for determining iron(iii) in extracted solution the spectrometer should be calibrated. As mentioned before the molar extinction coefficient of iron(iii) in ferric ammonium sulphate/1M sulphuric acid solution had been determined by Steele and Douglas [64]. In this study, the molar extinction coefficient of iron(iii) in ferric sulphate/1M sulphuric acid solution has been found as the same 2240 at 304 nm. Four experiments have been done. Each time some amount of ferric iron sulphate nine hydrates was added into 1M sulphuric acid solution (150 cc) then ferric iron amount was calculated by using the extinction coefficient as 2240 at 304 nm. The results are shown in Table 3.5. Also graph which plotted absorption vs molar concentration can be seen in Figure 3.5.

Table 3.5.: Calibration data of spectrometer for iron(iii).

Ex. No	Absorption at 304 nm	mg Fe(iii)/l in solution	Cal.mg Fe(iii)/l in solution
1	0.089	2.228	2.220
2	0.243	6.082	6.058
3	0.062	1.515	1.546
4	0.168	4.190	4.193

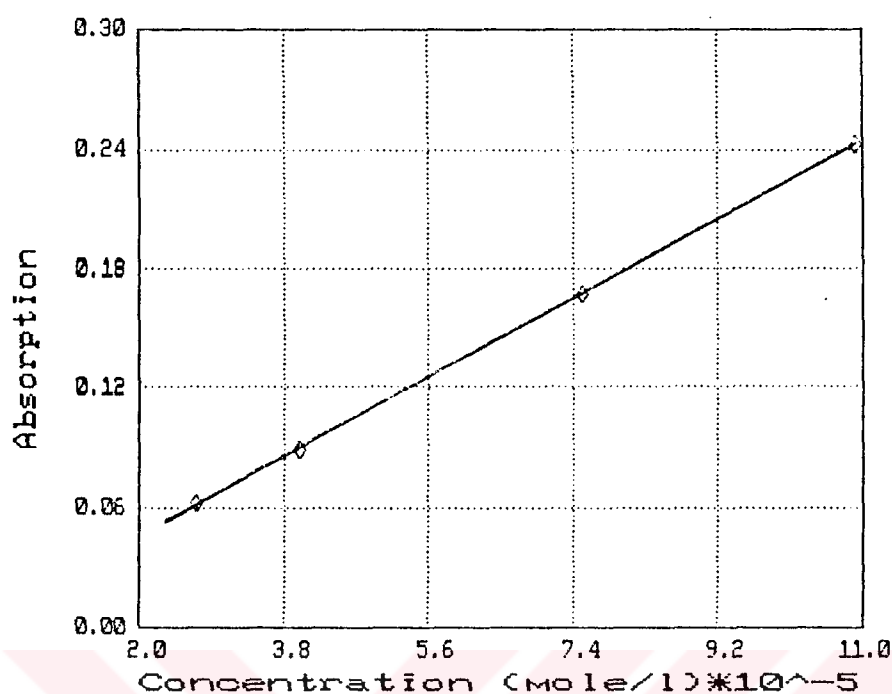


Figure 3-5: The graph of calibration, absorption vs molar concentration of iron(iii).

Kinetic work has been done by using three kinds of Silenka E-glass fibres under ultra-violet radiation and blackout conditions. Experiments have been carried out as mentioned before. First test showed that it was possible to monitor extracted iron(iii) in solution by using ultra-violet spectroscopy. The experimental data of commercially sized fibres is given in Table 3-6a,b, the results of silane sized fibres are shown in Table 3-7a,b and the water sized fibres results are in Table 3-8a,b. The kinetic curves of commercially sized, silane sized and water sized fibres plotted by using these data are given in Figure 3-6,3-7,3-8 respectively.

Table 3.6a: The amount of extracted iron(iii) from the commercially sized fibres in 1M sulphuric acid under ultra violet radiation.

Ex. No	Time, h	Absorption at 304 nm	Extracted Fe(iii) mg/g fibre
1	6	0.520	0.648
2	23.5	0.897	1.118
3	30	1.030	1.284
4	47	1.200	1.496
5	71	1.310	1.633

Table 3.6b: The amount of extracted iron(iii) from the commercially sized fibres in 1M sulphuric acid under blacked-out condition.

Ex. No	Time, h	Absorption at 304 nm	Extracted iron(iii) mg/g fibre
1	6	0.232	0.289
2	23.5	0.517	0.644
3	30	0.684	0.853
4	47	0.845	1.053
5	71	0.985	1.228

Table 3.7a: The amount of extracted iron(iii) from the silane sized fibres in 1M sulphuric acid under u.v.light (at 256 nm).

Ex. No	Time, h	Absorption at 304 nm	Extracted Fe(iii) mg/g fibre
1	6	0.193	0.241
2	23.5	0.475	0.592
3	30	0.564	0.703
4	47	0.670	0.835
5	71	0.795	0.991

Table 3.7b: The amount of extracted iron(iii) from the silane sized fibres in 1M sulphuric acid under blacked-out condition.

Ex.	Time,h	Absorption at 304 nm	Extracted Fe(iii) mg/g fibre
1	6	0.087	0.108
2	23.5	0.185	0.231
3	30	0.255	0.318
4	47	0.310	0.386
5	71	0.396	0.485

Table 3.8a: The amount of extracted iron(iii) from the water-sized fibres in 1M sulphuric acid under ultra-violet radiation.

Ex. No	Time,h	Absorption at 304 nm	Extracted Fe(iii) mg/g fibre
1	6	0.098	0.122
2	21	0.380	0.474
3	29	0.435	0.542
4	45	0.477	0.622
5	94	0.598	0.746

Table 3.8b: The amount of extracted iron(iii) from the water-sized fibres in 1M sulphuric acid under blacked-out condition.

Ex. No	Time,h	Absorption at 304 nm	Extracted Fe(iii) mg/g fibre
1	6	0.049	0.059
2	21	0.129	0.161
3	29	0.192	0.240
4	45	0.267	0.333
5	94	0.316	0.394

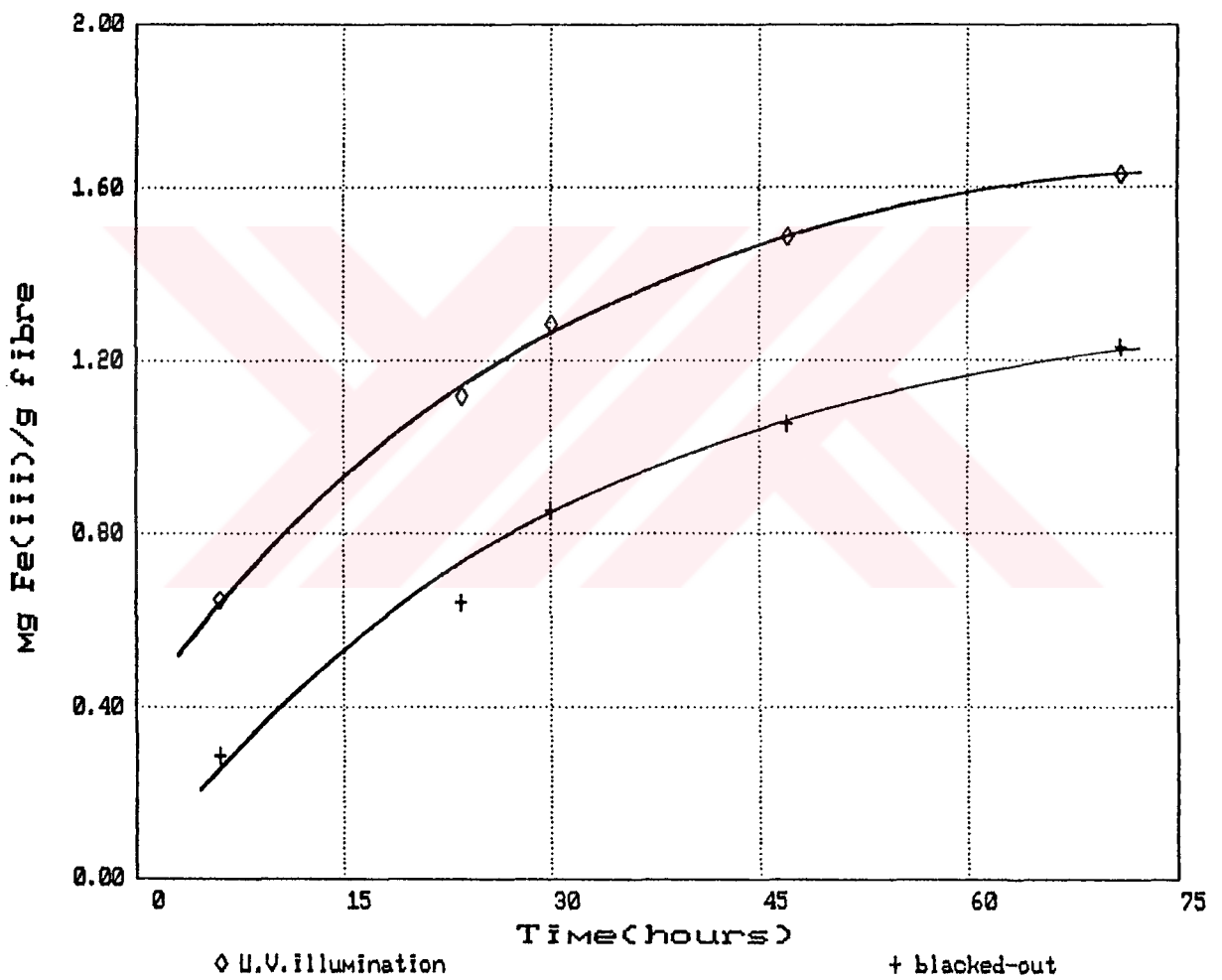


Figure 3.6: Extracted iron(III) amount of 1 g commercially sized E-glass fibre in 1M sulphuric acid under u.v. light and blacked-out conditions.

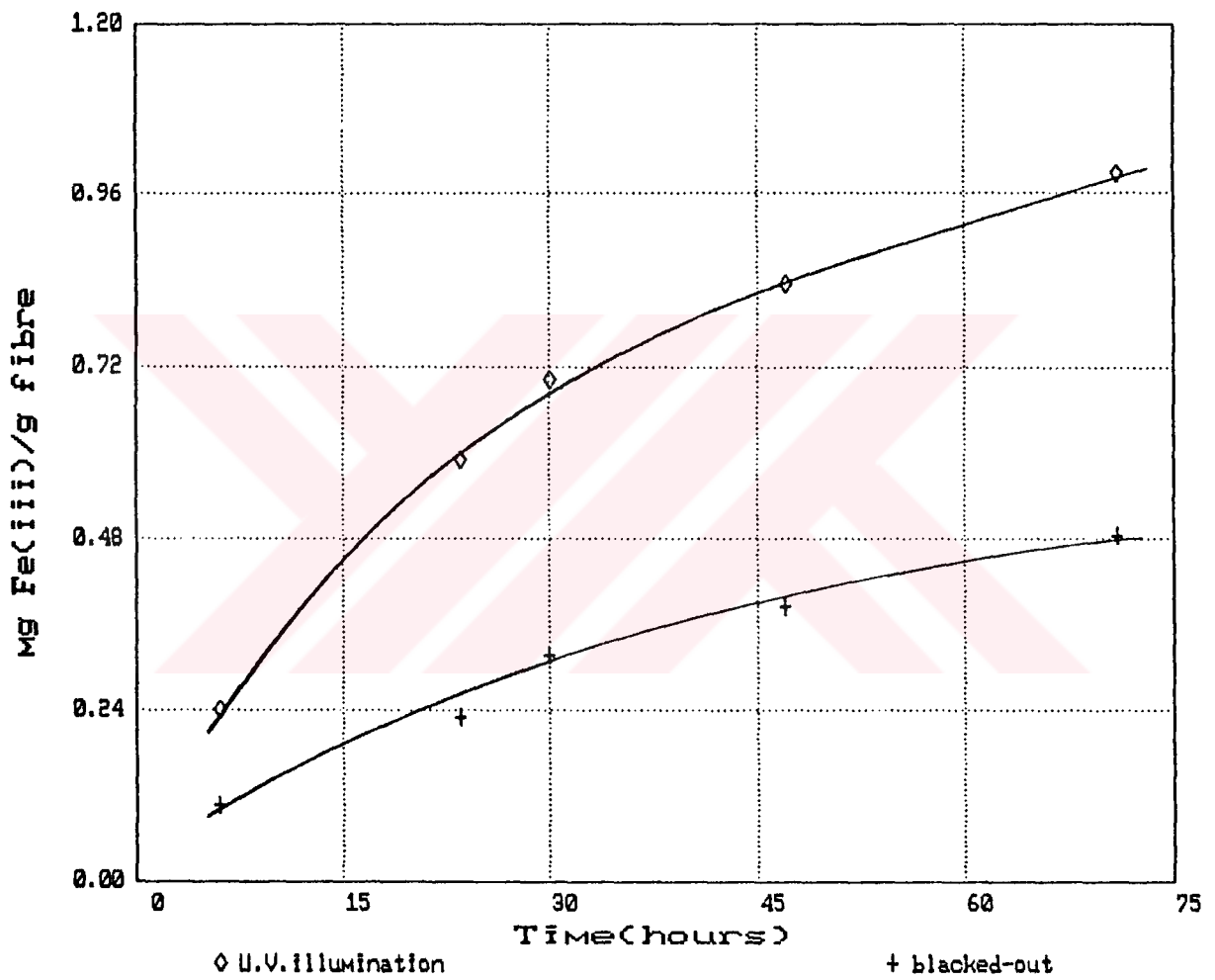


Figure 3-7: Extracted iron(III) amount of 1 g silane sized E-glass fibre in 1M sulphuric acid under u.v. light and blacked-out conditions.

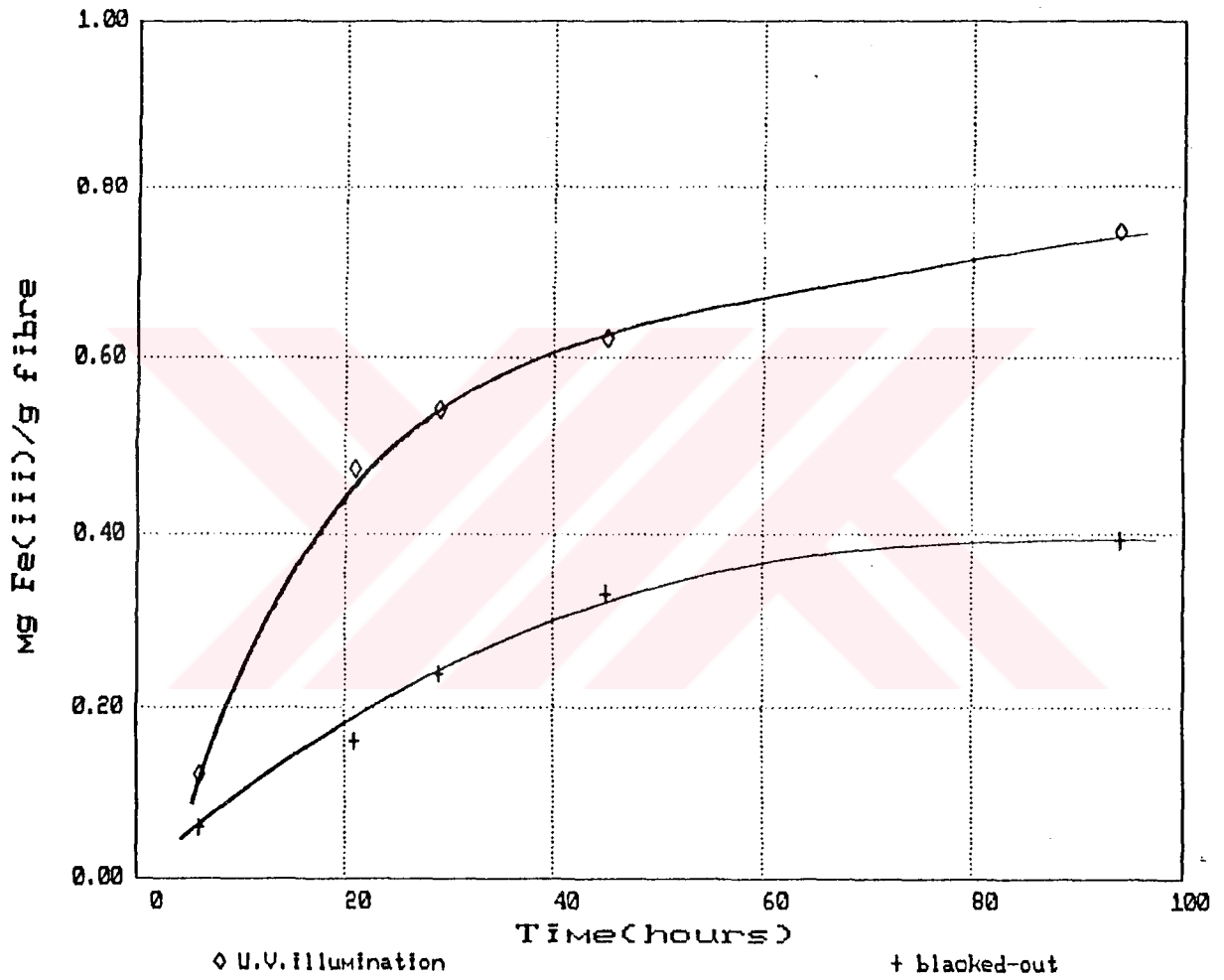


Figure 3-8: Extracted iron(III) amount of 1 g water sized E-glass fibre in 1M sulphuric acid under u.v. light and blacked-out conditions.

Some ferric sulphate was added to the 1M sulphuric acid solution corresponding to 1.14×10^{-4} mole/l iron(iii) sulphate. It was observed that the extraction rate was small under this condition. The data of these experiments is given in Table 3.9. Also the kinetic curves can be seen in Figure 3.9.

Table 3.9a: The amount of extracted iron(iii) from the water-sized fibres in 1.14×10^{-4} M ferric iron sulphate/1M sulphuric acid solution under U.V.light (at 256 nm).

Ex. No	Time, h	Absorption at 304 nm	Extracted iron(iii) mg/g fibre
1	6	0.095	0.118
2	21	0.307	0.382
3	29	0.405	0.504
4	45	0.485	0.601
5	94	0.559	0.696

Table 3.9b: The amount of extracted iron(iii) from the water-sized fibres in 1.14×10^{-4} M ferric iron(iii) sulphate/1M sulphuric acid solution under blacked-out.

Ex. No	Time, h	Absorption at 304 nm	Extracted Fe(iii) mg/g fibre
1	6	0.045	0.033
2	21	0.116	0.144
3	29	0.190	0.236
4	45	0.240	0.299
5	94	0.309	0.385

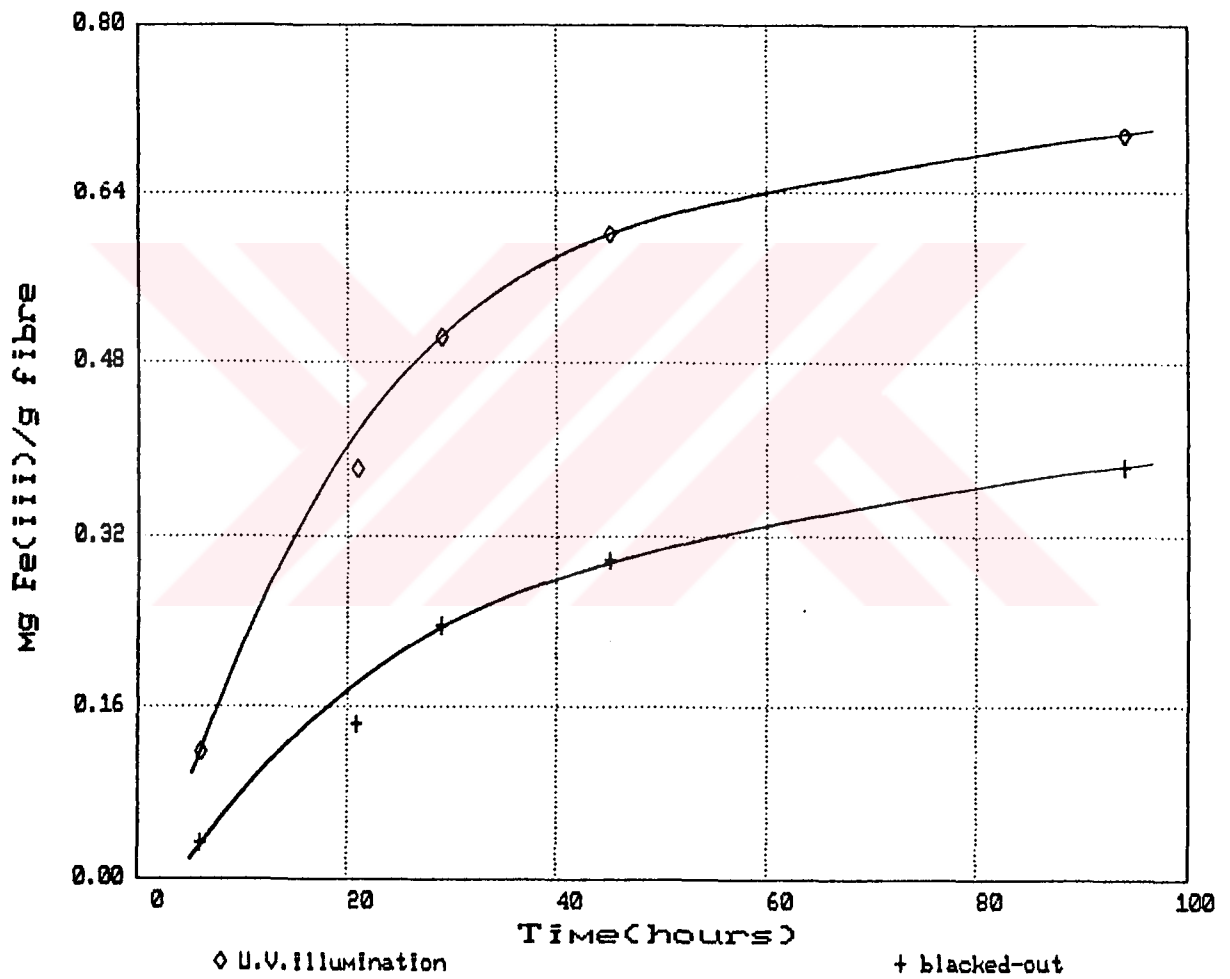


Figure 3-9: Extracted iron(III) amount of 1 g water sized E-glass fibre in 1.14×10^{-4} M ferric iron sulphate/1M sulphuric acid solution under u.v. light and blacked-out.

CHAPTER 4: DISCUSSION

4.1. STRESS CORROSION OF FIBRES

The average failure times, characteristic times and Weibull parameters are given in Table 4.1, 4.2, 4.3, 4.4 for all the experiments. Significant changes in Weibull parameters can indicate any possible change in the mechanism. The slopes calculated from the Weibull plots give very similar values of w , the shape modulus, and hence it can be assumed that the same stress corrosion mechanism is taken place both of illuminations. However there are significant differences of characteristic times between u.v. light and blacked-out for each fibre. These results shown in Figure 4.1, 4.2, 4.3, 4.4 would indicate that the stress corrosion mechanism is accelerated by u.v. light.

Table 4.1.: The average stress corrosion failure times and Weibull parameters of commercially sized E-glass fibres under u.v light and blacked-out in 1M sulphuric acid solution. (taken from Table 1a, 1b Appendix).

Condition	Av.failure time/10^4 s	Char.fail.time into to/10^4 s	Weibull parameter	
Blacked-out	12.196	11.51	9.97	0.674
Under u.v.	3.855	10.51	3.67	0.759

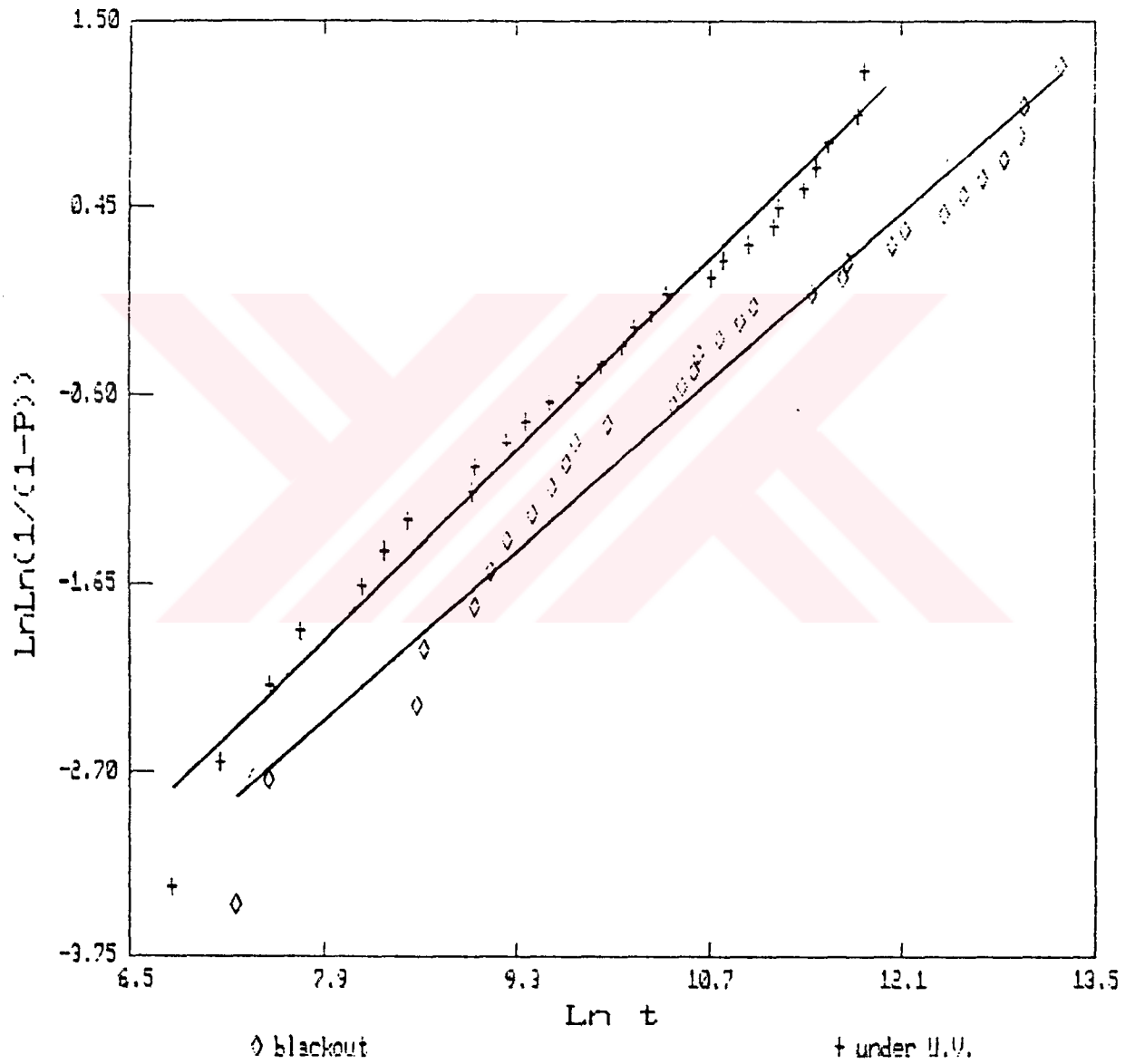


Figure 4.1: Weibull plots for stress corrosion failure times of commercially sized fibres in 1M sulphuric acid solution.

It is clear that ultra-violet radiation reduces the failure times for all fibres. Also it can be seen that the effect of illumination on the water-sized fibres is more significant than for commercial fibres. This result demonstrates that the applied size decreases effect of the illumination. On the other hand, the failure times of the water-sized fibres are longer than commercial fibres. This is presumably because the water-sized fibres have been handled less. It is well-known the mechanic damages occurred during the production of rovings causes the strength losses of fibres.

Table 4-2.: The average stress corrosion failure times and Weibull parameters of γ -amino propyltrihydroxy silane sized E-glass fibres under u.v light and blacked-out in 1M sulphuric acid solution.(taken Table 2a,b Appendix).

Condition	Av.failure time/ 10^4 s	Char.fail.time into	/ 10^4 s	Weibull parameter
Blackedout	14.614	11.61	11.02	0.683
Under u.v.	7.345	11.05	6.29	0.747

Table 4-3.: The average stress corrosion failure times and Weibull parameters of water sized E-glass fibres under u.v light and blacked-out in 1M sulphuric acid solution.(taken Table 3a,b Appendix).

Condition	Av.failure time/ 10^4 s	Char.fail.time into	/ 10^4 s	Weibull parameter
Blackedout	14.599	11.69	11.94	0.719
Under u.v.	4.620	10.54	3.78	0.652

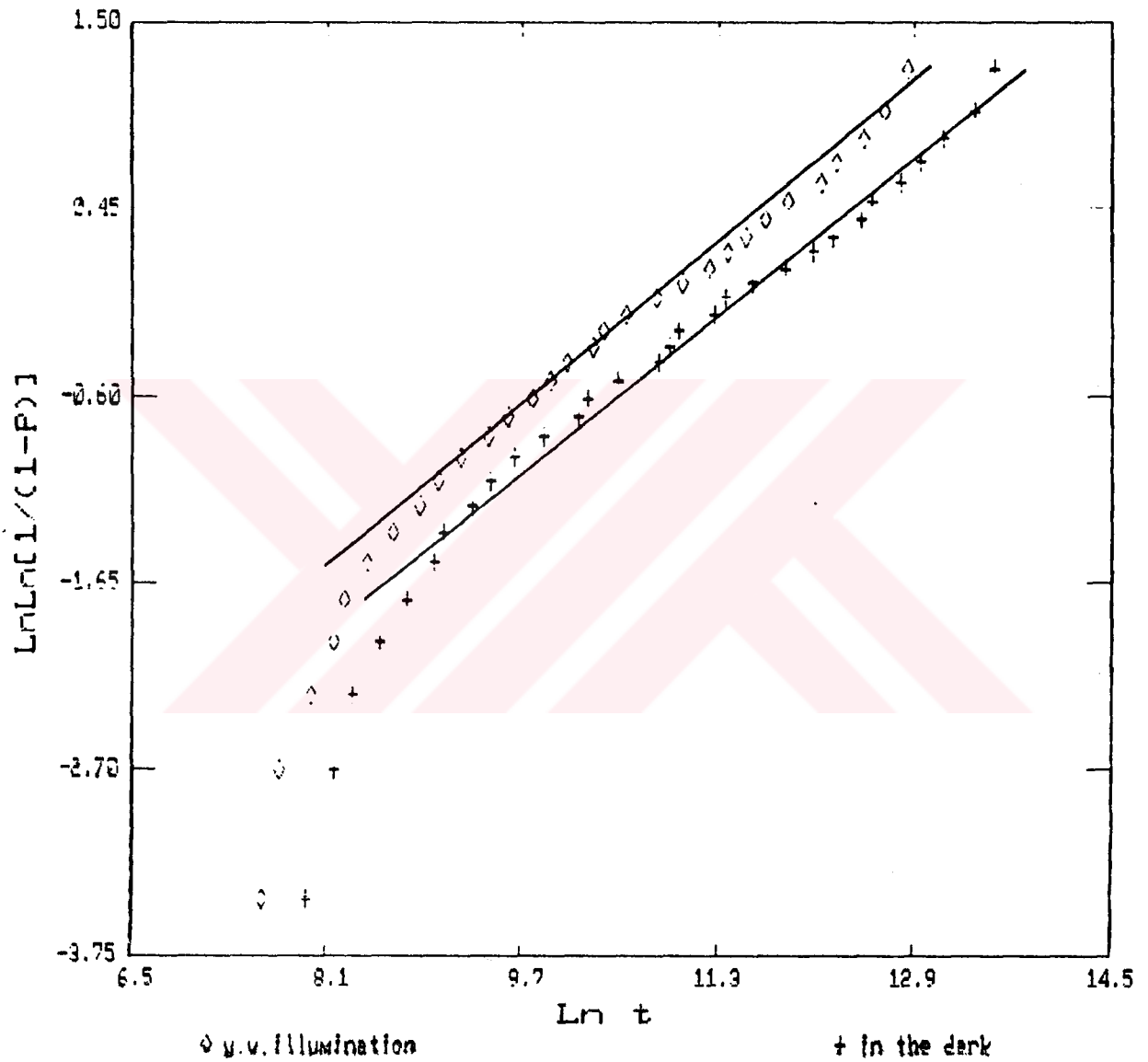


Figure 4.2: Weibull plots for stress corrosion failure times of γ -aminopropyltriethoxy silane sized fibres in 1M sulphuric acid.

As mentioned before the mechanism of stress corrosion in E-glass filaments has been studied very widely till now. Three observations provided the key to the mechanism. The first was that constitution of the ion exchange could lead to a reversal of the initial strength loss. The second was that the maximum strength loss was related to alkali metal content of the glass for ion exchange under specific conditions. The third observation was that filaments could crack spontaneously before the residual strength had reached zero. Also it had been observed that acidic solutions were more detrimental to strength than alkaline solutions.

Table 4.4.: The average stress corrosion failure times and Weibull parameters of water sized E-glass fibres under u.v light and blacked-out in 0.5 w% iron(iii) sulphate/1M sulphuric acid solution (taken Table 4a,4b Appendix).

Condition	Av.failure time/ 10^4 s	Char.fail.time into to/ 10^4 s	Weibull parameter
Blackedout	16.786	11.96 ; 15.64	0.754
Under u.v.	7.471	11.09 ; 6.55	0.755

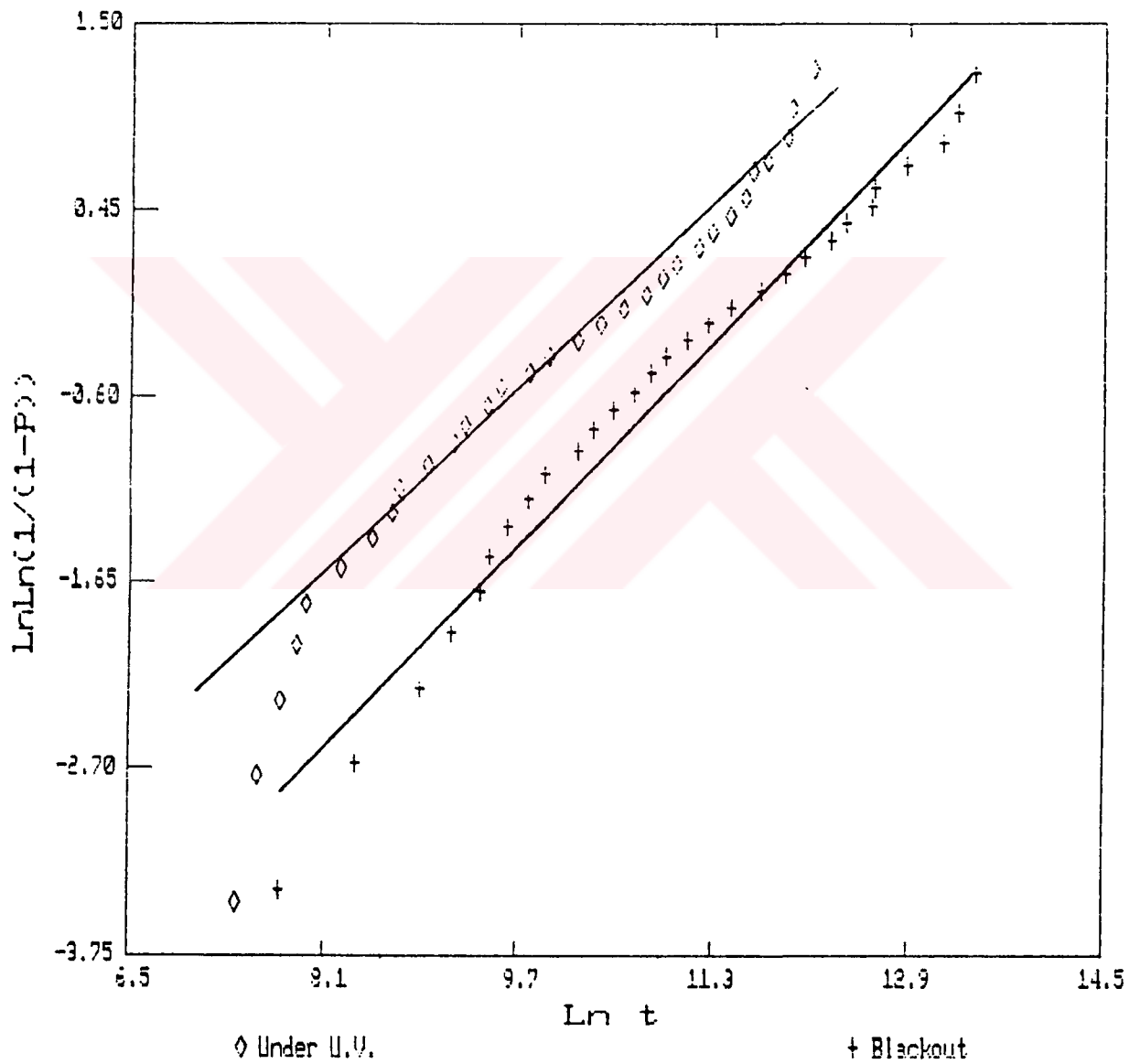


Figure 4-3: Weibull plots for stress corrosion failure times of water sized fibres in 1M sulphuric acid.

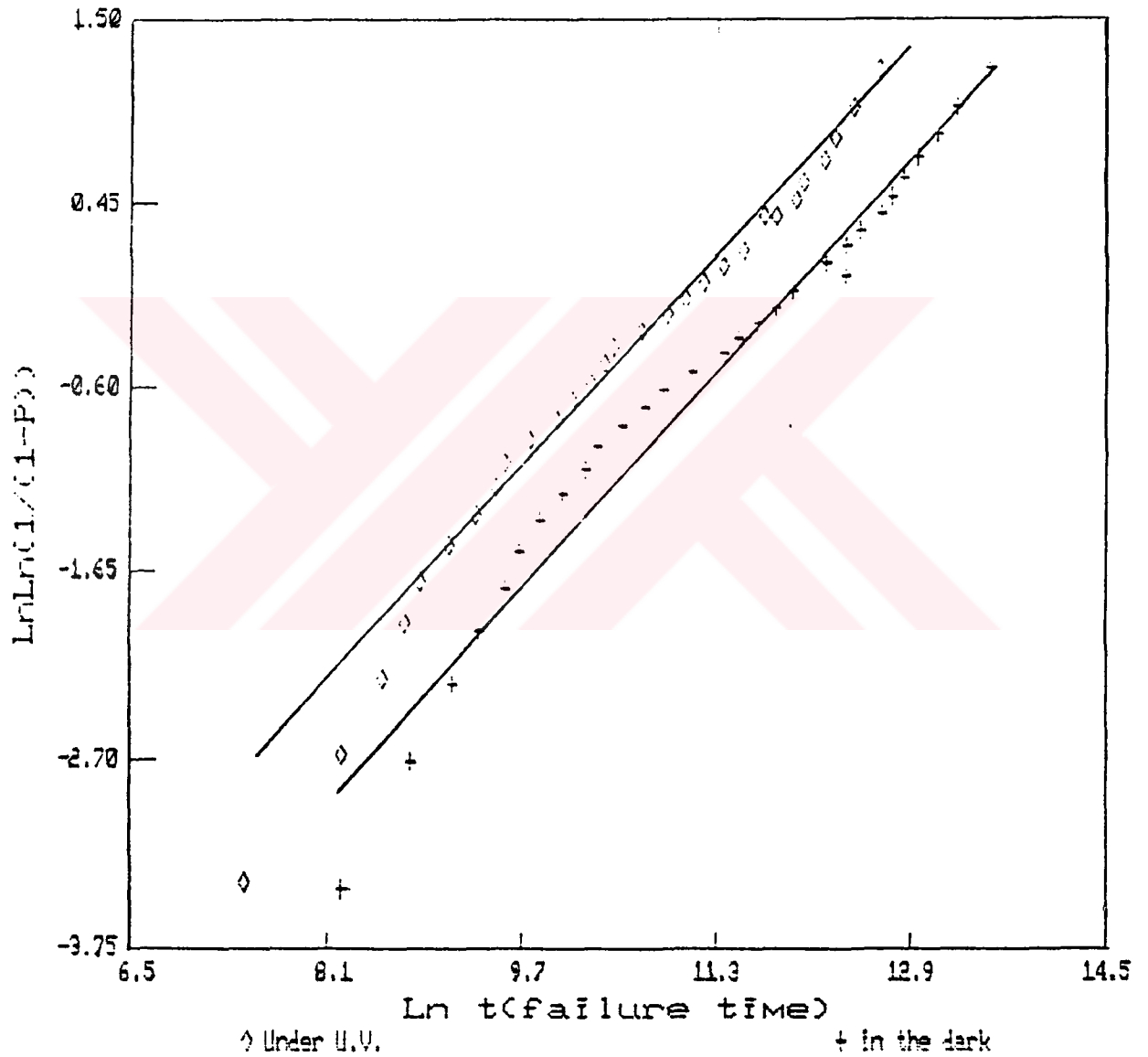


Figure 4-4: Weibull plots of water-sized fibres in 0.5 w% iron(III) sulphate/1M sulphuric acid solution.

It was observed that small cracks (flaws) could achive on the surface of corroded filaments under the light microscope. While these small cracks are growing in the filament the failure is achived any time later. As a result it has been decided to examine the surface of corroded filaments. Fibres used in this study were leached in 1M sulphuric acid for two weeks, then the surface of filaments were examined by using electron microscope. As shown in Figure 4-5 small flaws can be occured on the surface. It means that these fibres contain a lot of alkali metal ions. Metcalfe et al studied with different kinds of glass composition. They found that fibres containing more alkali ions had some flaws on the surface but there was not any crack on the surface of less alkali content fibres. Our result also comfirmed that less alkali content E-glass fibres with a nominal composition; SiO_2 :52, Al_2O_3 :14.3, B_2O_3 :10, CaO :19.2, MgO :3.3, Na_2O :0.3, K_2O :0.2, Fe_2O_3 :0.38, supplied from Cam Elyaf San.A.Ş. and NEG-Japan were leached in the same solution for three weeks but it could not be seen any crack on the surface. On the other hand, as mentioned before high alumina and bor content glasses have excellent chemical durability because of blocking alkali ions.

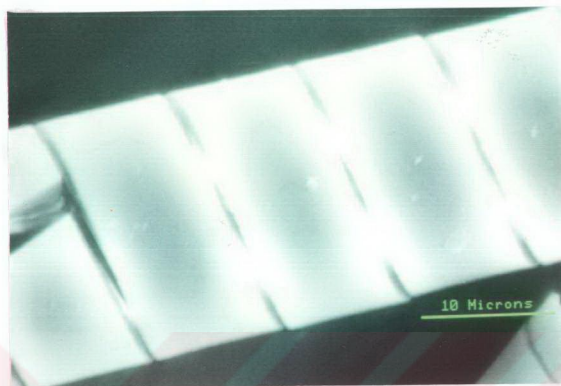


Figure 4-5a: Silenka silan sized fibres in 1M sulphuric acid for 2 weeks.

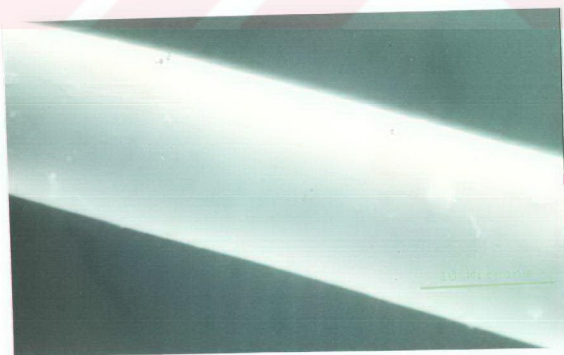


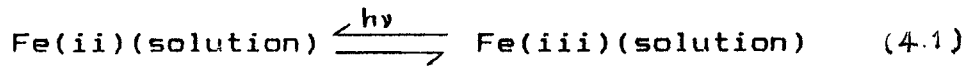
Figure 4-5b: CE water sized fibres in 1M sulphuric acid for 3 weeks.

It is well established that transition metal ions can change their valence state under the action of incident radiation in the ultra-violet region. Since iron is the most commonly found impurity in glass and, as already suggested [51] may effect the stress corrosion mechanism, hence the effect of ultra-violet radiation on its valency may qualify the observed acceleration of the reaction.

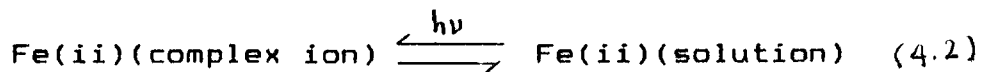
It has been established from spectroscopy that ferrous iron is six fold coordinated by bridging oxygens in glass. Absorption spectra for ferric iron tend to be weak but it is believed to be four fold coordinated by non-bridging oxygens. The radiation may affect the iron present either in the sulphuric acid or the glass. Steele and Douglas [65] studied the absorption of iron in some glasses. Also Sheard [2] confirmed iron absorption in sulphuric acid in which glass fibres have been immersed. Jones et al [66] studied the effects of illumination on the stress corrosion of E-glass filaments. Their results have confirmed that ultra-violet light of wavelength 256 nm influences the process.

If ultra-violet radiation incident on the solution changes the valency of iron, this would effect the equilibria between the ferrous and ferric iron in the glass fibre and the solution, and that between the

ferrous complex and the ferrous in solution. These phenomenons can be shown as below ;



would favour the dissolution of ferrous iron from the complex into the solution.



This would upset the equilibrium between the ferrous iron in glass and the complex, facilitating the removal of calcium and aluminium ions, and hence accelerating the stress corrosion. However the effect of radiation on the valency of iron in the glass fibres must also be considered, even though it is likely that much of the incident radiation is absorbed by the solution, before reaching the immersed glass fibres.

The idea of putting ferric sulphate into the corrosive solution was to slow down the rate of stress corrosion. It is discussed previously that under the action of ultra-violet radiation thus causing to replace the lost iron ions.



Adding much more Fe(iii) to the solution should decrease the extent of leaching of Fe(iii) from the glass to keep the equilibrium constant the same. The iron sulphate solution increase the number of $\text{Fe}^{3+}(\text{aq})\text{SO}_4^{2-}$ ion pair in the corrosive solution and it could be possible that the change are due to an increase in involvement of SO_4^{2-} in the corrosion mechanism.

4.2. KINETIC RESULTS

If iron is considered to play an important role in the mechanism of stress corrosion its behaviour in glass and corrosion environment should be examined more closely. Therefore it was decided that the amount of iron(iii) should be determined in the corrosion solution.

As shown in Figure 3-6,3-7,3-8 the amount of leached iron(iii) from all kinds of fibres under ultra-violet radiation was more than blacked-out. On the other hand, as shown in Table 3-6 the most iron(iii) had been leached from commercially sized fibres because applied size was being prepared in stainless steel equipments. Also leaching from silane sized fibres was less than commercially sized fibres but more than water sized fibres.

The mechanisms of iron leaching from different E-

glass fibres have been found similar in acidic solution and iron(iii) sulphate-acidic solution under u.v. light and blacked-out conditions. All curves shown in Figure 3-6,3-7,3-8,3-9 can be simulated by the following equation:

$$W = t / (a*t+b) \quad (4.4)$$

Where W is the amount of extracted Fe(iii) in mg/g fibre, t is the leaching time in hour, a,b are constants of equation. The correlation coefficients and constants are given in Table 4-5.

Table 4-5: Correlation coefficients and constants of different E-glass fibres.

Fibre type	Condition	a	b	R^2 Cor.
Com.sized	U.V. light	0.571	5.917	0.981
	Blacked-out	0.640	17.083	0.988
Sil.sized	U.V. light	0.760	20.392	0.999
	Blacked-out	1.734	45.760	0.989
Water sized	U.V. light	0.448	45.667	0.980
	Blacked-out	1.262	94.292	0.995
Water sized	U.V. light	0.604	46.724	0.992
Fe3+ sol.	Blacked-out	-0.942	185.12	0.988

Graphs shown in Figure 4-6,4-7 were plotted to compare the effects of different corrosion solutions and illuminations on the leached iron(iii) amount from water sized fibre. It is easy to see that the presence of iron(iii) in corrosion solution decreases the leaching amount of iron under both illuminations. These results also confirm that iron(iii) in glass fibre affects the

stress corrosion of E-glass fibres under different illuminations.

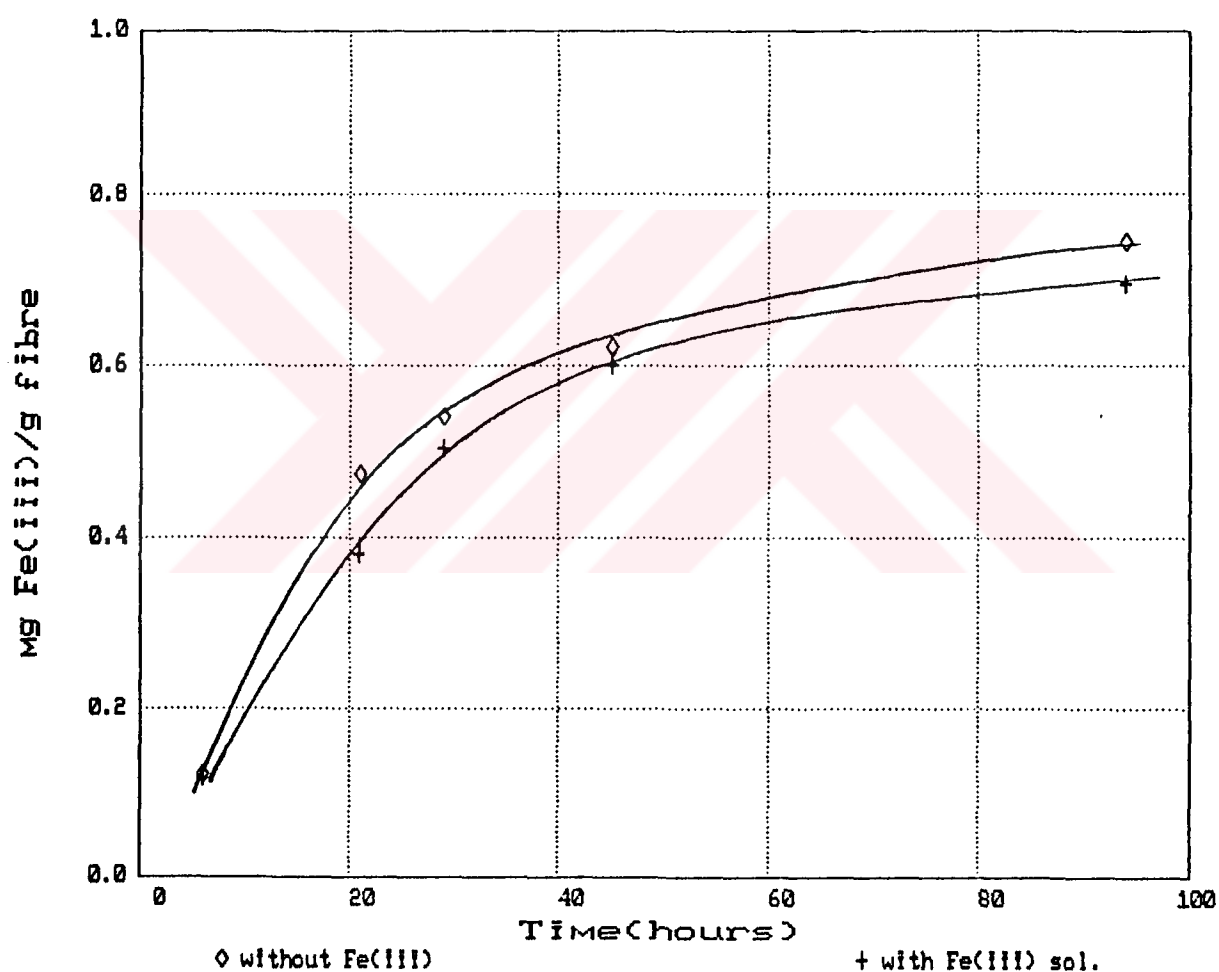


Figure 4.6: Weight of leached iron(III) in 1M sulphuric acid under ultra-violet radiation, with and without added iron(III) as iron(III) sulphate ($1.14 \times 10^{-4}M$).

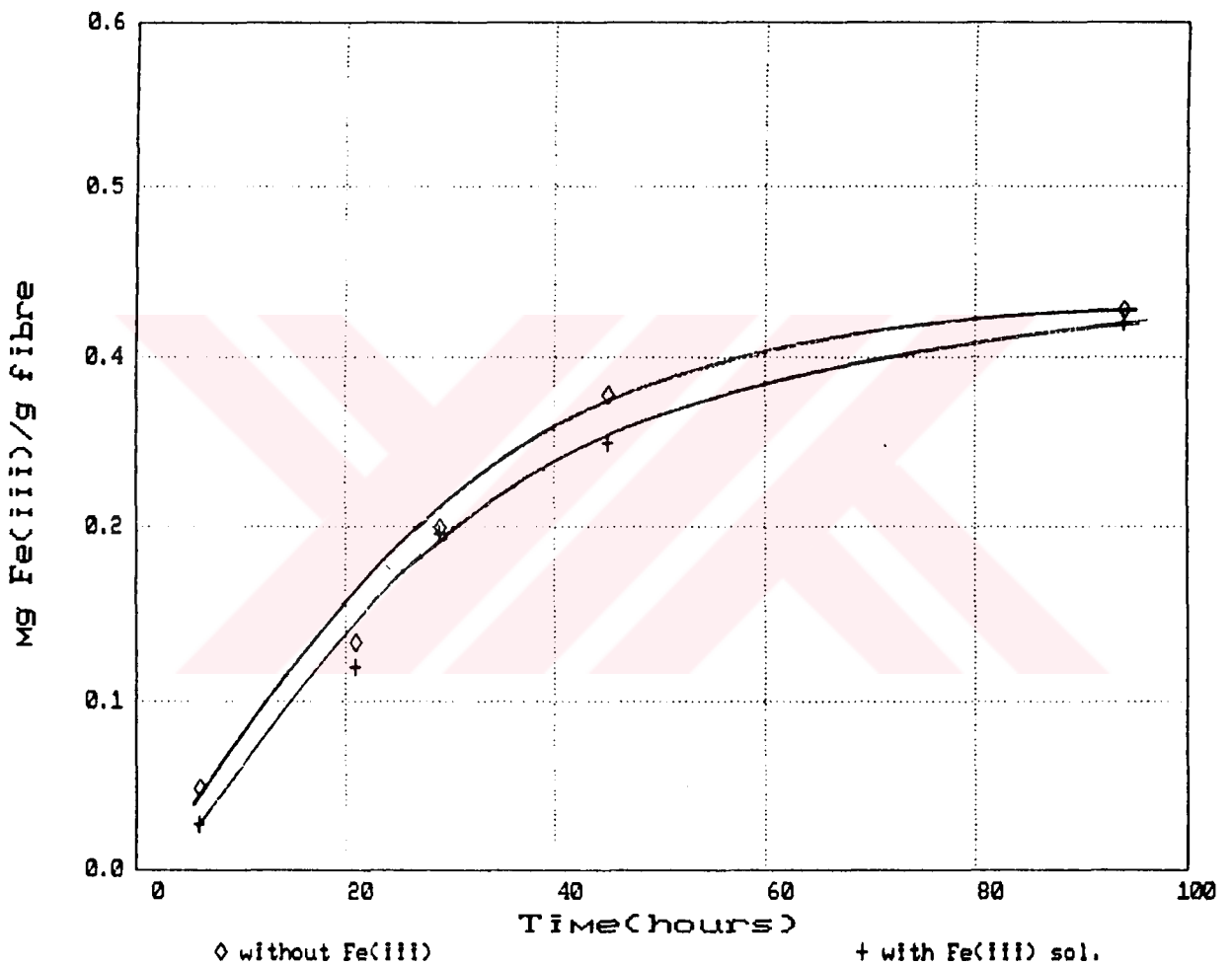


Figure 4-7: Weight of leached iron(III) in 1M sulphuric acid under blacked-out condition with and without added iron(III) as iron(III) sulphate ($1.14 \times 10^{-4}M$).

The ultra-violet spectrum of the aqueous sulphuric acid containing the glass leachants has a strong absorption with a maximum at ≈ 295 nm [66]. This u.v. spectrum is typical of an iron(iii) solution given by Steele and Douglas [65] for ferric ammonium sulphate.

The extraction of acid-soluble oxide constituents in E-glass fibres was studied by Thomas [67]. He found that the weight change resulting from leaching in 1.5N HNO_3 for times ranging up to ≈ 500 min can be expressed by the following equation:

$$\text{Log } w = -0.157 \text{ Log } t + 1.969 \quad (4.5)$$

$$\text{Log } w = -0.051 \text{ Log } t + 1.802 \quad (4.6)$$

where w is the weight change in percent, t is the leaching time in minutes. Equation (4.5) applies for times ranging up to 30 min and Eq. (4.6) from ≈ 30 to 500 min. Also he suggested that leaching was to be diffusion controlled and surface area, moisture absorption and weight loss measurements showed that leaching from E-glass was controlled by acid strength and time.

CHAPTER 5: CONCLUSION AND SUGGESTION

5.1. CONCLUSION

In this study, strength loss and iron(iii) extraction of three kinds of Silenka E-glass fibres have been studied. Strength loss has been monitored by testing failure times of stressed fibres immersed in 1M sulphuric acid solution. Weibull statistic has been applied to establish of experimental results shown that failure times of three types of fibres are dependent upon the incident illumination during the stress corrosion process.

Iron(iii) being in E-glass fibre as an impurity causes more stress corrosion under u.v. light than blacked-out because of charge transfer. But it was seen that the mechanism of both illuminations were the same. However, u.v. light is encouraging the stress corrosion of all fibres. At the end of this study, it was decided that the amount of iron(iii) should be examined in leached fibre or solution. It was possible to check iron(iii) in extracted fibre by using electron micro probe analyzer, but it was more difficult than determining in solution. By using ultra violet spectrometer, the amount of extracted iron(iii) found in

solution was tested. The extraction results showed that under ultra-violet radiation iron(iii) was extracted from E-glass fibres more rapidly than under blacked-out conditions reaching an apparent equilibrium at a lower concentration in the corrodent. Also when in an acidic solution contained ferric sulphate, more iron was retained in the E-glass fibre. The stress corrosion results show that the same mechanism operates in acidic ferric sulphate solution compared to aqueous sulphuric acid and thus confirming the iron complexation theory. As a result, it can be said that iron(iii) as an impurity is effected by u.v. light and causes strength loss.

5.2. SUGGESTIONS

The retardent iron(iii) can be tested by using chemical micro probe analyzer. Also it is well known that ion extraction from glasses strongly depends on temperature. In this study, temperature was controlled in $\pm 2^{\circ}\text{C}$ because of heating and cooling system. With a more sensitive system, it would be possible to control in a small range.

There is an equilibrium between ferrous and ferric iron in E-glass fibre. The ratio of $\text{Fe(ii)}/\text{Fe(iii)}$ in the extraction solution could be determined in further work. On the other hand, the effect of u.v. light on the

composite can be studied more detail in the future.

Kinetic studies were carried out with open beakers at the same conditions of stress corrosion because of ultra-violet radiation. In order to eliminate solvent evaporation and to be permitted U.V. radiation the silica container can be used in further work. Also corrosion solution it means sulphuric acid could be changed with another acidic solution or acid salt.



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APPENDIX

Table 1a: Stress corrosion failure times of commercially sized E-glass fibres in 1M sulphuric acid under blacked-out at 20°C.

Sample Number	Diameter μm	Strain %	Time /s $\times 10^{-4}$	Ln t	P(f)	LnLn(1/(1-P))
1	15.3	0.352	3.42	10.44	0.406	-0.65
2	14.8	0.321	32.449	12.69	0.844	0.62
3	14.7	0.321	0.802	8.99	0.156	-0.77
4	15.1	0.336	43.365	12.98	0.938	1.02
5	14.8	0.355	24.524	12.41	0.781	0.42
6	14.8	0.347	42.507	12.96	0.906	0.86
7	13.7	0.325	1.419	9.56	0.281	-1.11
8	12.3	0.309	0.560	8.63	0.125	-2.01
9	14.1	0.301	18.535	12.13	0.750	0.33
10	13.8	0.311	0.179	7.49	0.063	-2.74
11	15.0	0.302	9.390	11.45	0.625	-0.02
12	14.3	0.315	1.233	9.42	0.25	-1.26
13	12.6	0.337	2.136	9.97	0.375	-0.76
14	13.5	0.300	0.142	7.26	0.031	-3.45
15	14.9	0.300	11.700	11.67	0.656	0.065
16	13.5	0.314	37.700	12.84	0.875	0.73
17	15.1	0.334	16.771	12.03	0.719	0.24
18	14.7	0.316	4.805	10.78	0.531	-0.28
19	14.0	0.300	4.136	10.63	0.5	-0.37
20	14.9	0.341	56.807	12.25	0.969	1.25
21	14.4	0.303	0.905	9.11	0.188	-1.57
22	13.7	0.318	0.527	8.57	0.094	-2.32
23	13.1	0.337	1.020	9.23	0.219	-1.4
24	12.2	0.316	1.681	9.73	0.344	-0.86
25	13.5	0.331	12.178	11.71	0.688	0.15
26	15.6	0.337	3.668	10.51	0.436	-0.55
27	14.9	0.346	28.206	12.55	0.812	0.52
28	14.9	0.358	5.583	10.93	0.563	-0.19
29	15.3	0.350	6.170	11.03	0.594	-0.1
30	14.5	0.318	3.974	10.59	0.469	-0.46
31	15.1	0.332	1.584	9.67	0.312	-0.98

Table 1b: Stress corrosion failure times of commercially sized E-glass fibres in 1M sulphuric acid under u.v.light (av.256 nm) at 20 °C.

Sample Number	Diameter μm	Strain %	Time /s $\times 10^{-4}$	Ln t	P(f)	LnLn(1/(1-P))
1	14.2	0.321	7.387	11.21	0.793	0.45
2	15.1	0.337	2.033	9.92	0.483	-0.42
3	14.1	0.324	0.228	7.73	0.138	-1.92
4	14.6	0.313	0.127	7.15	0.069	-2.64
5	13.8	0.304	2.585	10.16	0.552	-0.22
6	14.5	0.302	1.173	9.37	0.379	-0.74
7	14.7	0.332	1.404	9.55	0.414	-0.63
8	16.3	0.306	7.168	11.18	0.759	0.35
9	15.4	0.347	0.090	6.8	0.034	-3.36
10	13.7	0.306	0.818	9.01	0.031	-3.46
11	14.0	0.291	4.951	10.81	0.69	0.16
12	14.2	0.300	1.733	9.76	0.448	-0.52
13	13.2	0.320	2.944	10.29	0.586	-0.13
14	12.9	0.334	5.928	10.99	0.724	0.25
15	14.6	0.313	0.794	8.98	0.276	-1.13
16	14.8	0.338	2.386	10.08	0.517	-0.32
17	15.1	0.339	4.525	10.72	0.655	0.06
18	13.5	0.319	13.731	11.83	0.966	1.22
19	13.6	0.314	0.423	8.35	0.21	-1.45
20	13.2	0.314	3.286	10.4	0.621	-0.03
21	15.3	0.332	8.843	11.39	0.827	0.56
22	14.7	0.348	1.020	9.23	0.345	-0.86
23	12.2	0.306	9.676	11.48	0.862	0.68
24	14.5	0.341	0.183	7.51	0.103	-2.22
25	15.5	0.343	0.501	8.52	0.241	-1.29
26	16.5	0.301	10.587	11.57	0.897	0.82
27	16.4	0.307	13.061	11.78	0.931	0.98
28	14.7	0.352	0.36	8.19	0.172	-1.67

Table 2a: Stress corrosion failure times of silane sized E-glass fibres in 1M sulphuric acid under blacked-out at 20 °C.

Sample Number	Diameter μm	Strain %	Time / 10^{-4} s	Ln t	P(f)	LnLn(1/(1-P))
1	14.6	0.364	13.869	11.84	0.677	0.12
2	14.9	0.346	4.951	10.81	0.484	-0.41
3	14.9	0.371	0.794	8.98	0.194	-1.53
4	15.8	0.349	65.344	13.39	0.935	1.01
5	13.8	0.332	5.81	10.97	0.548	-0.23
6	15.9	0.391	1.935	9.87	0.355	-0.82
7	14.5	0.365	0.353	8.17	0.065	-2.7
8	14.6	0.385	1.258	9.44	0.29	-1.07
9	13.8	0.356	28.21	12.55	0.806	0.5
10	15.1	0.342	76.681	13.55	0.968	1.24
11	14.1	0.318	8.497	11.35	0.613	-0.05
12	14	0.383	2.585	10.16	0.387	-0.71
13	14.3	0.338	0.852	9.05	0.226	-1.36
14	15.2	0.374	0.411	8.32	0.097	-2.28
15	15.5	0.358	0.284	7.95	0.032	-3.43
16	15.5	0.398	1.521	9.63	0.323	-0.94
17	15	0.344	0.512	8.54	0.129	-1.98
18	14.8	0.372	2.772	10.23	0.419	-0.61
19	15.2	0.355	10.694	11.58	0.645	0.04
20	15.6	0.308	41.665	12.94	0.871	0.72
21	14.4	0.318	20.484	12.23	0.742	0.3
22	14.5	0.377	1.083	9.29	0.258	-1.21
23	15.8	0.363	25.782	12.46	0.774	0.4
24	14.4	0.331	50.383	13.13	0.903	0.85
25	14.9	0.346	4.951	10.81	0.484	-0.41
26	16	0.352	0.637	8.76	0.161	-1.74
27	14.9	0.348	35.505	12.78	0.839	0.6
28	15.6	0.379	17.456	12.07	0.71	0.21
29	15.3	0.335	5.364	10.89	0.516	-0.32
30	13.7	0.321	7.765	11.26	0.581	-0.14

Table 2b: Stress corrosion failure times of
silane sized E-glass fibres in 1M sulphuric
acid under u.v.light (av.256 nm) at 20 °C.

Sample Number	Diameter μm	Strain %	Time / 10^{-4} s	Ln t	P(f)	LnLn(1/(1-P))
1	13.9	0.335	0.379	8.24	0.161	-1.74
2	14.7	0.375	1.121	9.41	0.355	-0.82
3	14	0.338	2.885	10.27	0.516	-0.32
4	15.7	0.335	26.302	12.48	0.903	0.85
5	14.9	0.381	0.223	7.71	0.065	-2.7
6	15.5	0.368	0.704	8.86	0.258	-1.21
7	14.1	0.351	4.805	10.78	0.613	-0.05
8	15.6	0.325	11.701	11.67	0.774	0.4
9	14.8	0.314	1.75	9.77	0.419	-0.61
10	15.2	0.376	0.196	7.58	0.032	-3.43
11	14.5	0.394	0.818	9.01	0.29	-1.07
12	15	0.331	7.461	11.22	0.677	0.12
13	14.3	0.342	37.325	12.83	0.968	1.24
14	14.7	0.317	18.535	12.13	0.839	0.6
15	14.8	0.335	8.668	11.37	0.71	0.21
16	14.3	0.356	3.126	10.35	0.548	-0.23
17	14.3	0.385	0.289	7.97	0.097	-2.28
18	15.3	0.363	0.98	9.19	0.323	-0.94
19	15.1	0.354	5.928	10.99	0.645	0.04
20	15.3	0.347	0.454	8.42	0.194	-1.53
21	14.9	0.339	2.339	10.06	0.484	-0.41
22	13.8	0.357	3.78	10.54	0.581	-0.14
23	15.4	0.326	9.971	11.51	0.742	0.3
24	14.8	0.309	31.176	12.65	0.935	1.01
25	15.4	0.326	14.149	11.86	0.806	0.5
26	15.5	0.346	2.033	9.92	0.452	-0.51
27	14.6	0.352	0.56	8.63	0.226	-1.36
28	14.1	0.371	0.346	8.15	0.129	-1.98
29	15.1	0.346	20.898	12.25	0.871	0.72
30	14.7	0.348	1.447	9.58	0.387	-0.71

Table 3a: Stress corrosion failure times of water sized E-glass fibres in 1M sulphuric acid under blacked-out at 20°C.

Sample Number	Diameter μm	Strain %	Time /s $\times 10^4$	Ln t	P(f)	$\text{LnLn}(1/(1-P))$
1	15.3	0.353	3.560	10.48	0.4	-0.67
2	14.4	0.341	11.937	11.69	0.633	0.003
3	13.3	0.363	5.472	10.91	0.5	-0.37
4	15.8	0.332	29.361	12.59	0.8	0.48
5	15.2	0.355	9.297	11.44	0.6	-0.09
6	14.4	0.369	0.726	8.89	0.1	-2.25
7	15.3	0.354	20.898	12.25	0.733	0.28
8	14.1	0.374	0.230	7.74	0.033	-3.38
9	15.5	0.346	38.848	12.87	0.867	0.7
10	15.0	0.363	23.799	12.38	0.9	0.83
11	15.9	0.327	2.033	9.92	0.3	-1.03
12	14.7	0.360	1.197	9.39	0.166	-1.7
13	15.4	0.353	0.432	8.37	0.066	-2.67
14	15.9	0.340	4.219	10.65	0.433	-0.57
15	13.8	0.332	59.125	13.29	0.933	1.0
16	15.9	0.339	7.688	11.25	0.567	-0.18
17	16.2	0.329	3.033	10.32	0.366	-0.78
18	14.9	0.319	16.940	12.04	0.7	0.19
19	15.3	0.375	4.853	10.79	0.467	-0.46
20	15.7	0.355	1.284	9.46	0.2	-1.5
21	16.1	0.336	6.486	11.08	0.533	-0.27
22	14.9	0.344	1.161	9.36	0.133	-1.94
23	15.0	0.368	1.491	9.61	0.233	-1.33
24	14.9	0.367	2.664	10.19	0.33	-0.9
25	15.6	0.350	1.785	9.79	0.266	-1.17
26	16.4	0.342	29.954	12.61	0.833	0.58
27	14.8	0.329	68.010	13.43	0.967	1.22
28	16.3	0.349	14.435	11.88	0.667	0.09
29	15.8	0.325	52.439	13.17	0.9	0.83

Table 3b: Stress corrosion failure times of
water sized E-glass fibres in 1M sulphuric acid
under u.v.light (av.256 nm) at 20°C.

Sample Number	Diameter μm	Strain %	Time /s $\times 10^{-4}$	Ln t	P(f)	LnLn(1/(1-P))
1	14.8	0.329	0.960	9.17	0.344	-0.86
2	14.2	0.354	0.267	7.89	0.25	-1.25
3	16.1	0.320	11.149	11.86	0.906	0.86
4	16.1	0.322	18.168	12.11	0.969	1.25
5	14.6	0.385	0.281	7.94	0.188	-1.57
6	14.9	0.363	0.375	8.23	0.063	-2.74
7	15.6	0.340	5.258	10.87	0.656	0.06
8	15.5	0.343	2.074	9.94	0.5	-0.37
9	15.3	0.328	9.113	11.42	0.781	0.42
10	16.1	0.322	12.424	11.73	0.875	0.73
11	15.9	0.330	11.019	11.61	0.844	0.62
12	15.7	0.339	0.606	8.71	0.281	-1.11
13	16.6	0.345	0.571	8.65	0.219	-1.4
14	14.3	0.354	0.190	7.55	0.156	-1.77
15	14.8	0.368	0.160	7.38	0.031	-3.45
16	15.3	0.351	0.228	7.73	0.094	-2.32
17	15.6	0.349	1.040	9.25	0.375	-0.76
18	14.4	0.352	2.637	10.18	0.531	-0.28
19	15.6	0.340	4.617	10.74	0.625	-0.02
20	15.7	0.327	5.639	10.94	0.684	0.14
21	15.0	0.365	0.771	8.95	0.313	-0.98
22	14.3	0.327	10.378	11.55	0.813	0.52
23	15.0	0.355	1.785	9.79	0.469	-0.46
24	15.7	0.334	15.328	11.94	0.937	1.02
25	15.9	0.363	7.097	11.17	0.719	0.24
26	15.8	0.352	3.818	10.55	0.594	-0.1
27	16.7	0.367	1.419	9.56	0.438	-0.55
28	16.1	0.349	7.922	11.28	0.75	0.33
29	15.8	0.343	0.487	8.49	0.125	-0.65
30	15.0	0.366	1.258	9.44	0.406	-0.19
31	14.8	0.377	3.189	10.37	0.563	

Table 4a: Stress corrosion failure times of
water sized E-glass fibres in 0.5 w%
ferric iron sulphate/1M sulphuric acid under
blackened-out at 20 °C.

Sample Number	Diameter μm	Strain %	Time /s $\times 10^{-4}$	Ln t	P(f)	LnLn(1/(1-P))
1	15.9	0.353	13.193	11.79	0.581	-0.14
2	15.4	0.350	34.112	12.74	0.306	0.49
3	14.8	0.372	1.419	9.56	0.161	-1.74
4	13.9	0.344	39.386	13.11	0.903	0.85
5	15.8	0.335	14.875	11.92	0.613	-0.05
6	15.4	0.352	19.681	12.19	0.677	0.09
7	15.7	0.366	2.270	10.03	0.258	-1.21
8	15.3	0.349	6.551	11.09	0.452	-0.51
9	16.2	0.395	3.742	10.53	0.355	-0.82
10	15.7	0.348	75.918	13.54	0.968	1.23
11	15.4	0.348	23.096	12.35	0.645	0.04
12	15.9	0.328	37.325	12.83	0.839	0.60
13	15.1	0.368	0.923	9.13	0.097	-2.28
14	14.9	0.383	1.584	9.67	0.194	-1.54
15	14.1	0.398	2.717	10.21	0.29	-1.07
16	15.4	0.363	5.205	10.86	0.419	-0.61
17	15.8	0.336	9.676	11.48	0.516	-0.32
18	15.9	0.357	11.242	11.63	0.548	-0.23
19	15.2	0.360	4.480	10.71	0.387	-0.71
20	15.6	0.341	8.497	11.35	0.484	-0.41
21	14.5	0.378	0.650	8.78	0.065	-2.7
22	14.7	0.389	1.150	9.35	0.129	-1.98
23	14.6	0.349	57.955	13.27	0.935	1.01
24	15.1	0.380	31.176	12.65	0.774	0.40
25	16.1	0.368	3.033	10.32	0.323	-0.94
26	15.6	0.394	0.371	8.22	0.032	-3.42
27	16.1	0.350	42.084	12.95	0.871	0.72
28	14.5	0.365	1.896	9.85	0.225	-1.37
29	15.8	0.357	26.041	12.47	0.742	0.30
30	14.4	0.355	23.328	12.36	0.71	0.21

Table 4b: Stress corrosion failure times of water sized E-glass fibres in ferric iron sulphate/1M sulphuric acid under u.v.light (av.256 nm) at 20oC.

Sample Number	Diameter μm	Strain %	Time /s $\times 10^{-4}$	Ln t	P(f)	LnLn(1/(1-P))
1	15.2	0.356	3.157	10.36	0.468	-0.46
2	14.1	0.362	15.482	11.95	0.8	0.48
3	15.2	0.326	9.971	11.51	0.7	0.19
4	14.7	0.357	2.459	10.11	0.4	-0.67
5	15.9	0.381	1.116	9.32	0.233	-1.33
6	15.6	0.341	3.420	10.44	0.5	-0.37
7	14.5	0.359	1.404	9.55	0.3	-1.03
8	15.0	0.366	13.061	11.78	0.767	0.38
9	15.8	0.337	11.937	11.69	0.733	0.28
10	15.9	0.334	4.304	10.67	0.533	-0.27
11	15.3	0.375	1.733	9.76	0.333	-0.9
12	14.6	0.338	16.439	12.01	0.833	0.58
13	15.9	0.383	0.517	8.55	0.1	-2.25
14	15.3	0.344	19.485	12.18	0.867	0.7
15	15.8	0.342	21.320	12.27	0.9	0.83
16	14.6	0.398	0.619	8.73	0.133	-1.94
17	15.8	0.365	30.255	12.62	0.967	1.22
18	14.9	0.385	0.162	7.41	0.033	-3.38
19	14.9	0.360	2.159	9.98	0.367	-0.78
20	15.4	0.371	0.887	9.09	0.2	-1.5
21	14.5	0.366	1.296	9.47	0.267	-1.17
22	15.8	0.337	6.170	11.03	0.6	-0.09
23	15.0	0.367	2.828	10.25	0.433	-0.57
24	15.7	0.353	7.168	11.18	0.633	0.003
25	15.9	0.342	24.524	12.41	0.933	1
26	15.8	0.329	8.412	11.34	0.667	0.09
27	16.7	0.340	5.310	10.88	0.567	-0.18
28	16.1	0.379	0.371	8.22	0.067	-2.67
29	15.8	0.409	0.704	8.86	0.167	-1.7

CURRICULUM VITAE

The author who was born in Sivas in 1962 leaved high school namely Kongre Lisesi in 1979. Then he entered Technical University of Istanbul in 1979 and became Chemical Engineer in 1983. He started MSc programme at the Chem. Eng. Department and had got MSc degree in 1986. At the same year, he started PhD study, finished lectures in 1987. He was also succesful in the assistant lecturer exams and joint as a junior member of staff in 1984. After completed his compulsory military service in 1988, he started working at Cam Elyaf Sanayii A.Ş., subsidiary of Türkiye Şişe Cam Fabrikaları A.Ş., as a production engineer. In 1989 he was sent to England to study MSc in Glass Science and Technology in the Sheffield University, after coming back he began working at the same factory in 1990. He is married and has a doughter called Gökçe.