

**MECHANISMS OF WEATHERING
OF
AUTOCLAVED CELLULOSE FIBRE CEMENT**

Autoclaved CFC Weathering; Assumptions and Reality

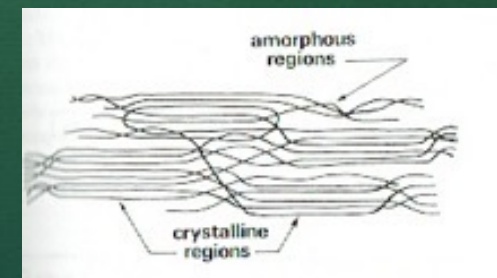
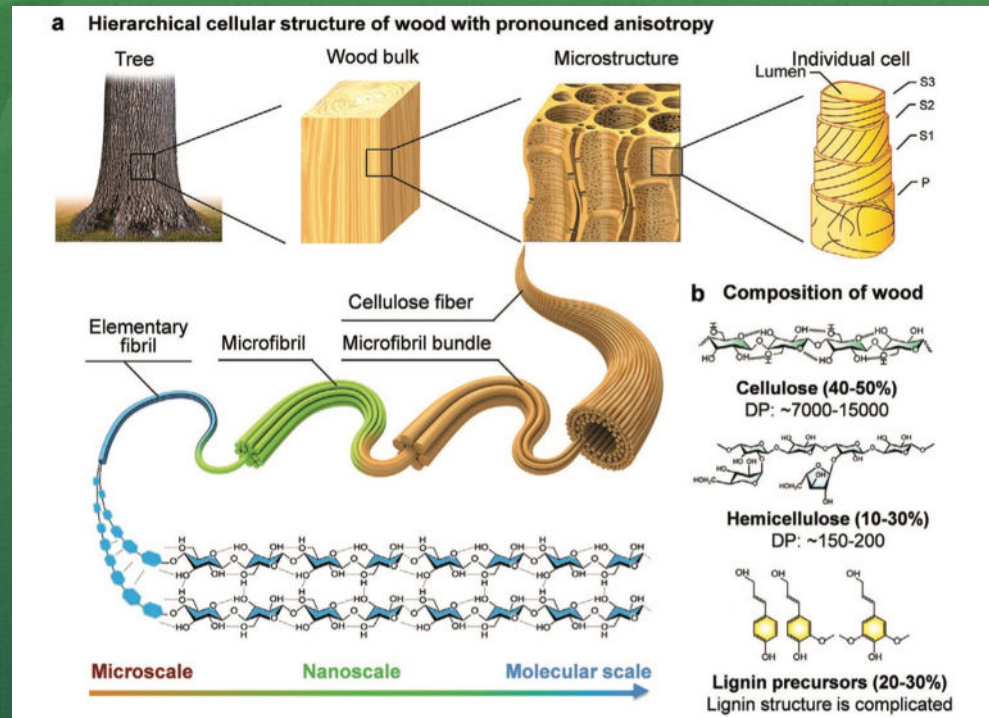
Assumption	Reality	Effect on CFC Strength	Effect on CFC Integrity	Comment
Cellulose rots within CFC	It does not rot	No effect	No Effect	Protected by alkalinity of matrix
Cellulose DP reduces	It does but only slowly	No effect until very high DP Loss	No Effect	DP reduced by alkaline oxidation
Cellulose % decreases	It does but only slowly	No effect until very high % Loss	No Effect	DP and % Cellulose decrease together
Matrix Carbonates	Matrix carbonates very slowly	Increases slightly	Porosity reduced: integrity improved	No chance of leaching
Matrix Carbonates and dries	Matrix shrinks on drying after carbonation & has higher moisture movement	No Effect	Could induce cracking on drying	Cracking depends on creep rate

Cellulose Structure

Hierarchy of structure

- Tree
- Wood
- Tubular Cells
- Cellulose Fibre ***
- Microfibril Bundles
- Microfibrils
- Elementary Fibrils
 - Amorphous regions
 - Crystalline Regions

*** Cellulose Fibre as used in CFC
DP is ~2000 as received



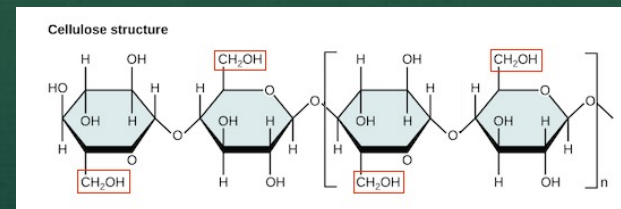
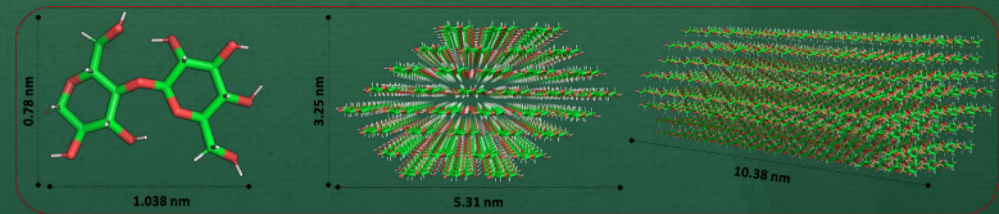
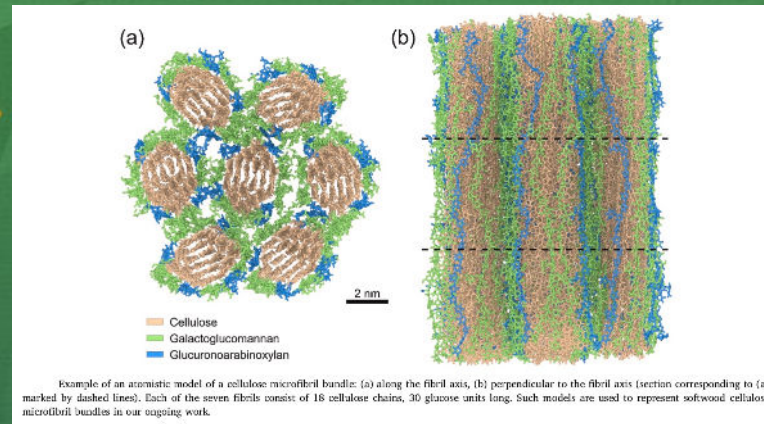
Cellulose Microstructure

Microfibrils are bundled together in groups

The number of individual microfibrils are in layers such that their cross-section is approximately round

The layers are bound together by hydrogen bonds

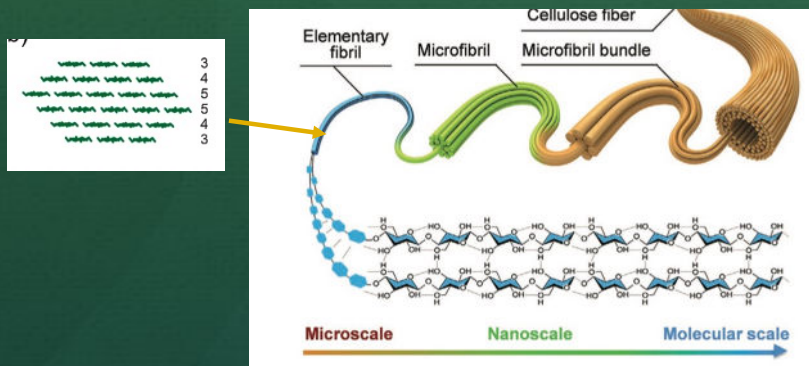
Cellulose elementary fibrils are long chains of cellobiose units (2 joined glucose molecules)



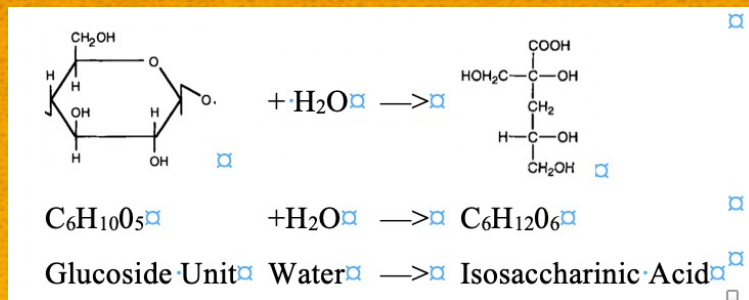
Cellulose Degradation

Two ways for Cellulose to Degrade

- Rotting by living organisms e.g. bacteria and fungi
- Protected by the constant alkalinity of the matrix
- Despite carbonation i.e. reaction of CO_2 with Ca^{2+} , the matrix remains alkaline because of the Na^+ and K^+ from the cement. Bacteria and fungi for the most part require acidic conditions for easy breakdown of cellulose and this means that the organisms must generate acids to reduce the pH of the matrix and this is not energetically feasible.
- De-polymerisation by chemical processes
- Alkalis in the cement matrix facilitate alkaline oxidation of the cellulose in the presence of air and even in the absence alkalis can cause alkaline hydrolysis or chain breaking
- These processes are resectively
 - Peeling
 - Chain breaking (microfibril breaking)
- Peeling is the removal of glucose molecules one by one from the end of elementary fibrils
- Chain breaking involves the simultaneous breaking of all the elementary fibrils in a microfibril (maybe 30 or so parallel chains)
- Peeling is about 1000 times faster than chain breaking so the predominant method of alkaline degradation of Cellulose is Peeling and is slow at room temperatures.
- Peeling is facilitated by cellulose refining which opens up the fibres particularly at their ends where the microfibrils are pulled out and their ends may be damaged



Peeling



Ca^{2+} stabilizes the peeling reaction by removing the released Glucoside unit as insoluble Calcium Isosaccharinate.

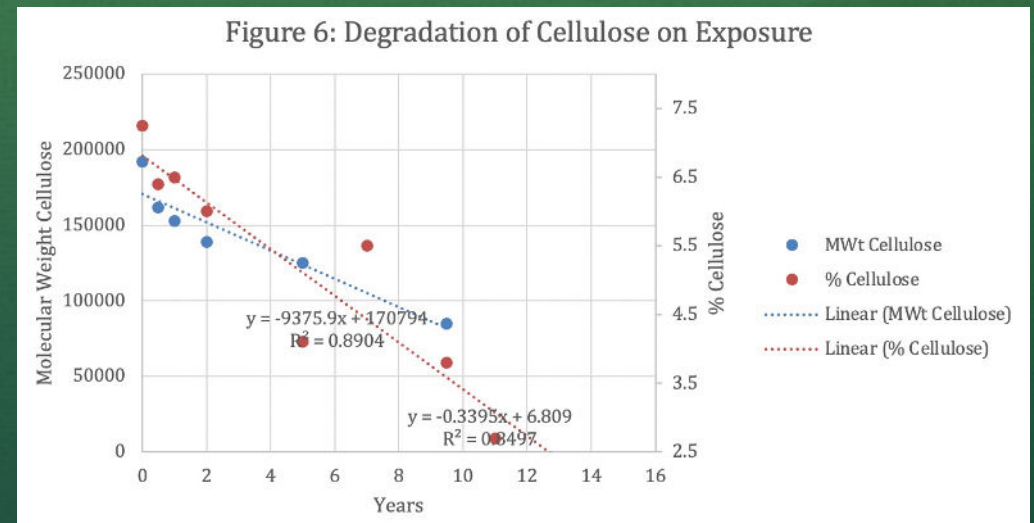
- each cellulose polymer chain has reducing end at one end and a complementary oxidising end at the other end.
- Peeling occurs at the reducing end of the chain and each peeling reaction removes one glucose unit from the end of the chain.
- The glucose ring molecule is broken open converting the ring 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.
- 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.

Cellulose Peeling in extreme exposure

Changes in Cellulose DP and % vs Exposure

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

Changes cellulose in time



Changes in Matrix

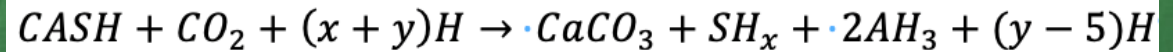
Carbonation or reaction with CO_2 in the presence of water is the main factor changing the matrix on exposure.

Ignoring the first 6 months exposure carbonation proceeds linearly with time at a slow rate.

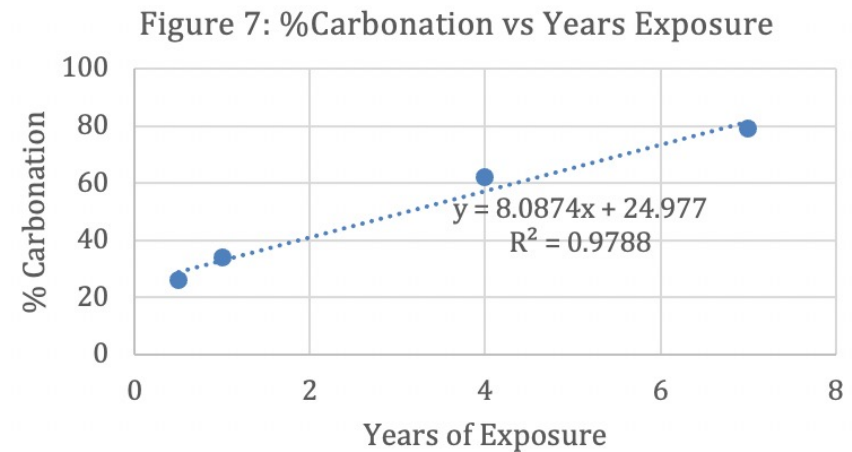
Porosity of the matrix diminishes with carbonation because one mole of $\text{Ca}(\text{OH})_2$ occupies less volume than one mole of CaCO_3 .

Reducing the matrix porosity, increases matrix strength and fibre/matrix bond

Matrix shrinks on drying after carbonation & has higher moisture movement



Where $\rightarrow \cdot C = \cdot \text{CaO}$, $\cdot S = \cdot \text{SiO}_2$, $\cdot A = \cdot \text{Al}_2\text{O}_3$ and $\cdot H = \cdot \text{H}_2\text{O}$

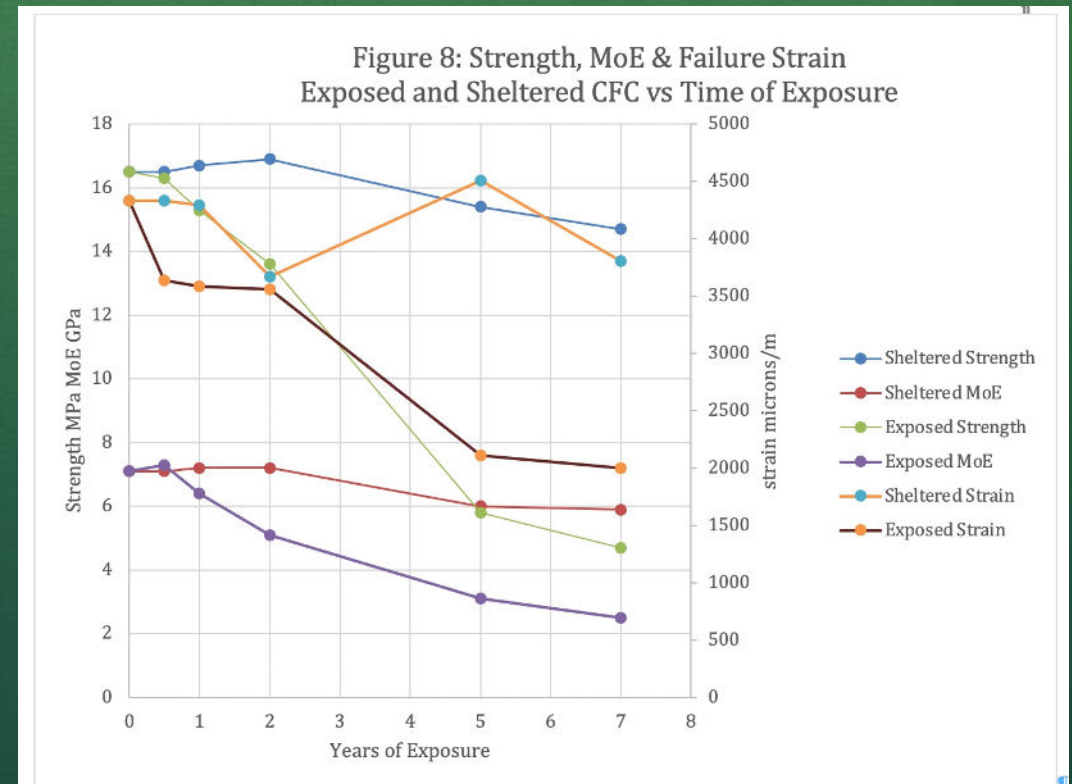


Overall Effect on CFC

extreme exposure

CFC Changes with Age

Age at Test	Sheltered	Exposed	Sheltered	Exposed	Sheltered	Exposed
Yrs	MoR MPa	MoR MPa	MoE GPa	MoE GPa	Failure Strain	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



Overall Effect on CFC

Normal Exposure

Comparison of some exposed CFC
with newly made CFC

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

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

Why no cracking with Carbonation?

Effect of Carbonation

- 100% of the CaO present in the CFC is susceptible to Carbonation
- 100% Carbonation
 - Induces irreversible moisture movement equal to the original moisture movement
 - Doubles the reversible moisture
- The effect of carbonation in one cycle of wetting and drying is proportional to the %age of carbonation occurring in that cycle
- Roughly one cycle of carbonation with wetting and drying occurs daily assuming
 - Carbonation occurs mainly during the night
 - Drying occurs during the warmer day

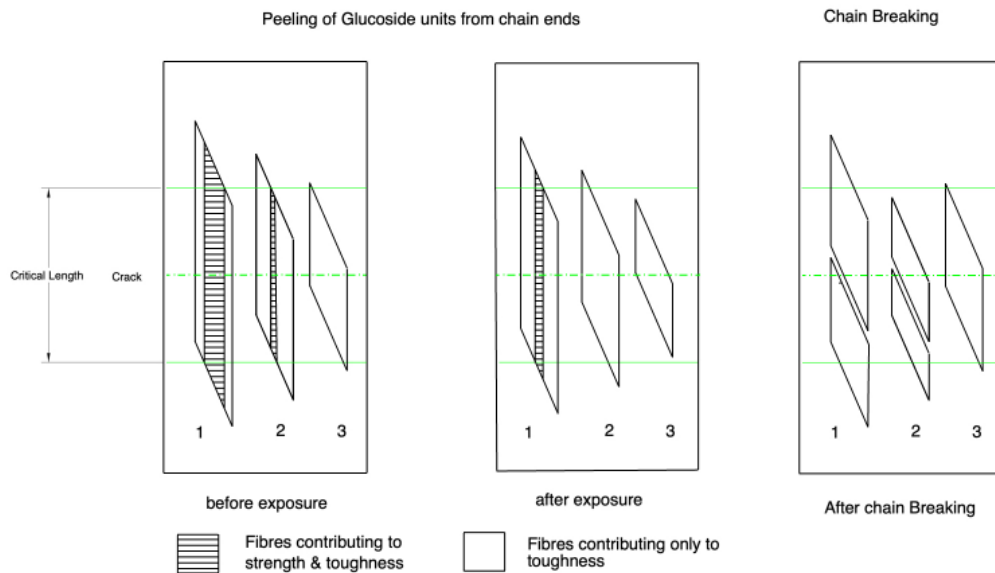
Creep Test and Results

- Load approximately 7MPa
- Creep of specimens ~ 1.6 mm/m/day
- Irreversible shrinkage $\sim 0.3-0.5$ mm/m
- Reversible Moisture Movement only about 25% of the potential MM due to partial drying say 0.5 mm/m
- Potential creep is greater than the combined irreversible shrinkage due to carbonation and the reversible moisture movement
- Also there will be some thermal expansion due to warming during drying
- **RESULT NO CRACKING**



Cellulose Degradation and CFC Strength

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



Each parallelogram represents a bunch of equal length fibres whose centres are linearly distributed across a crack in the CFC

- From critical fibre length theory
 - only a proportion of fibres contribute to strength
 - For a tensile strength of say 10MPa this is about 30-40% of the fibres.
- During the same time period of alkaline oxidation every individual fibre will be reduced in length by the same amount
- Only those fibres that are reduced in length to less than the critical length will no longer contribute to the strength
- Degree of polymerisation is a measure of the average length of cellulose chains
- DP can therefore vary significantly with only a small effect on CFC strength, hence the slow decline of strength with exposure and DP

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.



Thanks for listening