# MECHANISMS OF WEATHERING OF AUTOCLAVED CELLULOSE FIBRE CEMENT

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## ABSTRACT

It has been generally assumed that cellulose fibres of the cellulose fibre cement (CFC) will be susceptible to rotting. It is demonstrated here that this is not true for the bulk of the cellulose within the body of the fibre cement which is protected from attack by moulds and other organisms by the persistent alkalinity of the cement matrix. However, the persistent alkalinity of the matrix in the presence of Oxygen, results in degradation of the cellulose by alkaline oxidation and decline in the cellulose due a reduction in its degree of polymerisation (DP).

It has also been commonly assumed that any reduction in DP will reduce the mechanical properties of the CFC; however, it is also demonstrated here that there must be significant reduction of cellulose DP before there are significant changes to the mechanical properties of the CFC. This is firstly because the bond strength of the fibre within the CFC matrix is increased by carbonation of the matrix which compensates for the implied reduction in fibre length as a result of reduction in DP. However, after detailed consideration of the structure of the fibres within the fibre cement it becomes apparent, an effective reduction in fibre length and thus strength and mechanical properties will not appear until the DP is severely reduced.

A further common assumption is that carbonation of the matrix will result in the destruction of the CFC. This is certainly not the case and in fact carbonation results in a decrease in porosity which increases the fibre/matrix bond and increases the matrix strength. These two effects tend to counteract the effects of any deterioration that may have otherwise appeared in the CFC.

It is also known that carbonation of the matrix will result in shrinkage of the CFC on drying and that cracking may result. However, modern formulations of CFC result in a product that carbonates slowly and can creep. It is clear that for each cycle of carbonation and drying which occurs roughly daily, the amount of carbonation will be small as will the resulting potential shrinkage strain. Thus the potential shrinkage on drying can be dissipated by creep and the possibility for cracking is reduced or essentially eliminated.

All of these assertions are substantiated with data from a period of 40 years of experience with autoclaved fibre cement and research into the specifics of field performance of CFCs.

Keywords:

Mechanisms of weathering; cellulose degradation; carbonation of cementitious materials; mechanical properties of cellulose fibre cement

## INTRODUCTION

### Historical Perspective[i]

When it was decided to remove asbestos from fibre cement an extensive program was undertaken in James Hardie Industries in conjunction with Australia's CSIRO Paper industry group. The research focused on improving the bond of the cellulose fibre with the matrix by refining as practiced in the paper industry. This resulted in determination of an optimum cellulose freeness whereby the strength of the CFC was maximised. The research group had long experience of assessing weathering of asbestos/cement products and the original Autoclaved Cellulose Fibre Cement (Mk I-CFC) had been exposed to external conditions without finding any significant problems.

Despite this, a major problem developed on the introduction of Mk I-CFC and after relatively short exposure to mostly dry climates, Mk I-CFC sheets failed dramatically in explosive cracking. This was very surprising because the properties of Mk I-CFC were very similar to their antecedent Asbestos/Cellulose Reinforced Fibre Cement. In particular, Mk I-CFC was only slightly weaker and its moisture movement was only marginally larger.

These failures prompted urgent changes in manufacturing to tighten the specifications and ensure that the tightened specifications were meticulously adhered to. They also prompted intense research efforts to understand the reasons for the failures and to make formulation changes to eliminate the problems.

### Solving the problems with Mk I-CFC

The major problem with the Mk I-CFC seemed to be its moisture movement and a literature search revealed that incorporation of Alumina into the autoclaved matrix would reduce the moisture movement. A major experimental effort resulted in searching and incorporating various alumina containing materials into the formulation. Ultimately it was found that inclusion of alumina in the form of Alumina Trihydrate (ATH) resulted in reduced moisture movement. After the initial discovery of the efficacy of ATH further work concentrated on optimising the formulation by varying the cement/silica ratio and adjusting the ATH level.

Assessment of each formulation was undertaken by measuring their mechanical properties, moisture movement, cellulose content and cellulose degree of polymerisation (DP) and percentage of carbonation as manufactured and after various periods of exposure to natural and accelerated conditions. Laboratory accelerated tests were undertaken using heat/rain tests and accelerated carbonation by exposure to high concentrations of Carbon Dioxide.

External exposures were undertaken in and around Sydney and at a dedicated exposure laboratory in tropical Queensland. In all instances CFCs were exposed without protection such as coatings or sealers and allowed to experience whatever the climate would throw at them. In the tropical Queensland laboratory, CFC exposure was maximised by mounting specimens facing North at the latitude angle.

Three iterations of the original formulations were developed over a period of about 12 months and the final iteration was extensively evaluated internally and externally. The final iteration has stood the test of time and is still used with few problems. Formulations were separately developed for internal applications and structural boards.

### Occasional problems with CFCs

Despite the generally favourable performance of CFCs thus developed there was a concern that cellulose would rot in service and this was evaluated over a lengthy period of time. In practice and under normal conditions it is found that where water penetration has occurred, it is due to some mechanical problem such as cladding damage or inappropriate fixing details. Nevethless it has been assumed by some that water penetration may be caused by failure of the CFCs due to

1. rotting of the cellulose fibres and

2.    deterioration of the matrix due to carbonation and subsequent leaching of matrix components,

thus allowing water to penetrate the building envelope and rot to develop in the frames and other components.

This author was asked to evaluate these claims and was given access to the all of the information derived from the investigations referred to above which he had initiated during the development of the modern CFCs and to the results derived since his departure from James Hardie. This paper is the summary of his conclusions.

## General comment on such Claims

When water penetration has occurred, samples are usually cut from affected areas and photographs taken of the affected areas. Where this has occurred it is the experience of this author, from inspections (or photographic evidence) and the need to cut samples from the building envelope that there was no evidence of significant deterioration of the CFC. Indeed mechanical testing of the limited number of samples of CFC showed that some of the CFC samples exceeded the current strength requirements of the AS/NZS 2908.2:2000 "Cellulose-cement Products, Part 2: Flat sheets". It is possible that damage could have occurred during sampling that may have suggested prior deterioration to an inexperienced observer. It was also significant that most of the water penetration occurs at or near vulnerable places such as external corners and window or other penetrations of the building envelopes.

Let us now move on to considering mechanisms of weathering of CFC and the evidence for them. Firstly though, weathering of CFC is determined by its overall structure, the structure of its components and their interaction. Careful interpretation of the results of testing is also important to reveal the true behaviour of CFC.

## STRUCTURE OF CFC AND ITS COMPONENTS

### Overall structure

CFC consists of multiple thin layers typically between 0.25-0.33mm thick. Thus an 8mm thick sheet will be consist of 24 or 32 layers. Each layer has a fibre rich face and a matrix rich face. Because of the manufacturing process the fibre rich face always becomes the front face of the sheet and the back face of the sheet is fibre poor.

CFC is very porous with pores that are open to the atmosphere and compromise around 40% of the total volume. CFC is hydrophilic and the pores will usually contain ~10% by weight of water which will fill ~30% of the free volume. The amount of water present in the pores varies with the absolute humidity of the atmosphere and is present as liquid films in the interior of the pores and as more tightly bound water closer to the matrix or cellulose fibres.

CFC is strong in the plane of the sheet and because of the manufacturing process the long direction is usually stronger than the cross direction. Also, the sheet is relatively weak perpendicular to the plane due to the presence of the fibre rich and fibre poor surfaces that are in contact at the junction of the adjacent layers. There are also very few fibres that cross the boundary between the layers so contrary to what has been suggested, the fibres do not assist water movement perpendicular to the plane of the sheet. Nor do they allow fungal hyphae easy access from front to back of sheet.
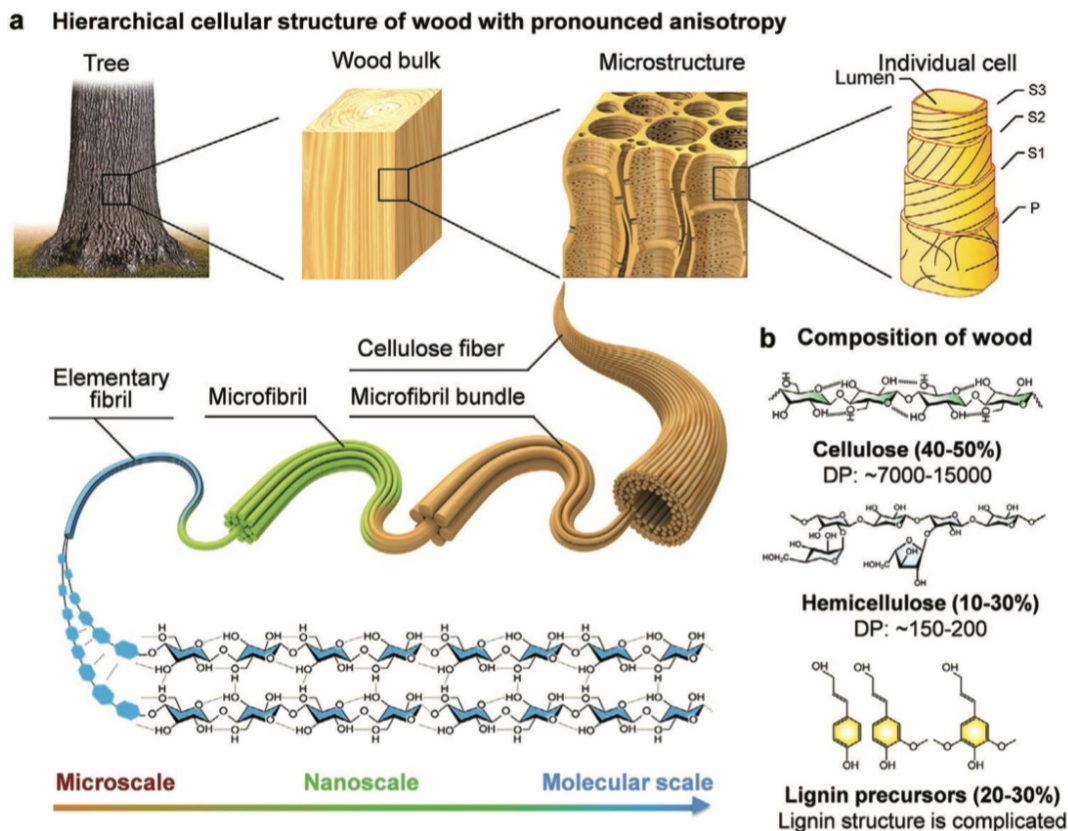
### Cellulose Fibres



Figure 1: Hierarchy of wood structure [ii]

Cellulose fibres in CFC have been extracted from wood in the pulping process and significantly modified both physically and chemically. As shown in Fig 1: in whole wood cellulose fibres form tubular structures bound together by lignins. Internally cellulose fibres have a complex hierarchal structure of cellulose molecules

combined in microfibrils which are also combined in fibril bundles (also known as macrofibrils) that together form a 3 layered cell wall structure. The fibres also contain other polysaccharides such as hemicelluloses which surround the microfibrils and macrofibrils binding them together.

When pulped a major part of the lignins and a proportion of the hemicelluloses are dissolved and the typical in-wood cellulose degree of polymerisation (DP) of 7000-15000 is reduced to around DP 2000. After pulping and drying the cellulose fibres collapse into flattened ribbons.

Cellulose fibres are further treated by mechanical refining prior to their incorporation into the fibre cement. During the refining process the structure of the cellulose fibres is disrupted and micro fibrils are pulled from the fibres. Fibres may also be reduced in length and in some cases split longitudinally. Refining improves the bonding of the fibres to the matrix of the fibre cement and improves their ability to reinforce the matrix by increasing their surface area.[iii]
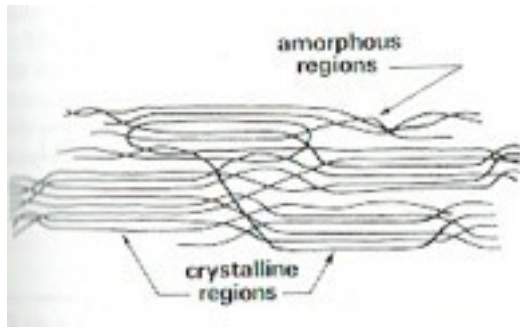


Figure 2: molecular structure of cellulose microfibrils[iv]

As shown in Figure 2, microfibrils consist of chains of cellulose divided into crystalline and amorphous regions. The crystalline regions are immensely strong, having a Modulus of Elasticity in excess of 70GPa or about 70% higher than high strength steel. The amorphous regions are much softer and imbue flexibility to the microfibrils. This combination of properties produces high strength but flexible structures in the wood. The flexibility of the wood fibres also allows good bond with the cement matrix in fibre cement.

During autoclaving to cure the fibre cement, cellulose DP decreases further to around 1000 (Molecular weight 180,000). Indeed the decrease in DP is a limitation on the extent and intensity of the autoclaving process which would seriously weaken the cellulose fibres and the strength of the fibre cement if it were continued too long or if the autoclave temperature were increased beyond the present levels of around 180°C.

Figures 3a and 3b[v] illustrate the complex structure of the microfibrils.
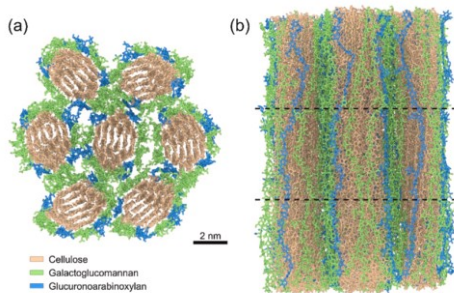


Figure 3a structure of microfibrils

Figure 3b Idealised section of the possible different sized microfibrils

Figure 3a (a) shows a section through a bundle of 7 microfibrils making up a macrofibril. The brown roughly parallel bunches are the ends of parallel cellulose chains and the blue and green represents the hemicelluloses binding the microfibrils into the macrofibril. Figure 3a(b) shows the same structure but as a section parallel to cellulose chain lengths.

Figure 3b shows some idealised sections of different sized microfibrils. The last of these shows a section through a fibril which has 8 layers of side-by-side parallel chains containing respectively 3,4,5,6,6,5,4,3 chains. This as with the other different sized microfibrils results in a microfibril of approximately circular cross section.
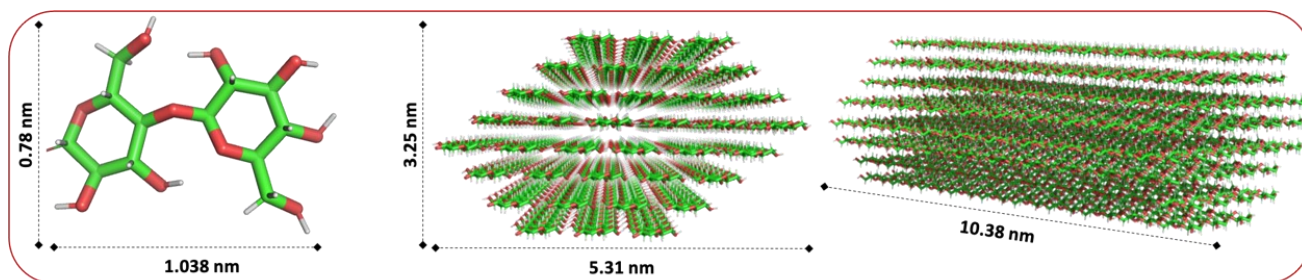
Figure 4[vi] scaled structure of a microfibril

Figure 4 illustrates the structure of the crystalline portion of the cellulose microfibril from Figure 3b (c). Individual cellulose chains in each layer are bound together by hydrogen bonding. Each layer is also bound to layers above and below by hydrogen bonding. It is this compact structure of hydrogen bonds that gives the crystalline cellulose microfibrils their strength and rigidity.
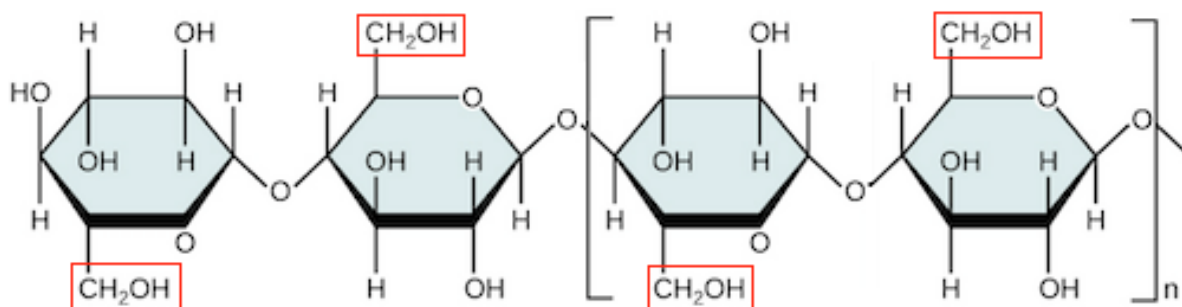


Figure 5 Cellulose molecular structure.

Cellulose itself is composed of repeating cellobiose units, i.e. the two flat structures in the square brackets above. Each cellobiose units consists of two consecutive glucose anhydride units. It is clear from the above that there is ample opportunity for forming hydrogen bonds between adjacent cellulose chains. Each glucose unit is ring shaped and contains 5 carbon atoms and one oxygen atom. There is some strain within the rings because of the natural bond angles that would be present in free atoms are not allowable because of geometry of the ring. It should be noted that although we illustrate the cellulose structure as a being flat, it is not flat in reality and the rings have the "structure" as modelled in Figure 6. (The same structure is also illustrated in Figure 1 at the "Molecular Scale")



Figure 6: Models of Cellobiose[vii]
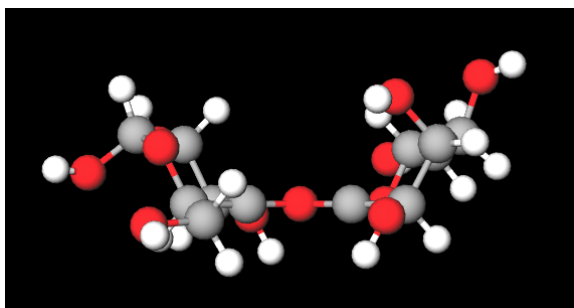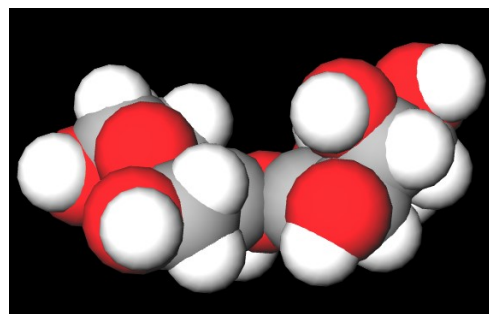
Ball and Stick Model                          Van der Waals Spheres

https://embed.molview.org/v1/?mode=vdw&cid=16211032

**Structure of the Matrix**

The composition of the matrix of autoclaved fibre cement is a mixture of crystalline Al substituted Tobermorite i.e. Calcium Aluminosilicate Hydrate, unreacted coarse Silica, and a variety of amorphous Calcium Alumino Silicates and hydrated minerals derived from the Portland Cement. Calcium dominates cations present but since all Portland Cement contains Sodium and Potassium, the matrix always contains a significant amount of each of these metal ions.

During low temperature curing prior to autoclaving the Portland cement hydrates and releases Calcium Hydroxide (CH) into the pore water. This reaches its maximum at around 12 hours after manufacture of the CFC which is then subjected to autoclaving at ~10BAR or 180°C. During autoclaving this CH reacts with the free silica and properly cured CFC will contains less than 0.5% Calcium Hydroxide after autoclaving. It also contains a residual amount of unreacted silica depending on the proportions of the original mix.

Hydrated CFC is hydrophilic and its water content varies with the absolute humidity of its surroundings. In a standardised laboratory atmosphere, it will contain around 10% by weight of water which occupies about 30% of the pore space. About 1/3 of this water is present in films that coat the inside of the pores and the remainder is intercalated to various degrees in hydrated minerals.

The CFC expands on absorption of water and shrinks when water is lost to the environment. There are two distinct responses to the change in water content which reflect the bond between the water lost and its location in the mineral structure. From the saturated state to equilibrium with standard lab conditions water loss is ~50% of the saturation volume giving about 30% of the shrinkage, and the loss of the remaining water produces 70% of the shrinkage. The shrinkage due the first part of this curve is attributable to surface tension within the pores while the second part of the curve is attributable to the loss of intercalated water from within the crystals of the matrix.

Because of the manufacturing process the matrix contains open pores thus water vapour, other gases or liquids can pass directly through the thickness of the CFC sheets. The rate at which this can happen depends mainly on the manufacturing process and to a lesser extent on the formulation of the CFC. This open porosity means that CFC is potentially susceptible to chemical attack and indeed it is well known that CFC is susceptible to carbonation i.e., reaction between the matrix and Carbon Dioxide from the atmosphere.

**Interface between the Cellulose Fibres and the Matrix**

The surface of the cellulose fibrils expresses multiple hydroxyl groups that are functionally equivalent to water molecules. If the cellulose fibres are in contact with the matrix materials then hydrogen bonds can form between the fibres and the matrix material binding them together.

During manufacture the fibres and the matrix materials are placed together in suspension in water. Therefore it is certain that both the fibres and the matrix materials will have an adherent film of water molecules on their surfaces and prior to significant curing of the cement materials layers of loosely bound water molecules will remain between the fibres and the cement. As curing continues the cement particles will become increasingly hydrated absorbing the bulk of the water and reducing the number of layers of water between the fibres and the cement and thereby increasing the bond between the fibres and matrix.

This process is further enhanced during the autoclaving stage where a series of reactions takes place which remove a further amount of free water and convert the matrix to Alumina Substituted Tobermorite. At the end of autoclaving the pressure in the autoclave is reduce to atmospheric pressure resulting in the evaporation of around 30% of the total free water while the temperature is also reduced from 180°C to 100°C. The total amount of water between the fibres and the matrix is also reduced which improves the chances of a direct and stronger bond between them.

Finally as indicated above, once the CFC is exposed to normal atmosphere, more water evaporates until its pores are roughly 30% filled with water. Evaporation of this water causes a reduction in the volume of the CFC equivalent to about 0.15% (i.e. 0.05-0.08% linearly) and the strength of the fibre-matrix bond is further improved.

# LONG TERM CHANGES IN CFC ON EXPOSURE TO NORMAL ENVIRONMENTS

## Cellulose Fibres

Cellulose fibres are subject to several effects that can cause them to break down as determined by the DP test. These are

1. mechanical and chemical effects during their extraction from whole wood or during refining and
2. chemical effects due to alkaline oxidation, alkaline degradation or biological degradation.

We have previously described their early breakdown due to extraction and processing to make the fibres suitable for use in CFCs, so we will not be concerned further. We will concentrate on possible effects after the CFC has been subject to exposure in normal working environments.

Cellulose is actually quite a stable material and biological degradation can only take place under specific conditions. For example wood eating termites would be unable to digest wood without the aid of gut bacteria that provide enzymes that decompose the wood. Fungi and free living bacteria can of course cause decay of whole wood but in general they require not only cellulose-degrading enzymes but also they must generate an acidic environment where the enzymes are effective. There are also some rare bacteria that can work in slightly alkaline conditions but they still require a lot of energy to bring about decomposition of the cellulose.

As a consequence of the presence of alkaline earth ions of $Na^+$ and $K^+$ in the cement, CFC is alkaline in nature and remains alkaline up to the end of complete carbonation when the total available Calcium Hydroxide has been converted to $CaCO_3$[viii]. $Na^+$ and $K^+$ are strong alkalis, do not form insoluble carbonates and therefore remain in solution in the internal free water. Thus the interior of the CFC's is protective of the cellulose fibres from biological attack.

Biological attack can occur in the cellulose on the front surface of the CFC because fibres are exposed on this surface. However if the surface is painted (as recommended by all manufacturers) attack on the fibres is minimal because paints usually contain mould inhibitors. Fibres at all of the other film interfaces within the fibre cement are protected by the alkaline matrix as the energy that any biological agent would require to neutralise the matrix is more than could be obtained from any cellulose that it could extract.

However, cellulose fibre is susceptible to two processes whereby its polymer chains shorten and their DP reduces. [ix] [x] These processes are respectively known as

1. "alkaline oxidation" or "peeling" which is stepwise reduction of the free ends of a cellulose chain and
2. "alkaline hydrolysis" or "alkaline degradation" which is breaking of the cellulose polymer chain in its interior.

### *Alkaline Oxidation or Peeling:*

a) Reflecting the orientation of the glucose monomer units within the polymer chain, each cellulose polymer chain has reducing end at one end and a complementary oxidising end at the other end.
b) Peeling occurs at the reducing end of the chain and each peeling reaction removes one glucose unit from the end of the chain.
c) The glucose ring molecule is broken open converting the ring into linear water soluble isosaccharinic acid and the new end of the chain may either become a new reducing moiety or may be modified to block further peeling.
d) The isosaccharinic acid combines with $Ca^{2+}$ ions from the matrix to become insoluble Calcium Isosaccharinate allowing further peeling to take place. The presence of the $Ca^{2+}$ ions in the environment of the cellulose facilitates the peeling reaction.

The peeling reaction can be summarised by the following equation

$$C_6H_{10}O_5 \quad\quad + H_2O \quad \longrightarrow \quad C_6H_{12}O_6$$

Glucoside Unit    Water    $\longrightarrow$    Isosaccharinic Acid
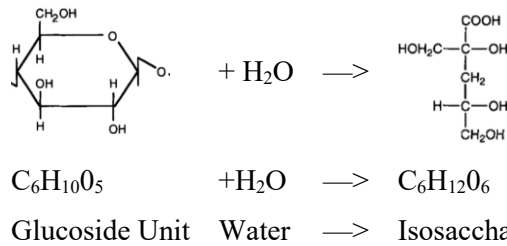
As the Isosaccharinic Acid is produced, it combines with $Ca^{2+}$ ions and precipitates as insoluble Calcium Isosaccharinate.

### *Alkaline Hydrolysis or Alkaline Degradation:*

a) Alkaline degradation only occurs in the amorphous portions of the cellulose fibrils (see Figure 2 above) because the crystalline portions of the cellulose chains consist of tightly packed layers bound together by hydrogen bonds. Tight packing does not allow easy access of the bonds within each chain and even if the separation is effected between two monomers within the chain there is a possibility of self-healing.

b) Alkaline degradation in the amorphous regions is also slow because to effect the breakage of a complete micro-fibril requires the simultaneous breaking of numerous chains e.g. referring to Figure 3b a) 18 chains would need to be broken simultaneously to break that microfibril.

c) Although the amorphous region allows more scope to the movement of the polymer molecules, there is still a chance that a break could self-heal because the polymer molecules are more restrained than the free end of a cellulose chain.

d) Breaking the chain does not result in release of isosaccharinic acid but formation of a permanent break would allow peeling to take place thereafter at the chain break.

There is a considerable difference in the reaction rates for peeling and chain breaking and Van Loon and Glaus found that peeling is the dominant reaction mechanism for the obvious reasons in the discussion above. In addition in their investigations of degradation of cellulose in radioactively contaminated cloth (presumably from clothing) they also estimated that the cellulose would not be completely degraded until $10^7$ years. I suspect that cellulose in CFC would be completely degraded in less time than this because CFC allows access to oxygen from the air unlike the Van Loon and Glaus experiments in which oxygen would only be available for a short time with sealed materials being confined because of their radioactivity.

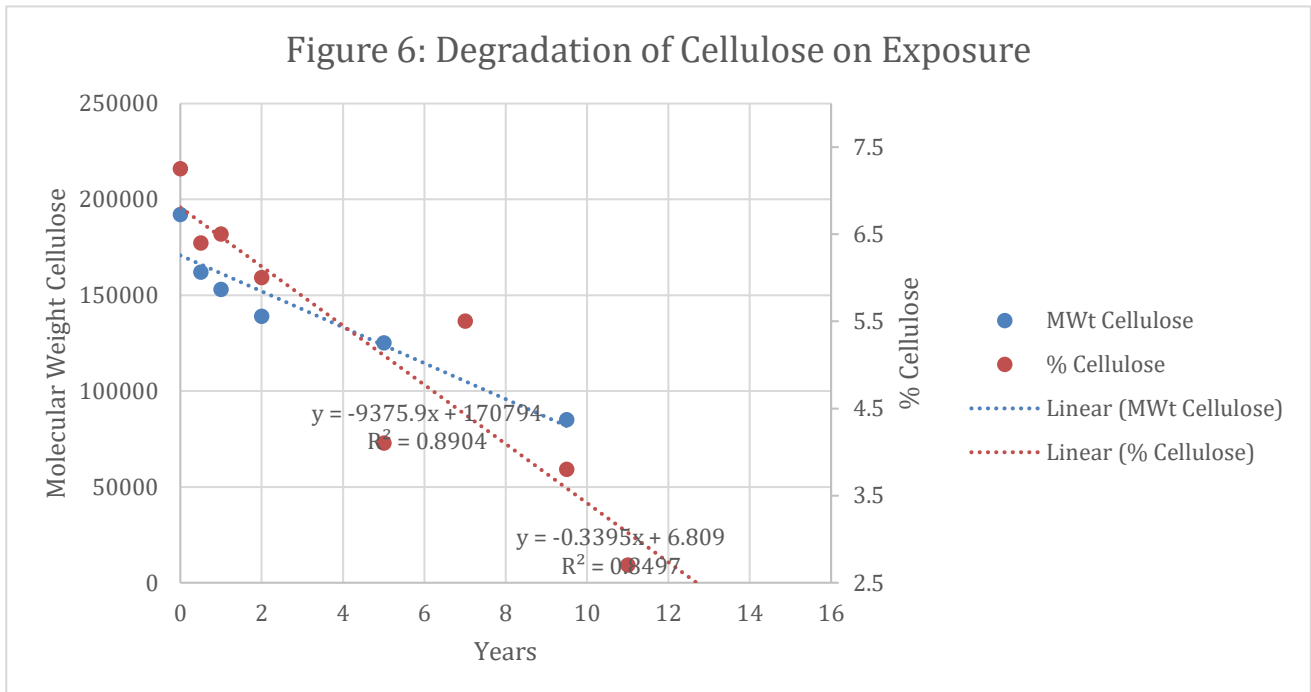### *Evidence for Cellulose Degradation by Peeling*

In any event peeling is the dominant means by which cellulose weathers and is a slow reaction as demonstrated by our experience with CFC's. Table 1 and Figure 6 show the changes in Molecular Weight and Cellulose percentage relative to the years of exposure. Nearly all of the cases reported in Table 1, the CFC specimens were exposed without protection in natural atmospheric conditions in a tropical environment which significantly accelerates the rates of reaction[1].

Sets of 6 specimens were returned at regular intervals and tested for cellulose content and cellulose DP. Specimens were expected to show most rapid change early after exposure so the return intervals were 6 months, 1, 3, 7 and 10 years. However as you will see below in Figure 6, our expectations differed from the results achieved.

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[1] The exposure of the last two specimens exposed for 9.5 and 11 years respectively was less certain than the first 5 specimens but seemed to continue the trend so have been included.

| Years Exposure | Molecular Weight | % Cellulose |
|---|---|---|
| 0 | 192000 | 7.25 |
| 0.5 | 162000 | 6.4 |
| 1 | 153000 | 6.5 |
| 2 | 139000 | 6 |
| 5 | 125000 | 4.1 |
| 7 | | 5.5 |
| 9.5 | 85000 | 3.8 |
| 11 | | 2.7 |

Table 1: Changes in Cellulose DP and % vs Exposure



Figure 6: Degradation of Cellulose on Exposure

$y = -9375.9x + 170794$
$R^2 = 0.8904$

$y = -0.3395x + 6.809$
$R^2 = 0.8497$

It will be seen from the chart and the table that the cellulose percentage and its DP decline linearly with time. The interpretation of this behaviour is that the predominant method of degradation is peeling of the cellulose fibres i.e. removal of glucose molecules to reduce the Cellulose DP. The glucose molecules are converted in the presence of $Ca^{2+}$ ions to insoluble Calcium Isosaccharinate ($Ca(C_6H_{12}O_6)_2$) which remains in the CFC after weathering of the cellulose fibres. Since it is no longer part of the cellulose molecules it does not contribute to the strength of the CFC.

Calcium Isosaccharinate, if not removed from the matrix would register as Cellulose when burnt in the cellulose determination test because it is organic. However it is removed during the during the acid digestion of the fibre cement that removes $CaCO_3$ resulting from carbonation of the matrix which would artificially increase the apparent CFC Cellulose content.

**Matrix**

***Carbonation:*** The main changes within the matrix are related to carbonation or reaction between Carbon Dioxide in the air and hydrated Calcium Silicates (CSHs), Alumina substituted Calcium Silicates (CASHs) and Calcium Aluminates (CAHs) in the presence of water films in the pores of the matrix. While the reactions of the

CSHs, CASHs and CAHs are somewhat different it is certain that all of the Calcium contained within these species is available for reaction with $CO_2$ to form $CaCO_3$. In the general case where we have CASHs we can write a universal equation to describe the reaction as follows

$$CASH + CO_2 + (x + y)H \rightarrow CaCO_3 + SH_x + 2AH_3 + (y - 5)H$$
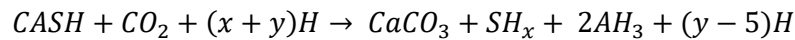
Where   C = CaO, S= $SiO_2$, A= $Al_2O_3$ and H = $H_2O$

CASH represents all the hydrated Calcium alumino Silicates with no regard for ratio of the ingredients.

The reaction may be split into two components where the CH of the CASH is assumed to react independently with one molecule of $CO_2$ to give $CaCO_3$ and release one molecule of water shown independently on the right side above. The water (x+y) that forms the silica gel ($SH_x$) and alumina trihydrate ($AH_3$) is assumed to be available in the internally absorbed water.

Apart from the water molecule released from the CaO reaction, none of the products of the reaction are labile and none of the solids is soluble in water. Alumina Trihydrate is a dry solid and silica gel is a porous hydrophilic insoluble material (used elsewhere as a desiccant to keep sensitive materials dry).

***Carbonation effect on Shrinkage and Moisture Movement:*** However, carbonation produces from each cycle an irreversible shrinkage in the bulk material and an increase in its reversible moisture movement. If carbonation is carried to 100% in one cycle, then the magnitude of the irreversible shrinkage is roughly equal to the uncarbonated moisture movement and the reversible moisture movement is doubled. Whether CSF survives a cycle of carbonation therefore depends on the magnitude of the cycle and the ability of the CSF withstand particularly the irreversible shrinkage without breaking.

The rate of carbonation of unprotected CSF in external exposure was evaluated[xi] with the following generic results shown in Figure 7.

As can be seen there is a good linear relationship between the percentage carbonation and the years of exposure providing that we ignore the first 6 months of exposure. Some of the apparent carbonation at zero time is due to actual carbonation of the fresh materials that does occur during manufacture from drawing air through the wet films on the machine and a further amount may be due to carbonation during storage. For our purposes we ignore this and assume that the rate of carbonation is linear during exposure at a rate determined from figure 7.

From Figure 7 we can determine that the average rate of carbonation for unprotected CSF is 0.025%/day.



Figure 7: %Carbonation vs Years Exposure

$y = 8.0874x + 24.977$
$R^2 = 0.9788$
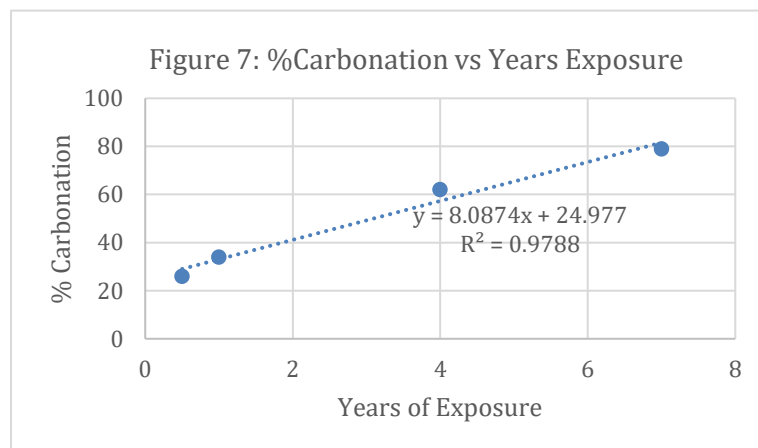
***Creep:*** Moisture movement of the usual formulations CSF is between 1.2 and 1.9 mm/m so the irreversible shrinkage will lie between 1.2 and 1.9 mm/m assuming 100% carbonation has occurred. In external exposure assuming that we have had a one carbonation and drying cycle per day, the daily implied shrinkage will lie between 1.2*0.025/100= 0.0003mm/m or 0.3 ppm and 1.9*0.025/100= 0.0005 mm/m or 0.5 ppm.

In a simple experiment the author[xii] determined creep rates in fibre cement loaded with moderate loads much less than the required 7MPa. These varied between 16 ppm in the first day of exposure and 1.6 ppm on

subsequent days. No failures occurred during the period of the experiment that continued for approximately one month under stressed conditions. It will be clear from this experiment that the creep capacity of the CFC was more than adequate to withstand the daily strain induced by a cycle of carbonation. Creep also proceeds at a rate that is sufficient to completely de-stress the CFC within one day so that there is little or no residual stress that would compromise the CFC during subsequent cycles of carbonation and drying.

***Porosity and Fibre/Matrix Bond:*** Carbonation also reduces the porosity of the CFC as follows. The basic carbonation reaction is

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
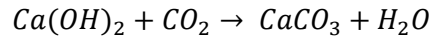
The specific gravity of $Ca(OH)_2$ is 2.34 g/cc and $CaCO_3$ is 2.711 g/cc. Thus the molar volume of $Ca(OH)_2$ is 74/2.34 = 31.6 cc/mole and the molar volume of $CaCO_3$ is 100/2.711 = 36.89cc/mole. This means

- Porosity of carbonated CFC diminishes progressively as carbonation continues and rates of carbonation tend to decrease although this is minimal
- Since the hydrated cement minerals are in contact with the cellulose fibres their expansion during carbonation tends to increase the bond between fibres and matrix and will maintain the CFC strength or increase it slightly in the early stages of exposure when deterioration of the cellulose fibres is at a minimum.

The maximum compressive strength ($\sigma_{ult}$) of a porous material is related to its porosity ($\alpha$ )by a relationship similar to the following

$$\sigma_{ult} \propto (1 - \alpha)^3$$

Thus, the strength of the matrix will tend to increase with carbonation since its porosity declines. Since the modulus of elasticity tends to increase with the strength, the stiffness of the CFC will also tend to increase with carbonation.

### Effects on the CFC in total

***Strength:*** Table 2 and Figure 8 below compare the flexural strength or modulus of rupture (MoR), modulus of elasticity (MoE) and failure strain of the unprotected panels exposed in tropical Queensland and sheltered samples kept in the laboratory to determine any natural deterioration that could occur.

| Age at Test Yrs | Sheltered MoR MPa | Exposed MoR MPa | Sheltered MoE GPa | Exposed MoE GPa | Sheltered Failure Strain | Exposed Failure Strain |
|---|---|---|---|---|---|---|
| 0 | 16.5 | 16.5 | 7.1 | 7.1 | 4335 | 4335 |
| 0.5 | 16.5 | 16.3 | 7.1 | 7.3 | 4335 | 3639 |
| 1 | 16.7 | 15.3 | 7.2 | 6.4 | 4294 | 3585 |
| 2 | 16.9 | 13.6 | 7.2 | 5.1 | 3669 | 3557 |
| 5 | 15.4 | 5.8 | 6.0 | 3.1 | 4506 | 2112 |
| 7 | 14.7 | 4.7 | 5.9 | 2.5 | 3806 | 1998 |

Table 2: Comparison of CFC behaviour with age

Specimens held in a sheltered laboratory and exposed unprotected in a tropical climate

## Figure 8: Strength, MoE & Failure Strain
### Exposed and Sheltered CFC vs Time of Exposure
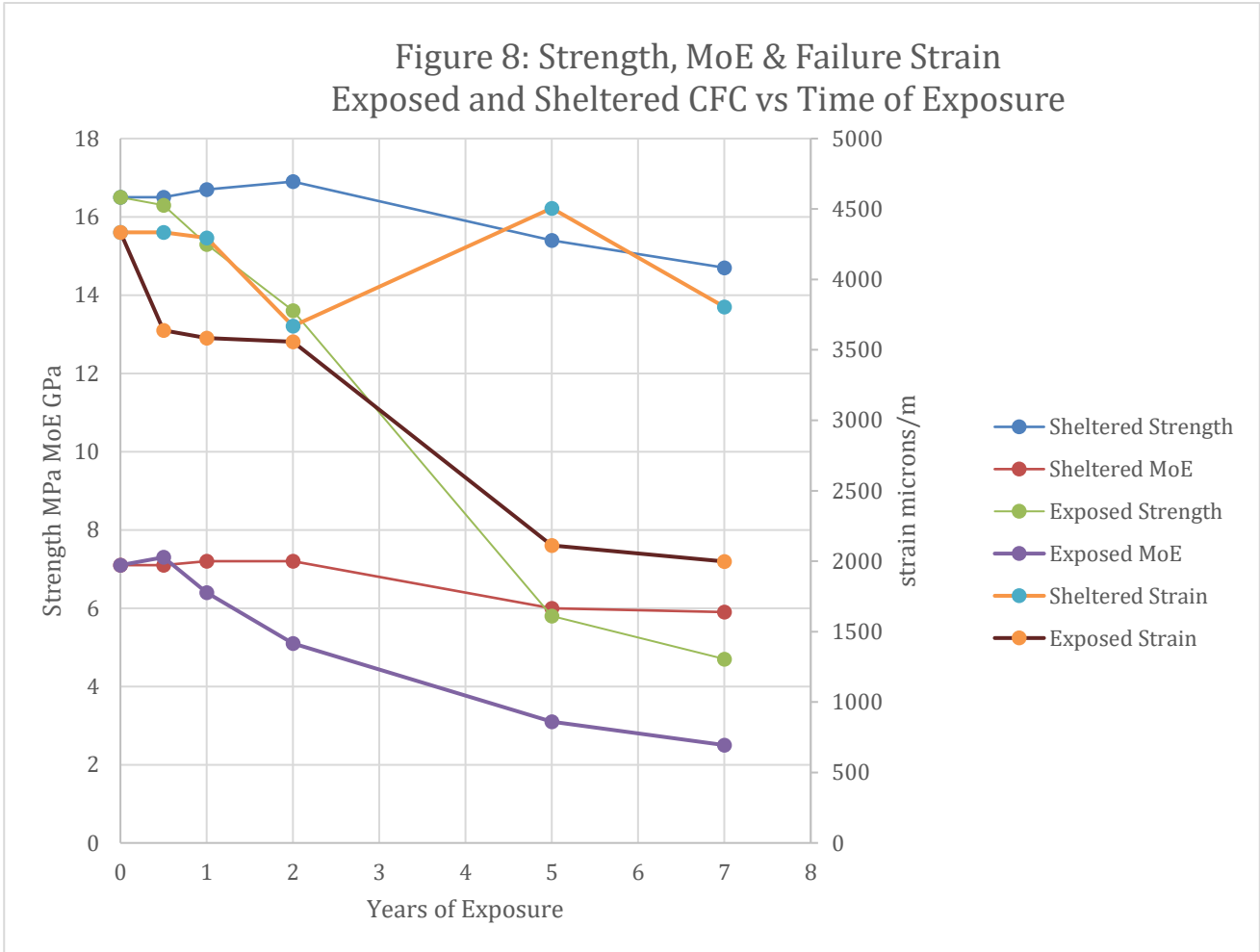


The table and graphs above show the comparative deterioration of CFC exposed to a tropical environment to one held in a laboratory for testing. The sheltered specimens show very similar behaviour to specimens that are installed as wall cladding and protected with a paint coating. As can be seen the sheltered specimens did show some deterioration in strength that is probably indicative of deterioration of the cellulose fibres due to alkaline oxidation. The strain to failure of the sheltered specimens also was little affected indicating that there was only slight deterioration of the fibres and probable increase in fibre/matrix bond. The change to exposed specimens was much greater indicating fibre damage as well as fibre bond increase. It is likely that protected specimens will also behave somewhere between these two extremes.

This indicated in the Table 3[xiii] showing air dry strengths of exposed painted boards compared with new production of equivalent boards.

| Material | MoR Long MPA | MoR Transverse MPA | MoR Mean MPA |
|---|---|---|---|
| Sample 1 | 16.9 | 10.6 | 13.7 |
| Sample 2 | 18.9 | 14.4 | 16.6 |
| New Manufacture | 20.1 | 14.5 | 17.3 |

Table 3: comparison of exposed and newly made materials

Sample 1 and sample 2 were taken from a jobsite after long exposure of unknown time. It will be seen that they fall between the sheltered samples and the severe exposure in a tropical environment as reported in Table 2 and Figure 4.

It is interesting to note that Table 2 shows the observed initial increase in strength with a reduction in strength with further exposure as reported for accelerated heat rain testing in Cooke 2000. This is also evident in the MoE results.

Akers and Studinka[xiv] studied the behaviour of both air cured and autoclaved cellulose fiber cement composites in natural and accelerated exposures. They found that 4 years natural weathering of both types of composite increased both the strength and modulus of elasticity. They concluded that this was mainly due to the carbonation of the matrix and the consequent increase in the fibre-matrix bond. They also noted that there had been a simultaneous reduction in the DP of the cellulose but that this was not associated with a reduction in the strength of the CFC.

Similar results for 5 years of natural weathering of CFC were reported by Sharman of BRANZ[xv] in. In this case sets of unpainted and painted specimens were exposed in various orientations. They reported that unpainted boards were affected more rapidly than painted boards and that both painted and unpainted boards exhibited similar behaviour to specimens subjected to accelerated testing.

**Explanation of the Behaviour**

To sum up field exposure of protected (painted) and properly fixed CFC has been shown to result in the following effects.

1. *Mechanical Strength:* in many cases there is an increase in strength and stiffness soon after exposure that is followed by a slow decline in both. At no stage up to several years after exposure is there any evidence that CFC will fail.
2. *Changes to the Cellulose Fibres:* the cellulose fibres are gradually degraded with simultaneous loss of DP and mass of cellulose. Despite the apparent loss of cellulose mass and DP, the strength of the boards remains high for an extended period of time. Apart from the top layer of cellulose fibre, which decays in unprotected CFC, there is very little evidence of rotting of the internal cellulose fibres except where there has been some other damage that has resulted in delamination of the CFC thus exposing internal cellulose fibres.
3. *Changes in Matrix Internal Chemistry:* the only obvious change in the internal chemistry of CFC is carbonation of the matrix which is benign if not beneficial. Full carbonation requires several decades to complete. The internal pH of CFC remains alkaline for decades despite carbonation.
4. *Changes to other Physical Properties:* the most obvious changes that also occur are increases in reversible moisture movement and the generation of irreversible shrinkage due to carbonation. The strain to failure during testing decreases as specimens age.

*Matrix*

As described above, carbonation of the matrix results in the formation of Calcium Carbonate and hydrated gels of Silica and hydrated Alumina Trihydrate which are all insoluble in water. Calcium Carbonate also occupies a volume greater than the Calcium Hydroxide that it replaces. Thus, there is no possibility of leaching of the matrix materials from the CFC. The strength of the matrix also increases due to the reduction in porosity of the CFC and the fibres become more tightly bound due to their close proximity to the expansion of Calcium Hydroxide on its conversion to Calcium Carbonate.

Carbonation proceeds slowly because the concentration of Carbon Dioxide in the atmosphere is low which limits the rate at which it can occur. If we assume a daily cycle of carbonation and drying it can be shown that the amount of irreversible shrinkage and reversible shrinkage due to one cycle is well within the daily creep capacity of the CFC. So, cracking of the CFC is not likely to occur and in fact is rarely a problem except if the CFC has been improperly fixed.
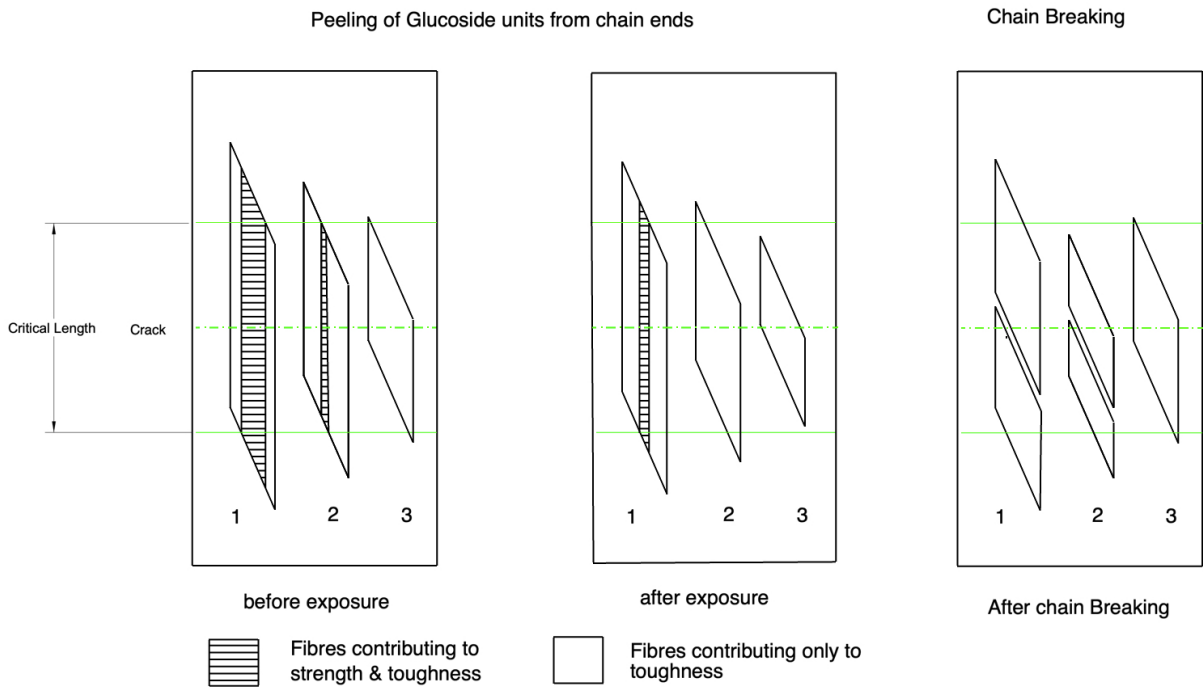
Protecting the CFC with a paint coating has the effect of further limiting the diffusion of $CO_2$ into CFC pores and thus slows the rate at which carbonation can occur. Importantly it also protects the surface of the CFC and the cellulose fibres thereon as well as the coating being reinforced by the cellulose fibres.

*Cellulose Fibres and Strength*

Cellulose fibres internally to the CFC are protected against fungal and other biological attack by the persistent alkalinity of the matrix. However, they are subjected to Alkaline Oxidation which destroys the cellulose and reduces its chain length or Degree of Polymerisation. One would expect therefore that this would result in a rapid loss of strength of the composite and while in the long run this may be true, observation of CFC in the field shows that almost complete loss of cellulose must occur before the boards are unsuitable for service. The question arises is what is the mechanism that drives this process? The answer lies in the following.

Because of the structure of cellulose fibre, degradation of the fibre proceeds by "peeling" that is one by one removal of glucoside units from the open ends of individual cellulose polymer chains. Reduction of cellulose DP does not proceed to any significant extent by chain breaking because individual cellulose polymer chains are strongly connected within bundles such that multiple polymer chains must be simultaneously broken to break the bundle containing them. It also depends on the mechanism by which short cellulose fibres reinforce the CFC.

Figure 9: Schematic of Fibre Bundles
Bridging a Crack during testing



Peeling of Glucoside units from chain ends

Chain Breaking

Critical Length    Crack

1    2    3

1    2    3

1    2    3

before exposure

after exposure

After chain Breaking

Fibres contributing to strength & toughness

Fibres contributing only to toughness

Consider Figure 9: that shows a simplistic schematic of fibres bridging a crack during a mechanical test and illustrates 2 scenarios – fibre peeling and fibre chain breaking.

According to the theory of short fibre reinforcement as developed by Hannant[xvi], after cracking of the matrix all the load applied by the test is supported by those fibres longer than a critical length. The critical length is determined from the length necessary to bond of the fibre strongly enough to ensure the fibre breaks during the test. Fibres shorter than this critical length will not contribute to the maximum strength but only to the toughness of the CFC as they require energy to pull out after cracks have developed.

In addition to this, both ends of the fibre bridging a gap must be able to carry the full breaking load of the fibre, for if one end of the fibre is less than ½ the critical length, then that end will pull out during the test and that fibre will only contribute to toughness of the CFC after breaking.

Figure 9 under the peeling scenario shows this situation. Each Block represents a set of fibres of equal length and the average lengths of each set is different. Individual fibres are not shown. The distribution of the centre point of each fibre within a bundle is assumed to be linear with respect to the crack. In other words, some fibres will be located with their centre point at the crack and others will have their centre point above or below the crack. The centre points of the fibres are assumed to be distributed equally on both sides of the crack.

Consider set 1 of "before exposure", the left most fibre is situated so that its bottom end below the crack is too short to remain in the matrix and will pull out during the test. Thus it does not contribute to maximum strength. The same applies to the rightmost fibre except that its top end will pull out.

In the centre is a block of fibres that all contribute to maximum strength and this is illustrated by the hatched area. The fibre at the leftmost edge of this block is just long enough below the crack to exert the full breaking load of that fibre while its upper end easily exceeds this length. The converse is true for the rightmost fibre in this block.

The hatched area of the set is proportional to the contribution of this group of fibres to the strength of the CFC. While the unhatched area is the contribution of this set to toughness.

Set 2 in "before exposure" is of shorter fibre length and while individual fibres are still at about the critical length, they are so distributed that only a small proportion contributes to maximum strength.

Set 3 in "before exposure" is composed of fibres that are all shorter than the critical length and therefore contribute only to toughness.

Now consider "after exposure" where all the fibres have been shortened due to "peeling". In this case the area of hatched proportion of set 1 has been reduced and has disappeared in set 2. The toughness has been decreased also because the fibres have all been decreased in length therefore their pull-out loads and lengths have been decreased.

Let us now assume that there has been chain breaking i.e., sets of fibres has been broken in their interior rather than on the end. Let us assume that sets 1and 2 in "before exposure" have been broken somewhere between the crack and the ½ critical length i.e. they have their chains broken. Then under this scenario it is clear that the DP would be rapidly decreased and not only that but that this would remove the fibres from contributing to maximum strength and result in reduction of the maximum strength. Toughness would also be reduced because of the reduction in the fibre lengths which would reduce the pull-out load that can be carried as well as the length over which the fibre would restrain breakage.

*Cellulose fibres and MoE*

Modulus of Elasticity is the slope of the stress/strain curve prior to crack formation and according to Hannant is proportional to the sum of the contributions of the matrix and the cellulose fibres weighted according to their respective volume fractions. Chain peeling or breakage would only have a small effect on the volume fraction of cellulose fibres until a major proportion of the fibres have been oxidised to Calcium Isosaccharinate irrespective of which mechanism has caused the change. Indeed, in the absence of other mechanisms, one would expect a slight increase in MoE due to carbonation and this is initially observed and is usually followed by a slow decline in MoE. It is likely that the decline in MoE with age is due to fatigue from the constant daily temperature cycling resulting in movement due to temperature and moisture changes.

*Cellulose Fibres and Strain to Failure*

In the protected situation there is little reduction in strain to failure while in the exposed situation the reduction is relatively rapid. This is because the cellulose fibre can contribute to strain to failure even as it pulls out from the matrix during the test. Thus, fibres that do not break because they have shortened still resist fracture of the test specimen but this increasingly reduces as the cellulose degrades. It is expected that CFC in normal service will not experience major changes in strain to failure in the early stages and will behave more like the sheltered specimens reported above.

# CONCLUSIONS

Field experience has shown that provided that it is properly installed and protected by a paint coating, Autoclaved Cellulose Fibre Cement performs well and is a durable long-lasting material suitable for many applications and exposure conditions. It has been found to meet the durability predictions of this author made when field experience was much more limited.

The performance of the CFC can be adequately explained by consideration of the properties of the components of the fibre cement, individually and in conjunction with each other.

1. Cellulose fibre is known to degrade slowly in alkaline conditions in the presence of oxygen from the air and but is protected from rotting by the same alkaline conditions. The complex structure of cellulose protects it from chain breaking and confines its degradation to the ends of the polymer chain thus degradation of the cellulose is a slow process.
2. The CFC matrix is subject to carbonation that reduces its porosity due to the formation of Calcium Carbonate from the Calcium present in the hydrated cement minerals. The matrix remains alkaline despite carbonation of the Calcium because of the presence of alkaline earth ions ($Na^+$ and $K^+$) that are present in the cement. Thus, the matrix provides protection of the cellulose against rotting.
3. The changing interaction of the cellulose fibres with the matrix during weathering is most important in determining the overall reaction of the composite material.

Accelerated testing of the CFC during development is normal practice and a rational way to predict long term behaviour. It can however be somewhat misleading and in this instance the accelerated testing resulted in behaviour that indicated a somewhat reduced life expectancy. This was due to

- much accelerated and intense fatigue from the exposure conditions than would be met in practice
- lack of protection due to deliberate intense exposure and absence of protective coatings that would normally be used in practice and
- a prediction of decay of cellulose which was promoted by delamination of the exposed edges of the specimens.

It is therefore necessary to be aware of the limitations of accelerated testing although it is not usually possible to determine in advance the relation of the accelerated regime to performance of the product in the field conditions.

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