

# “The effect of aluminous additives on the properties of Autoclaved Cellulose Fibre Cement”

By

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## **Abstract**

The earliest versions of autoclaved cellulose fibre cement were susceptible to cracking and failure in service. It was subsequently found that this was due to carbonation of the matrix and irreversible shrinkage and enhanced moisture movement that followed the carbonation. This was surprising because all of the properties of the newly developed cellulose fibre cement were better or similar to the autoclaved cellulose asbestos cement that they had just replaced. While carbonation had not previously been recognised it is certain that it occurred in asbestos cement but possibly did not lead to failure or cracking of the product and also the mechanism could have been different.

However once carbonation had been recognized as a possible cause of the problem, a literature search revealed that moisture movement had been reduced in autoclaved lime silica bricks by the introduction of aluminous materials. It was subsequently found that the addition of materials to autoclaved cellulose fibre cement such as Alumina Trihydrate, Bauxite or Metakaolin reduced its susceptibility to carbonation, softened it and reduced its moisture movement. This discovery has led to the development of the fibre cement formulations that are used today and have a history of successful use for more than 25 years.

This paper discusses the possible reasons why the carbonation in asbestos cement is different to the newly developed replacement products. The arguments are backed by published literature with models describing the reaction taking place during autoclaving of cement and silica containing aluminous additives.

**Keywords:** Autoclave, curing, fibre cement, mechanisms, models, chemistry, carbonation, durability

# 1 Development of Autoclaved Cellulose Fibre Cement from Autoclaved Asbestos Cement<sup>1</sup>

Asbestos cement was invented in the 1890's by Ludwig Hatschek who mixed asbestos fibre directly with Portland cement using a modification of the vat/cylinder paper machine. The mix was essentially an air cured formulation.

Autoclaved asbestos fibre cement (AAFC) was developed in Australia by the James Hardie Company<sup>i</sup> in the 1930's for the manufacture of asbestos cement pipes. Air cured asbestos cement pipe is particularly susceptible to Sulphate attack because a pipe trench forms a naturally draining cavity along which ground water can travel. If this groundwater contains sulphates then the pipe will suffer from sulphate attack and eventually will fail in service. It was found that autoclaved asbestos cement is resistant to sulphate attack and the James Hardie Company rapidly transformed its pipe manufacturing to the autoclave process to avoid this problem.

Where there is available cheap and abundant silica sand, autoclaved formulations have a considerable cost advantage because at least 50% of the costly cement is replaced by the cheaper sand despite the cost of fuel for the boilers and the additional process equipment required. Furthermore, because the curing process is essentially complete after about 2 days the manufacturing process is much more rapid and stock levels of product can be kept lower. There is therefore an incentive for the asbestos cement manufacturer to use this process for all asbestos cement products and the autoclave curing method rapidly became the standard method of manufacture for all asbestos cement products in Australia where there is available cheap and abundant silica sand.

Whether autoclaved or air cured, asbestos cement is a brittle material and special methods must be used to cut it and fix it into buildings. It has limited flexibility and is easily broken and cannot be nailed with conventional pointed nails used for wood. Indeed it is necessary to use nails with square ends that punch out a cylinder of asbestos cement into the wooden frame on which they are to be fixed. These problems are exacerbated with aged autoclaved asbestos cement because although its curing is complete, it carbonates which densifies it and increases the matrix fibre bond making it more brittle and harder to work without damaging it. AAFC is also a fairly dense material.

The problems described above were alleviated to a large extent by the development of autoclaved cellulose asbestos cement (ACAC) which incorporated a proportion of unrefined cellulose pulp into the mix. This

- increases the product's porosity thus reducing its density and material usage,
- makes it more flexible and less likely to be damaged during fixing,
- makes it nailable with conventional nails because of the introduction of pores which collapse when the nail is driven through and
- extends the period of easy use after manufacture because although the material still carbonates and becomes more brittle with age, the relatively young material starts with a higher flexibility.

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<sup>1</sup> It should be pointed out that this paper refers to asbestos cement which is no longer manufactured in Australia, most European Countries, USA and South Africa. It is however still manufactured in many other countries today.

The manufacture of Asbestos cement relies on the ability of asbestos fibres to form a filter layer and this is achieved with asbestos because of the length and fineness of the individual asbestos fibres. Some processing of the raw asbestos fibres was always undertaken in part to disperse them in water and in part to separate the fibres from the bundles in which they occur naturally. Dispersement and processing was usually carried out in a Kollergang mill or similar equipment. With the removal of the asbestos fibre the role of the filter fibre was taken up by the cellulose which has to be refined to enable it to filter the cement and to reinforce the composite.<sup>2ii</sup> Thus the final stage of development of autoclaved cellulose cement involved the removal of the asbestos and its replacement with refined cellulose.

## 1.1 Typical formulations of Fibre Cement Products

Table 1 shows typical formulations of various autoclaved fibre cement products

Table 1	Percentage of Material in Product			
Material	Air cured Asbestos Cement	Autoclaved Asbestos Cement	Autoclaved Asbestos Cellulose Cement	Original Autoclaved Cellulose Cement <sup>3</sup>
Portland Cement	92	46	42	46
Asbestos Fibre	8	8	8	
Cellulose Fibre	0	0	8	0
Refined Cellulose Fibre	0	0	0	8
Silica Flour	0	46	42	46
Total Dry Material	100	100	100	100

Typically the materials had the following specifications.

Ordinary Portland cement was usually about 300m<sup>2</sup>/kg a relatively coarse grind by today's standards.

Asbestos fibre was originally a mixture of different types and grades. The length of the fibres tended to be reduced to cheapen the blends but fibres of 4mm or more in length were still being used in the final days of the production of asbestos containing products in Australia.

Cellulose fibre was usually Kraft Softwood Pulp which was not refined for autoclaved asbestos cellulose products because it was added only to reduce density and to soften the product.

The same cellulose fibre was used in the early autoclaved cellulose cement but it was refined to develop its capacity to form films and to reinforce the cement matrix. The specification for the chemical properties of the cellulose became more stringent because it was found to interfere with the autoclave reaction and this was deleterious to the durability and the properties of the final product.

Silica flour is relatively pure silica sand (usually greater than 95% silica) that has been ground to about the same fineness as the cement. No differences were made to the fineness in the transition to autoclaved cellulose cement.

<sup>2</sup> Details of the manufacture of fibre reinforced cements and fibre cement film formation may be found in reference 2.

<sup>3</sup> Developed in 1980

## 1.2 Comparison of Autoclaved Asbestos/Cellulose Cement with Original Autoclaved Cellulose Cement developed in 1980

Table 2 shows typical properties of autoclaved Asbestos/Cellulose Cement with the original Autoclaved Cellulose Cement.

Property	AACFC	ACFC
Direct Tensile Strength	18 MPa	12 MPa
Young's Modulus of Elasticity	6 GPa	10 GPa
Strain to Failure	3 mm/m	1 mm/m
Energy at Failure	20 kJ/m <sup>3</sup>	0.5 kJ/m <sup>3</sup>
Moisture Movement mm/m	2.8-3.1 mm/m	2.9-3.3 mm/m

Flexural strength of ACFC was about 15% less than the AACFC and was thought to be adequate.

Before determining their mechanical properties the materials were equilibrated to atmosphere at a temperature of 23°C and 65% RH for around 7 days. After equilibration under these conditions the materials contain around 11% moisture relative to their oven dry weight.

The mechanical properties were determined in direct tension with attached strain gauges.

Strain to failure is the tensile strain to failure. Energy at failure is obtained by integrating the stress/strain curve to failure and dividing by the volume of test specimen.<sup>4</sup>

Moisture movement is determined by saturating the specimens in water for 24 hours, determining their length and then determining the difference in their length after they have been dried at 105°C for 24 hours. The moisture movement is the difference in length between the saturated and oven dried length divided by the oven dried length and expressed as mm per metre.

There are other observations not reported in Table 2 which are relevant to the performance. It has also been observed that AACFC creeps significantly more easily than ACFC.

At the time of introduction of the original formulation of ACFC, AACFC had been in satisfactory service for approximately 20 years. However relatively little was known about the factors that influenced its performance and developers of the new formulations concentrated on matching as closely as possible strength and moisture movement.

### **Field Observations**

Within 9 months of the release of the new product massive field failures were experienced particularly in the drier parts of Australia. Failures were much less in coastal and more humid regions but there were still some failures reported but probably an order of magnitude less than in the dry regions.

Failures were spectacular involving sheets cracking with what can only be described as mud cracks on a major scale. Often sheets were cracked around their periphery about 200-300 mm from the edge. They were also cracked perpendicular to the peripheral crack to the corners of edges of the sheet. After cracking the sheets warped, being dished so that the inside edge of the peripheral crack was at the highest point.

<sup>4</sup> This is somewhat unusual to express the energy at failure this way but was the standard way for reporting this parameter

Clearly the sheets had cracked and warped due to shrinkage but the magnitude of the cracking and similarity of the drying shrinkage of the new product to the former product did not offer any immediate explanation. At the time, the tensile properties of the sheet described in Table 2 were unknown and while with hindsight an explanation is fairly obvious from this information there was still a mystery as why sheets should fail so spectacularly and in such a short time.

For example it was known that although the moisture movement of the sheets was marginally more in the early ACFC than the formerly made AACFC, the flexural strains to failure were less but not by much. The strengths of the ACFC were certainly poorer than the AACFC but it was felt that its strength was adequate and was not the problem. Exposure conditions were certainly no different yet the failures indicated significantly greater shrinkage in the newer material.

A source of the failure was then sought and it was surmised that this may be due to carbonation. It was however thought at the time that since the matrix materials were not greatly different it would be difficult to imagine that this was the source of the problem.

An experiment to check this out was then undertaken as follows. A light metal frame was made and 1 sheet of the new material was rigidly fixed to each of its sides. The sheets were then damped with water, the whole panel enclosed in a tarpaulin. CO<sub>2</sub> was then injected into the interior of the frame.

It was observed that within a few minutes the surface of the sheet became warm and water vapour started to condense inside the tarpaulin. After a little more time the surface of the sheet became hot and wet and water started to run out of the tarpaulin. Within an hour of commencing the experiment the sheets had cracked and warped exhibiting the same behaviour as had been observed in the field i.e. a peripheral crack with cracks radiating to the corners or a longitudinal split parallel to the long direction of the sheet i.e. parallel to the machine direction.

Clearly the problem was in part due to carbonation of the matrix and the shrinkage that this induced. The question as to why this did not happen with the AACFC was still not immediately obvious but examination of Table 2 and the reported observations reveals the critical differences.

The moisture movement is about the same therefore the shrinkage in the field would be about the same. Subsequent investigations showed that assuming that the sheets had come to equilibrium with the atmosphere and were in this condition when they were fixed, normal movement in the field due to moisture absorption/desorption would be about 1/3 of the maximum laboratory measured moisture movement between the oven dry and saturated conditions. Comparing this to the tensile strain to failure shows that ACFC has a failure strain that is close to the expected field moisture movement thus is very likely to fail in service. By comparison AACFC has a tensile strain to failure that comfortably exceeds the expected field movement. However the expected number of failures of ACFC is not as great as was observed, so some additional explanation must be sought.

This is found in two factors. Carbonation induces irreversible shrinkage in the matrix of both varieties of fibre cement so one would expect that carbonation combined with the normal moisture movement would induce a total shrinkage greater than the strain to failure of the ACFC. Carbonation of course will have the same effect on AACFC so why does it not fail given that the magnitude of the total shrinkage would be greater than its strain to failure. The explanation for this is found in the creep capacity of the AACFC which is much greater than for ACFC and means that AACFC is more able to stress-relieve itself, if it is subject to a combination of carbonation and moisture shrinkage. This is sufficient to allow it to stretch without obvious cracking and it therefore performs well in field service.

This raises the question of why AACFC performs so much better than its successor. This is not a matter of greater strength and is explained by several factors as follows.

### *Properties of asbestos fibres*

The length of asbestos fibres is also important and even in the latter stages of AACFC production when shorter and poorer grade fibres were used for reasons of economy they tended to be longer than the cellulose fibres which replaced them. This means that after the matrix cracks, the longer asbestos fibres can pull out to a greater extent and the composite strain to failure is greater. It is also a fact that asbestos fibres very rarely occur in the composite as single fibres. It is more correct to say that fibre bundles are present in asbestos cement composites. The bond between the individual fibres is less than that of the fibre cement interface. This results in a fibre/fibre separation during failure resulting in greater strain to failure.

Finally asbestos fibres are stiff, straight and smooth. Thus they are relatively easier to pull out than cellulose and AACFC creeps under load much easier than ACFC.

Figure 1 compares asbestos and cellulose fibres where it will be seen that the cellulose fibres are not only irregular in shape but are soft and conform to the surfaces beneath them.



Cellulose Fibres



Chrysotile Asbestos fibres

Figure 1: Comparison of Cellulose and Asbestos fibres

One may ask why does the cellulose in AACFC not interfere with its creep capacity. This occurs because the Cellulose in AACFC is not refined and does not bond very well to the cementitious matrix. Thus they contribute little to the composite properties and do little to reinforce it. Their presence does however increase the composite's porosity which softens it and makes it easier to deform under load. Thus the combination of stiff asbestos fibres with an open porous structure means that its creep capacity is high.

We may conclude that the difference in performance of the two materials is due to the combination of properties of their respective components and mainly the contrasting properties of their particular reinforcing fibres. The use of asbestos fibre which produces a composite of high strain to failure and high creep capacity allowed its' composite to withstand the shrinkage induced by carbonation of the cementitious matrix.

### 1.3 Further development of Autoclaved Cellulose Cement - Addition of Aluminous Additives

Once it was found that carbonation of the matrix was a major problem and that the ACFC lacked ductility and creep capability means were sought to improve these properties. It was also obvious that although the moisture movement of the ACFC was roughly equivalent to that of the AACFC, that a reduction in moisture movement would also be desirable. A literature survey<sup>iii</sup> indicated that the addition of alumina containing admixtures to autoclaved lime silica brick reduced the moisture movement significantly and a range of aluminous admixtures was tried which included Kaolin, Alumina Trihydrate, and Bauxite. The initial research also included other minerals such as Limestone, Dolomite and various Iron Oxides but these were found to be no better than inert fillers and since they often had deleterious effects on the mechanical properties of the ACFC work on them ceased.

The effectiveness of these admixtures was found to be dependent on their chemical composition and their proportion in the matrix of the ACFC. Table 3 on the following page shows some of the results of inclusion of different admixtures with the results from early experimentation in Series 1 to 8 and the results of mature formulations in series 9 to 13. While the results should not be taken as complete some trends can be discerned.

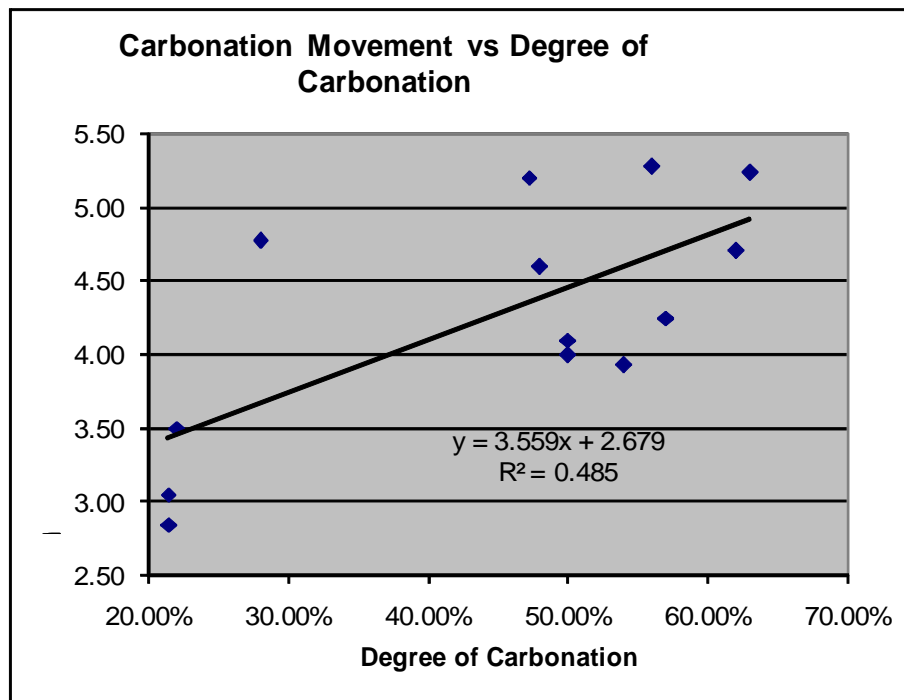


Figure 2: General Relationship between Degree of Carbonation and Carbonation Movement

If all of the results are considered together there is a weak relationship between Carbonation Movement and Degree of Carbonation as shown in Figure 2.

The weakness of the relationship is due to the fact that the results reported include different cement/silica ratios and different proportions of aluminous admixtures. This is exemplified best by the three points around 20% Carbonation degree which are from Series 11,12 & 13. These show that at the same low cement/silica ratio, inhibition of carbonation movement is greater at higher levels of aluminous admixture.

The type of aluminous admixture also affects the moisture movement of the resulting ACFC. Thus at the same cement silica ratio, Alumina Trihydrate is more effective than a mixture of Kaolin and Alumina Trihydrate as is shown by Series 10 and 12 which both have 4% of the Aluminous admixture.

Iron Oxide is shown as an example of other potential admixtures. It may be seen that far from improving the performance of the ACFC, it actually makes it worse.

Moisture movements and carbonation movements are all reduced with increasing amount of the aluminous admixture. This is exemplified in Series 1,2 &3 and with series 4 through 8.

It is also evident that the increasing the silica content and equivalently reducing the cement content also reduces the moisture and carbonation movements.

As seen in Series 1 2 and 3 increasing the addition of Alumina Trihydrate has the effect of reducing the rate of carbonation of specimens exposed to equivalent exposure conditions.

There are significant changes to the mechanical properties as the aluminous admixtures are increased. Thus increasing the admixture content at a given cement/silica ratio, generally increases flexural strains to failure, and decreases flexural strengths and flexural moduli of elasticity. The tensile properties are more mixed and no real trend can be discerned although there seems to be a real increase in the tensile strain to failure with reduction in cement/silica ratio.

Furthermore although not reported here propensity to creep also increases with increasing admixture content.

## **1.4 Discussion of Results**

**Moisture and Carbonation Movement** – reduction of the cement content and its replacement with silica reduces the amount of Calcium Silicate Hydrate (CSH) binding material present in the ACFC after autoclaving and replaces it with Silica. <sup>5</sup> Silica has no intercalated water as does the CSH and thus does not lose or take up water with humidity changes. Indeed because it is a rigid stiff material, it acts to restrain the binding material when this loses or takes up water in response to humidity changes or carbonation.

Furthermore, because the amount of moisture reactive binding material is reduced, there is less potential movement of the composite as a whole. Thus the effect of reducing the cement content is to reduce both moisture and carbonation movement.

The addition of aluminous admixtures also affects the rate of carbonation which slows as the admixture amount increases. This suggests that the inclusion of octahedral Al replacing octahedral Si in the matrix of autoclaved CSH (becoming C(AS)H) alters its chemistry making it less reactive to the  $\text{HCO}_3^-$  ions. It is possible that this is due to distortions within the crystal lattice of the CSH due to the necessity to rebalance the electronic charges ( $\text{Al}^{3+}$  compared to  $\text{Si}^{4+}$ ) which bind its water more tightly and restrict the entry of the reactive bicarbonate ions.

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<sup>5</sup> See the next section for detailed discussion of the autoclave reactions.



Table 3 Some Typical Properties of Formulations containing Aluminous Additives

	Series 1	Series 2	Series 3	Series 4	Series 5	Series 6	Series 7	Series 8	Series 9	Series 10	Series 11	Series 12	Series 13
Formulation													
Cement	50.60	47.90	45.10	49.20	48.50	47.85	46.50	47.85	35.20	26.10	27.00	26.85	26.70
Silica	41.40	39.10	36.90	40.30	39.75	39.15	38.00	39.15	52.80	60.90	63.00	62.65	62.30
Cement/(Cement+ Silica)	55.0%	55.1%	55.0%	55.0%	55.0%	55.0%	55.0%	55.0%	40.0%	30.0%	30.0%	30.0%	30.0%
Cellulose	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	7.00	7.00	7.00
ATH		5.00	8.00	2.00	3.00	4.00	6.00	2.00	4.00	4.00	1.50	1.75	2.00
Iron Oxide								1.00					
Kaolin											1.50	1.75	2.00
Bentonite			2.00	0.50	0.75	1.00	1.50	2.00		1.00			
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Moisture Movement mm/m	2.65	2.13	1.77						2.10	1.40	1.94	1.90	1.63
Carbonation Movement mm/m	5.24	4.60	4.77	4.25	5.28	3.93	4.10	4.71	5.20	4.00	3.50	3.05	2.85
Concurrent Carbonation Movement mm/m	2.59	2.47	3.00						3.10	2.60	1.56	1.15	1.22
Degree Carbonation	63.0%	48.0%	28.0%	57.0%	56.0%	54.0%	50.0%	62.0%	47.2%	50.0%	22.0%	21.4%	21.5%
Mechanical Properties at Equilibrium													
MoR MPa	23.70	22.60	20.95						22.70	10.00	13.78	13.54	13.42
MoE GPa	9.65	8.53	9.01						6.50	7.00	8.55	8.46	8.37
Flexural Strain to Failure m/m*10 <sup>-6</sup>	3492	4666	6541						8780	5850			
Tensile Strength MPa	13.3			13.8	12	11.7	11.8	12.4	9.5				
Youngs Modulus GPa	10.3			10.6	9.6	10.3	10.8	10	9.5				
Tensile Strain to Failure m/m*10 <sup>-6</sup>	1480			1340	1640	1190	1180	1320	3050				

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<sup>6</sup> Degree of carbonation is the proportion of the CaO present in the cement present in the formulation converted to CaCO<sub>3</sub> by reaction with CO<sub>2</sub> and water from the environment. It is found in practice that all of the CaO can be so converted which equates to 100% carbonation.

Moisture movement is the movement of the specimens in respect to moisture content while protected from carbonation. Carbonation movement is the movement due to carbonation and moisture change while the concurrent carbonation movement is the difference between the two i.e. the movement due to carbonation alone.

The effect of the Al on the carbonation movement is relatively small because carbonation movement is a combination of irreversible shrinkage due to the change of volume in passing from CSH to  $\text{CaCO}_3$  and the production of Silica Gel (hydrated silica) which is moisture unstable in its own right. If as may be surmised moisture movement after carbonation is due only to this Hydrated Silica ( $\text{SH}_x$ ) then the amount of  $\text{SH}_x$  produced by carbonation will be much the same in all of the formulations because the total amount of Silica replaced by Al is small and this is what we see in series 1 to 3.<sup>7</sup>

**Mechanical Properties** – Reduction in flexural strength and MoE of ACFC containing aluminous admixtures, with increasing strain to failure suggest that simultaneous weakening of the matrix and the matrix fibre bond strength. The reduction in the interaction of the matrix and the fibres means that longer fibres are more likely to pull out than break thus increasing the strain to failure and reducing the maximum strength.

Weakening of the matrix is also indicated by the reduction of the MoE which is normally correlated with matrix strength. Weakening of the matrix is most likely due to inbuilt strain in the crystal structure of the C(AS)H due to the replacement of Si atoms by Al ions of different electronic charge. The greater the degree of replacement the more is the inbuilt strain energy and the greater will be the reduction in inherent strength.

This is shown in series 11 to 13 where increasing amounts of aluminous admixture reduce the strength and MoR proportionately. A further effect is found when comparing Series 10 and 13 each with 4% of admixture. Here series 13 has 4% of 50:50 Kaolin:Alumina Trihydrate compared to 4% of 100% ATH in series 10. Series 10 shows significantly lower MoR and MoE which is a reflection of the greater amount of available Al in the Series 10 compared to the Series 13 mix<sup>8</sup>. There is not only less Al in total in pure Kaolin than in ATH but it is combined with Silica and is although in the correct coordination is not readily available for reaction with the cement and the other ingredients.

It is important to note that although ACFC becomes weaker and softer with the addition of aluminous admixtures (of the active kind), that these latter formulations have sufficient strength to withstand the stresses induced during fixing. It is also most important to note except in extreme circumstances such as in a violent storm, the stresses induced in the ACFC in service are much less than those to which it will be subjected during fixing so there is no major issue with their strength.

## 1.5 Conclusion

ACFC of the formulations shown in Series 9 and 10 are of the most typical external and internal of autoclaved formulations and have proven themselves over more than 25 years of service having had few problems with field failures. It can therefore be said that the additions of aluminous admixtures to ACFC and reduction in cement content with its substitution with silica are beneficial despite the loss of strength that is a consequence. The benefit of these changes and improvement in durability is due to the reduction in moisture movement coupled with an increase in strain to failure and improved capacity to creep.

## 2 Chemistry of Autoclaved Cement Silica Mixes

We now consider the chemistry of the autoclave reactions and the stability of the resulting products of that reaction. We will first consider the reactions that occur in mixtures of cement and silica and only and those occurring with partial substitution of the cement and silica by reactive aluminous admixtures. We will also consider what accounts for reactivity in aluminous admixtures.

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<sup>7</sup> Carbonation reactions may be the subject of another paper.

<sup>8</sup> Kaolin although not reported here has little effect on the mechanical properties of ACFC and being moisture sensitive itself increases its moisture movement.

## 2.1 Without Aluminous Additives

We refer here to Taylor<sup>iv</sup> for most of what follows in this section. It should be noted however that Taylor reports mainly on the work by Menzel and Kalousek on this subject who did not include cellulose in their work. There is no doubt that cellulose has an effect on the autoclaving reactions and most likely the products of those reactions however, the effect of cellulose and its associated wood derived materials has not been systematically evaluated.

Autoclaving in this context is the curing of the ACFC at temperatures above 150°C for extended periods usually more than 5 or 6 hours. As we have seen above ACFC contains silica which is finely ground which is necessary to ensure its reactivity with cement.

Menzel (reported in iv and whose results are shown in Figure 3 below), found that the ratio of cement to silica is important to the development of mechanical properties in any autoclaved product. He found an initial decline in compressive strength with the introduction of silica followed by an increase and final decline. He also found that the optimum cement:silica ratio for maximum strength is 65:35 which corresponds roughly to a CaO:SiO<sub>2</sub> of 5:6 for cement containing 65% CaO and 20% SiO<sub>2</sub>.

Taylor states that if Portland cement is cured in the absence of reactive silica then the fundamental chemistry of the products changes from a variety of Calcium Silicate Hydrate to an unrelated crystalline  $\alpha$ -C<sub>2</sub>S hydrate.  $\alpha$ -C<sub>2</sub>S hydrate crystallises in a tabular form and the resulting product is weak. This is probably because of the shape of these tabular crystals and their lack of contact with each other compared to the contact that is possible with the interlocking needle like crystals of other forms of CSH.

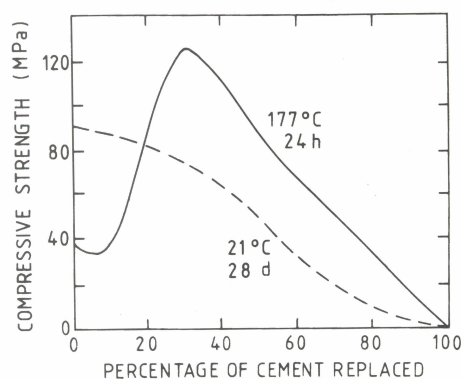


Figure 3: Compressive strength of Autoclaved Cement Silica Mixes from Menzel reported in and reproduced from Taylor ref 4 page 342

Menzel's results above demonstrate that the initial decline is due to the formation of a maximum amount of  $\alpha$ -C<sub>2</sub>S hydrate at around 10% Silica. Beyond this point the increase is due to the removal of Lime liberated from the cement by reaction with the silica and the formation of other types of CSH. The greatest strength corresponds to a maximum of the new type of high temperature CSH (htCSH) and the final decline is the result of the inclusion of larger and larger amounts of unreacted Silica which does not add to strength.

The optimum htCSH with an approximate composition of C<sub>6</sub>S<sub>5</sub>H crystallises to give 1.1nm Tobermorite. Taylor surmises that high degrees of crystallinity of Tobermorite may be deleterious to strength because extending the time of autoclaving, which is expected to increase the degree of crystallisation, reduces strength. However it is certain that extended autoclaving reduces shrinkage and recent studies in ACFC indicate that shrinkage is minimised with proper autoclaving and this is associated with obtaining well crystallised Tobermorite. It has been found that low shrinkage is obtained with an estimated 15% of crystalline Tobermorite<sup>v</sup>.

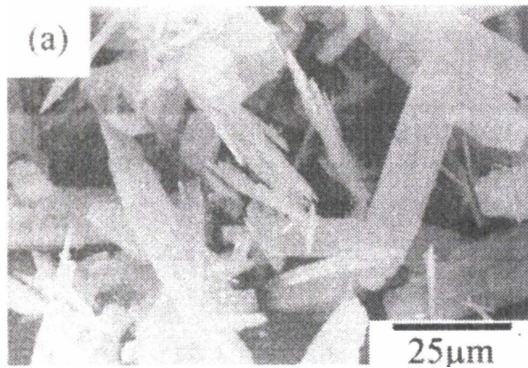


Figure 4:  $\alpha$ -C<sub>2</sub>S hydrate<sup>vi</sup>

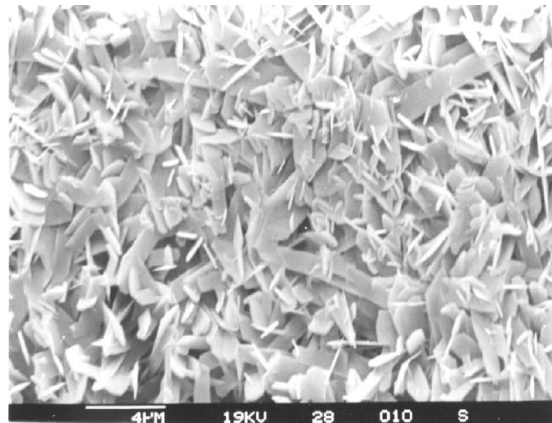


Figure 5: Tobermorite

Comparison of the structure of  $\alpha$ -C<sub>2</sub>S hydrate with Tobermorite shows the difference in morphology of the 2 materials. The  $\alpha$ -C<sub>2</sub>S hydrate is considerably coarser than the Tobermorite and while the porosity of the two structures is probably the same there is a considerable difference in the proportion of contact between individual crystals. It is suggested that the tobermorite structure is stronger because of the greater number of bonds between the individual crystals that hold the structure together.

If the time for crystallisation of Tobermorite is extended then it is likely that individual crystals will increase in size. However, the total number of crystals will not increase because crystalline Tobermorite will form at the expense of its amorphous predecessor and further crystallisation is most likely on the surface of existing crystalline material. Thus the total number of contacts between crystals will decrease and the strength will decline with extended autoclaving.

However, crystalline Tobermorite is known to have lower moisture movement than its amorphous predecessor which is probably because the amorphous material is more easily able to absorb or give up water because of its irregular structure. Thus it is beneficial to increase the degree of crystallinity of the Tobermorite in ACFC to minimise its shrinkage. However as we have seen above, conversion of the amorphous to crystalline htCSH is likely to reduce the strength of the final product. Thus there appears to be some optimum degree of crystallinity to achieve minimum shrinkage with maximum strength.

It is speculated that the amorphous htCSH may contribute to strength because of its ability to conform to the surface of Tobermorite crystals<sup>9</sup>, thus binding them together more tightly than would be possible due to face to face contact by the crystals themselves. While the strength of crystalline materials is usually greater than that of their amorphous equivalents because of the orientation of their internal bonds, the strength of their amorphous equivalents may not be much less. Thus the presence of amorphous material is necessary for the development of adequate strength and the matrix of the final product (ACFC) may be considered to be a composite of Tobermorite crystals embedded in an amorphous htCSH binder. Indeed unreacted silica grains and cellulose fibres are also embedded in this matrix along with up to 50% of void space. The whole is also structured due to its mode of formation on the Hatschek machine – a complex structure indeed!

The response of the cellulose to the autoclave is another factor that must be considered in the manufacture of ACFC. Cellulose can be damaged during autoclaving if this process is continued for too long. It is usual to use unbleached Cellulose in ACFC because it contains residual Lignin and hemicellulose as well as pure cellulose fibres. While all of these materials are attacked by alkalis

<sup>9</sup> The amorphous CSH will also bind better to the other materials present for much the same reason – tighter conformity and more intimate contact with their surfaces allowing for better bonding.

from the cement their rates of reaction with the alkalis are different and Lignin is preferentially dissolved compared to Hemicellulose which in turn is more reactive than the Cellulose. Thus the Lignin and the hemicellulose act to protect the Cellulose in the early stages. However if autoclaving is continued for too long the cellulose will be attacked and the properties of the ACFC are adversely affected.

Similarly the autoclaving temperature affects the rate at which all of these autoclave reactions take place. While there is a minimum temperature below which no reaction between the cement and the silica takes place one cannot increase the temperature indefinitely despite the fact that the reaction rates would increase. The rate of damage to the fibres will also be increased at higher temperatures and the products of the reaction between the cement and the silica are also different. Thus there is a small window of reaction conditions that produce optimum ACFC and typically autoclaving of ACFC is undertaken within the following ranges.

Temperature	170-185°C
Pressure	9-10 Atmospheres
Time to Temperature	2-6 hours
Time at Temperature	8-12 hours
Time to reduce pressure	2 hours

It has been found desirable to pre-cure the product for a minimum of 12 hours at room temperature or commonly at 70 to 80°C before introducing the product to the autoclave. It is found that failing to do this often results in poor strength ACFC. It is surmised that low final strength after autoclaving may be due to a combination of insufficient green strength of the precured product and insufficient free Lime (CH) to react with the free silica in the partially cured product. Insufficient strength in the unautoclaved product means that it is unable to withstand without damage the thermal stress gradients that are inevitably produced by the impingement of hot steam on the outside surfaces of packs of product during the time needed to raise their internal temperature.

This is supported by the work of Stark and Moser<sup>vii</sup> who demonstrate that the release at room temperature of CH is insignificant before about 6 hours and that it peaks at around 15 hours after the commencement of hydration. Thus fresh ACFC should not be introduced to the autoclave before 6 hours and preferably not until after 12 hours so that there is sufficient CH present to react with the silica.

It is also found that delaying autoclaving for periods in excess of 36 hours or more often results in poor ACFC. The reasons for this are that the formation of low temperature forms of CSH constrains the formation of the high temperature forms of CSH because they will form on the surface of these low temperature forms and this introduces lattice distortions. Furthermore delaying autoclaving results in the loss of water from the ACFC matrix because of hydration of the cement and in some cases evaporation. Thus there is less water available to support the reactions and as a consequence delaying autoclaving reduces the strength of the final product.<sup>10</sup>

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<sup>10</sup> Since the product of delayed autoclaving is often substandard little further testing has been done. Thus it is not known whether the other properties such as moisture movement are affected. However it may be surmised that the moisture movement will be intermediate between air cured and autoclaved product viz. higher than desirable.

## 2.2 With Aluminous Additives

We now discuss the effects of Aluminous admixtures on autoclaving.

We have seen above that not all Aluminous admixtures are effective in altering the properties of ACFC. For example it was originally surmised that cements with high alumina content (i.e. high  $C_3A$ ) would produce lower moisture movement ACFC than cements of low  $C_3A$  but this was soon found not to be the case. Similarly Peng<sup>viii</sup> has shown that Alumina does not produce any reduction in moisture movement but that Gibbsite and Boehmite (naturally occurring forms of hydrated alumina) do. As we have seen above synthetic Alumina Trihydrate is effective as are Kaolin:ATH mixtures and Kaolin itself although to a much lesser extent. Klimesch and Ray<sup>x</sup> have shown that Metakaolin is also effective in reducing ACFC moisture movement. Thus the type of Aluminous admixture is important in determining whether it will be effective or not. Their effectiveness is related to their structure so we first examine the structure of these materials.

### Structure of Aluminous Additives and Cement Compounds

Taylor<sup>x</sup> shows that the Aluminium contained in  $C_3A$  is tetrahedrally coordinated with Oxygen atoms. Figure 6 reproduced from Taylor (ref x) shows the structure where the  $Al^{3+}$  ions lie at the centre of each of the tetrahedra.

The  $Al^{3+}$  ions also lie close to the corners of a cube forming a ring joined by the Oxygen atoms which form the corners of linked tetrahedra.

Research from University of Waterloo<sup>xi</sup> describes the structure of the most common form of Alumina as shown in Figure 7.

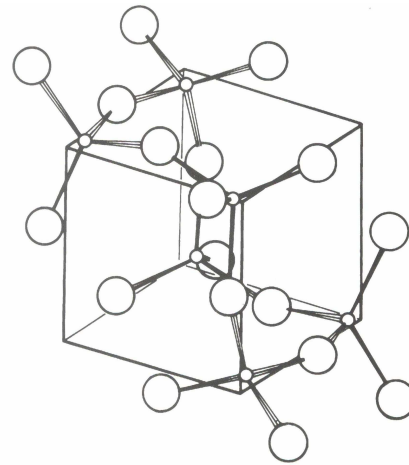


Figure 6 Structure of  $C_3A$

*“There are a few forms of aluminum oxide, and corundum being the most common. The structure of corundum can be viewed as a hexagonal close packed array of oxygen atoms with 2/3 of the octahedral sites occupied by  $Al^{3+}$  ions. Thus, the  $Al^{3+}$  ions are bonded to 6 oxygen atoms in a distorted octahedron. Each octahedron shares a face with one on the upper and one on the lower layers. The distortion is caused by repulsion between  $Al^{3+}$  ions in octahedra sharing the faces. Corundum is a dense (specific gravity of 3.97), hard (9 on the Mobs' scale, next only to diamond), high melting (melting point 2288 K), and insoluble in water. Crystals of corundum are usually prismatic or barrel-shaped bounded by steep pyramids.”*

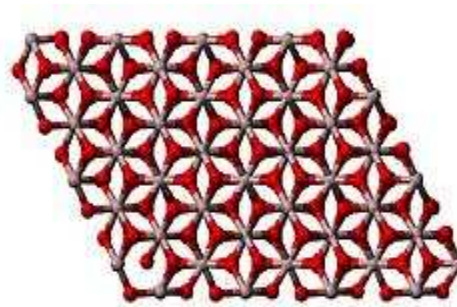


Figure 7 Structure of Corundum  
(from reference xi)

Thus while pure alumina has octahedrally coordinated  $Al^{3+}$  ions they are locked within a distorted lattice and in an insoluble and very hard material.



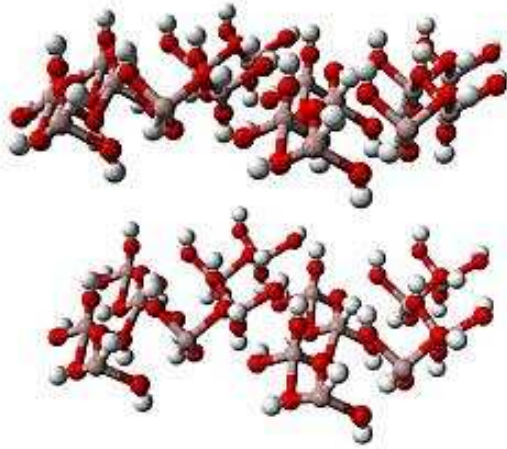


Figure 8: Ball and Stick model of <sup>xii</sup>Gibbsite

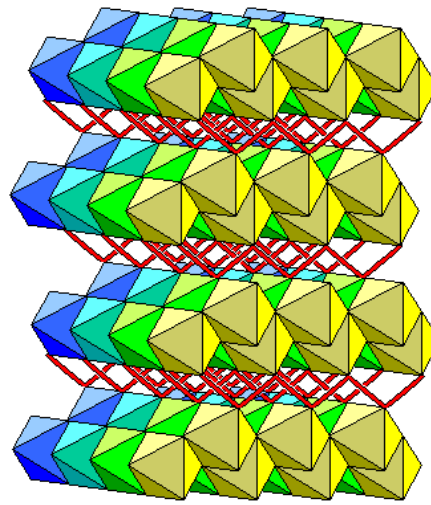


Figure 9: Structural model of Boehmite<sup>xiii</sup>

Figure 8 and 9 following from Wikipedia describe the structure of Alumina Trihydrate or Gibbsite.

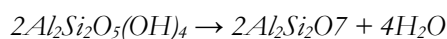
*“The structure of gibbsite is interesting and analogous to the basic structure of the micas. The basic structure forms stacked sheets of linked octahedrons of aluminium hydroxide. The octahedrons are composed of aluminium ions with a +3 charge bonded to six octahedrally coordinated hydroxides with a -1 charge. Each of the hydroxides is bonded to only two aluminium atoms because one third of the octahedrons are vacant a central aluminium. The result is a neutral sheet since  $+3/6 = +1/2$  (+3 charge on the aluminums divided by six hydroxide bonds times the number of aluminums) and  $-1/2 = -1/2$  (-1 charge on the hydroxides divided between only two aluminums); thus the charges cancel. The lack of a charge on the gibbsite sheets means that there is no charge to retain ions between the sheets and act as a “glue” to keep the sheets together. The sheets are only held together by weak residual bonds and this results in a very soft easily cleaved mineral.”*

Boehmite (ref <sup>xiii</sup>) also has the octahedral structure of Gibbsite with the octahedra lying together in sheets. Hydroxyl ions hold these sheets together through hydrogen bonding, shown schematically by red lines in Figure 9. This weak bonding gives Boehmite perfect cleavage parallel to the sheets, although the individual crystals are usually microscopic.

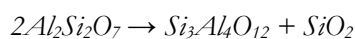
According to Wikipedia<sup>xiv</sup>, Kaolin or more strictly *“Kaolinite is a clay mineral with the chemical composition  $Al_2Si_2O_5(OH)_4$ . It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedra. Rocks that are rich in kaolinite are known as china clay or kaolin.”*

Kaolin type clays may undergo structural transformations on heating whose type depends on the degree to which it is heated. Thus

*“Kaolin-type clays undergo a series of phase transformations upon thermal treatment in air at atmospheric pressure. Endothermic dehydroxylation (or alternatively, dehydration) begins at 550-600°C to produce disordered metakaolin,  $Al_2Si_2O_7$ , but continuous hydroxyl loss (-OH) is observed up to 900°C and has been attributed to gradual dehydroxylation of the metakaolin<sup>v</sup>. Due to historic disagreement concerning the nature of the metakaolin phase, extensive research has led to general consensus that metakaolin is not a simple mixture of amorphous silica ( $SiO_2$ ) and alumina ( $Al_2O_3$ ), but rather a complex amorphous structure that retains some longer-range order (but not strictly crystalline) due to stacking of its hexagonal layers.*



Further heating to 925-950 °C converts metakaolin to a defect aluminum-silicon spinel,  $Si_3Al_4O_{12}$ , which is sometimes also referred to as a gamma-alumina type structure:



Upon calcination to  $\sim 1050^\circ\text{C}$ , the Spinel phase ( $\text{Si}_3\text{Al}_4\text{O}_{12}$ ) nucleates and transforms to Mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , and highly crystalline Cristobalite,  $\text{SiO}_2$

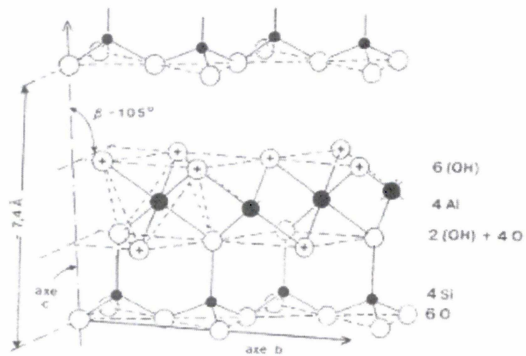
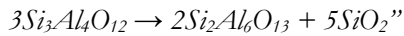


Fig 10: Ball and stick model of Kaolinite Structure (from ref xv)

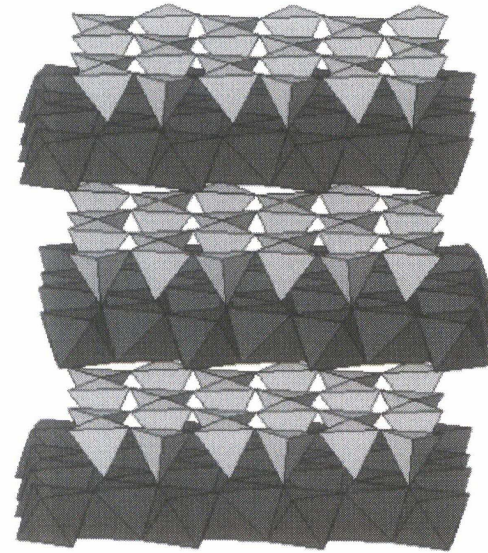


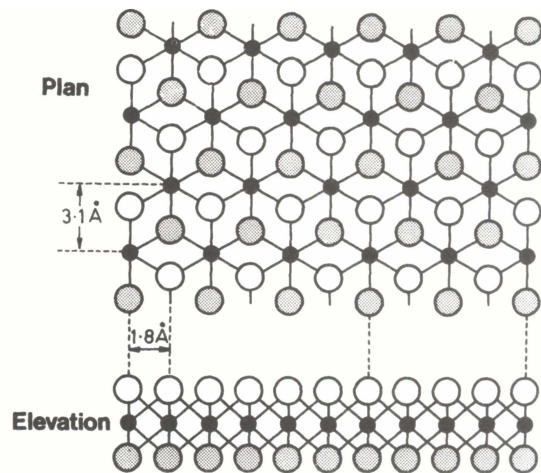
Figure 11: Structural model of Kaolinite showing layers of  $\text{Al}(\text{O},\text{OH})_6$  octahedra between layers of  $\text{SiO}_4$  tetrahedra (from ref xv)

Varga<sup>xvi</sup> has studied the transformation of Kaolin into Metakaolin and concludes that the structure of metakaolinite created from kaolinite at the temperatures higher than  $400^\circ\text{C}$  is still not clear because of the absence of XRD reflections which could show the metakaolinite structure exactly. What is generally known at the present time is that the double layer kaolinite structure is destroyed during calcination and that the metakaolinite crystal (if it exists at all) is full of defects. It may be surmised however, that octahedrally coordinated  $\text{Al}^{3+}$  ions are present in the metakaolinite structure and that these are exposed to reaction with alkaline materials of the cement due to the disordering of the Kaolinite structure.

Taylor shows that Lime (Calcium Hydroxide or CH) has a layered structure <sup>xvii</sup>as shown in Figure 12 below.

Taylor states that “the Calcium atoms are octahedrally and the oxygen atoms tetrahedrally, coordinated The interlayer forces are weak with negligible hydrogen bonding, thus giving good cleavage.” This implies that individual layers of CH may be present in the mix and that the octahedral Calcium atoms could be substituted with similarly coordinated Al atoms although this would require structural adjustment of the lattice and rebalancing of the charge with the addition of one more  $\text{OH}^-$  ion for each substituted Ca atom. This would tend to make Al substituted CH more alkaline than its unsubstituted analog. The degree to which the CH can be substituted is likely to be limited by the number of  $\text{OH}^-$  groups that can be added to the structure and this is the reason why the effectiveness of increasing amounts of Aluminous admixtures declines at higher levels of their inclusion.<sup>xviii</sup>





Structure of a single layer of  $\text{Ca}(\text{OH})_2$ . Small, solid circles represent calcium atoms, large open or shaded circles oxygen atoms; a hydrogen atom, not shown, completes the tetrahedral coordination of each oxygen atom.

Figure 12: Structure of Lime

We now consider the structure of Silica

Silica is usually added to autoclaved formulations as finely ground Quartz because it is found that the addition of amorphous silica such as Silica fume or Diatomaceous Earth results in ACFC with higher moisture movement. We have seen that the crystallinity of the resulting ACFC affects the moisture movement with high moisture movement being associated with low crystallinity.

Figures 13 and 14 show the structure of crystalline Quartz and Amorphous silica respectively.

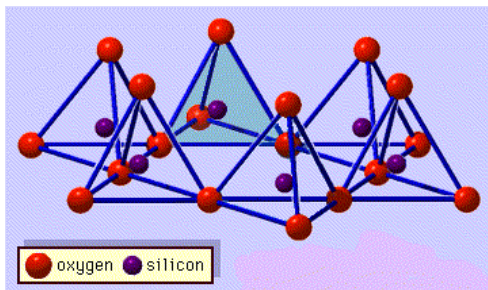


Figure 13: Silica Tetrahedra in Crystalline Silica

In contrast to the glass a regular structure exists within the crystal.

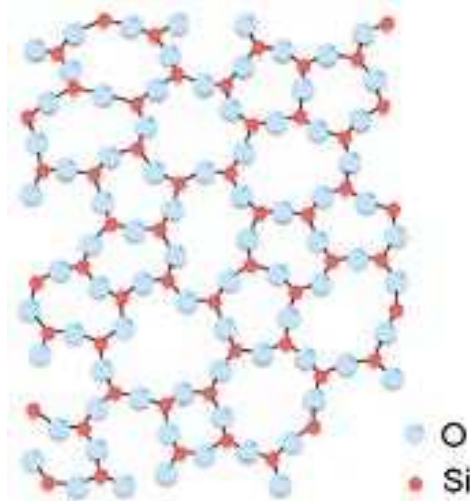


Figure 14: Silica Tetrahedra in Silica Glass

The amorphous structure of glassy Silica ( $\text{SiO}_2$ ). No long range order is present, however there is local ordering with respect to the tetrahedral arrangement of Oxygen (O) atoms around the Silicon (Si) atoms.

### **Structure of Hydrogarnet, 11 A° Tobermorite and Al substituted 11 A° Tobermorite**

As we have seen above 11 A° Tobermorite and its Al substituted homologue is the final product of the autoclave reaction. Klimesch and Ray<sup>xix xx</sup> have shown that Hydrogarnet precedes the formation of Al substituted Tobermorite during autoclaving. Hydrogarnet has the composition as expressed in the usual cement chemistry terminology as  $C_3AS_{3-x}H_{2x}$  where  $x=0$  to 3.

Klimesch and Ray have also found that the proportion of Hydrogarnet that forms within the first 3-4 hours of autoclaving, is dependent on the amount of Alumina present in the formulation and that the proportion rises with rising Alumina quantity. The amount of unreacted lime (CH) also decreases linearly with increasing Alumina quantity indicating that it is consumed in the chemical reactions occurring.

Subsequent to its formation Hydrogarnet breaks down during the formation of Al substituted Tobermorite and substantially disappears providing that the autoclave process is continued for long enough.

Taylor<sup>xxi</sup> states that Hydrogarnet is related in structure to Garnet which *“has a cubic structure in which the silicon, aluminium and calcium are in tetrahedral, octahedral and distorted cubic coordination respectively: each oxygen is bonded to one silicon, one aluminium and two calcium atoms. In the hydrogarnet, this structure is modified by omission of some or all of the silicon, the charge being balanced by replacing each of the oxygen atoms to which it was attached by hydroxyl”*.

11A° Tobermorite has a triple chain structure (dreierkette) as shown in Figure 15<sup>xxii</sup> where the triangles represent Silica tetrahedra linked in a chain with common Oxygen atoms at the corners. Each chain lies against 2 rows of Calcium atoms one of which lies within the layer (full circles) and one outside of it (open circle). OH groups necessary to maintain electrical neutrality and water molecules have been omitted to simplify the diagram.

2 of these triple chains make up the unit cell of the crystal which is 1.1nm (as shown in fig 15) or 11 A° lattice spacing. The chains are arranged in parallel to form sheets joined together by water molecules. Water molecules between the layers are tightly bound if close to the crystal surface.

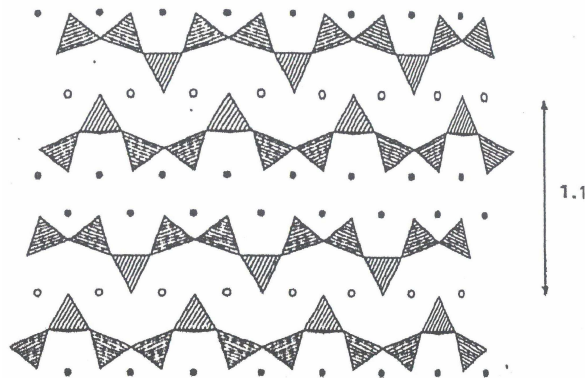


Figure 15: 11A° Tobermorite

However it is possible for water molecules to intercalate between the layers resulting in the observed moisture movement of this and similar materials.

Al substituted 11A° Tobermorite is similar in structure except that some of the Calcium atoms are substituted with Al atoms.  $Ca^{2+}$  ions with coordination number 6 (i.e. octahedral coordination) have an ionic radius of 1A° compared to  $Al^{3+}$  which has an ionic radius of 0.54A° at the same coordination number<sup>xxiii</sup>. Thus the substitution of  $Ca^{2+}$  with  $Al^{3+}$  will introduce strains into the crystal structure.

Since this will also introduce an unbalanced charge, additional OH groups must be introduced into the crystal to maintain electrical neutrality and these will replace the neutral water molecules.

Clearly this substitution will alter the 11A° Tobermorite and it is suggested that its structure will become somewhat more compact and chemically resistant to carbonation. Peng<sup>xxiv</sup> proposes a purely chemical reason for the increase in the resistance of Al substituted 11A° Tobermorite but it seems likely that steric hindrance effects are in play that also restrict the access of CO<sub>2</sub> because of lattice strain.

## **2.3 Chemical Reactions during autoclaving of Cement:Silica mixes with Aluminous Admixtures**

We now summarise the observations of the effects of aluminous additives on ACFC.

### ***Effectiveness of Various Aluminous Additives***

Aluminous additives

- reduce the moisture movement,
- reduce the strength and stiffness,
- increase the creep rate and
- reduce the rate of carbonation

of ACFC compared to ACFC without such additives.

There is an order of effectiveness for these additives and in order of their effectiveness we find that

$C_3A \approx \text{Alumina} < \text{Kaolin} \approx \text{Metakaolin} < \text{Kaolin/ATH(Gibbsite)} < \text{ATH(Gibbsite)} \approx \text{Boehmite}$

With the exception of C<sub>3</sub>A from the cement and Alumina which have no effect, the effectiveness of each material or combination is dependent on their concentration and they are more effective at higher concentrations than at lower. However there is evidence that each becomes increasingly less effective at higher concentrations although this limit of their effectiveness will certainly depend on the cement used and the ratio of cement to silica.

It is clear from the previous section that the effectiveness of the admixture depends on the presence and availability of octahedrally coordinated Al atoms. C<sub>3</sub>A has no octahedrally coordinated Al and while (Anhydrous) Alumina does contain octahedrally coordinated Al, it is contained within a distorted lattice and effectively unreactive to CH. Thus C<sub>3</sub>A and Alumina are not effective at all.

Kaolin is only marginally effective and this is in part because the proportion of octahedrally coordinated Al is small because of the presence of silica and various cations within its structure. Furthermore gaining access to the octahedral Al is difficult because of the presence of these other materials.

Metakaolin is more active than Kaolin because its structure has been disrupted by calcination. Klimesch and Ray (ref xx) have shown that Metakaolin does react with the CH and the material is a known pozzolan at room temperatures. The structure of metakaolin is not known but it must be amorphous because it has no XRD reflections. It is reasonable to assume that the octahedral coordination has been maintained in the debris of the disrupted Kaolin structure.

Kaolin/ATH is more effective than Kaolin alone and this is clearly because the proportion of octahedrally coordinated Al in this mixture is greater than in Kaolin alone.

ATH and Boehmite are the most effective of all of the additives because they contain the highest concentration of octahedrally coordinated Al.

### ***Chemical Reactions during Autoclaving***

Chemical reactions occurring during autoclaving are dependent on the prior low temperature hydration of the cement and the production of free lime (CH).

Klimesch and Ray clearly showed that the first reaction to occur in autoclaving is the formation of Hydrogarnet ( $C_3AS_{3-x}H_{2x}$  and  $x=0$  to 3) which in continued autoclaving and in the presence of excess silica, transforms into Alumina substituted 11A°Tobermorite. It is important to remember that Al in Hydrogarnet is octahedrally coordinated and that the other component atoms (i.e. Ca and Si) are also structurally the same in hydrogarnet as in their precursors.

Considering that the presence of significant amounts of Lime (CH) is necessary for good autoclaving, these observations suggest the following sequence of reactions.

After reaching autoclaving temperature (180°C and possibly from a lower temperature) the CH combines with the aluminous admixture to form an Al substituted CH (Als-CH) that is more reactive than the CH it replaces. Ca in CH is octahedrally coordinated, so octahedrally coordinated Al can readily substitute for the Ca. The reactivity of the substituted CH is greater than pure CH because in order to remove the electrostatic imbalance by the addition of Al for each Ca ion that is substituted another OH group must be added to the structure.

The Als-CH then reacts with the silica on the surface of the silica grains to form the hydrogarnet. This is possible because the lattice spacing of the Als-CH is similar to the lattice spacing of the silica and the solubility of Silica at autoclave temperatures. Furthermore the silica tetrahedra of the quartz lattice are identical with those in the hydrogarnet thus facilitating its formation.

As autoclaving proceeds the Hydrogarnet reacts with more Silica and the C:S ratio decreases. As this ratio decreases, the hydrogarnet approaches the Tobermorite C:S ratio (albeit with some of the Ca substituted with Al) and the altered Hydrogarnet recrystallises into the Tobermorite crystal habit.

As the active aluminous additives are removed as hydrogarnet, the remaining CH and silica react to form high temperature CSH to the limit of the remaining available free CH.

Taking a typical ATH containing formulation and assuming the following

- All of the alumina and iron oxide in the cement remain as hydrated version of  $C_3A$  or  $C_4AF$  after autoclaving
- All of the silica in the cement is trapped as CSH after hydration
- ATH is first consumed by free CH generated from the cement during low temperature hydration to make hydrogarnet and
- the remaining CH reacts with excess Silica,

we find that approximately 4% of the reaction products are converted to Hydrogarnet.

In the light of the arguments above it is reasonable to assume that this is crystalline and reactive. Since the hydrogarnet disappears with further autoclaving it is reasonable to assume that it reacts with silica and possibly CH to transform into an Al substituted Tobermorite. If we assume that the C:A ratio of the hydrogarnet is maintained and the C:S ratio of the final product is 6:5 as in Tobermorite then we will have converted approximately 8% of the final product to this material. Therefore given that crystallinity of the final product is usually around 15% then other material must be converted to Tobermorite and if Hydrogarnet acts as a catalyst for the formation of this Tobermorite then it must incorporate both CH and S into its structure.

The reactions therefore can be summarized in the following diagram.

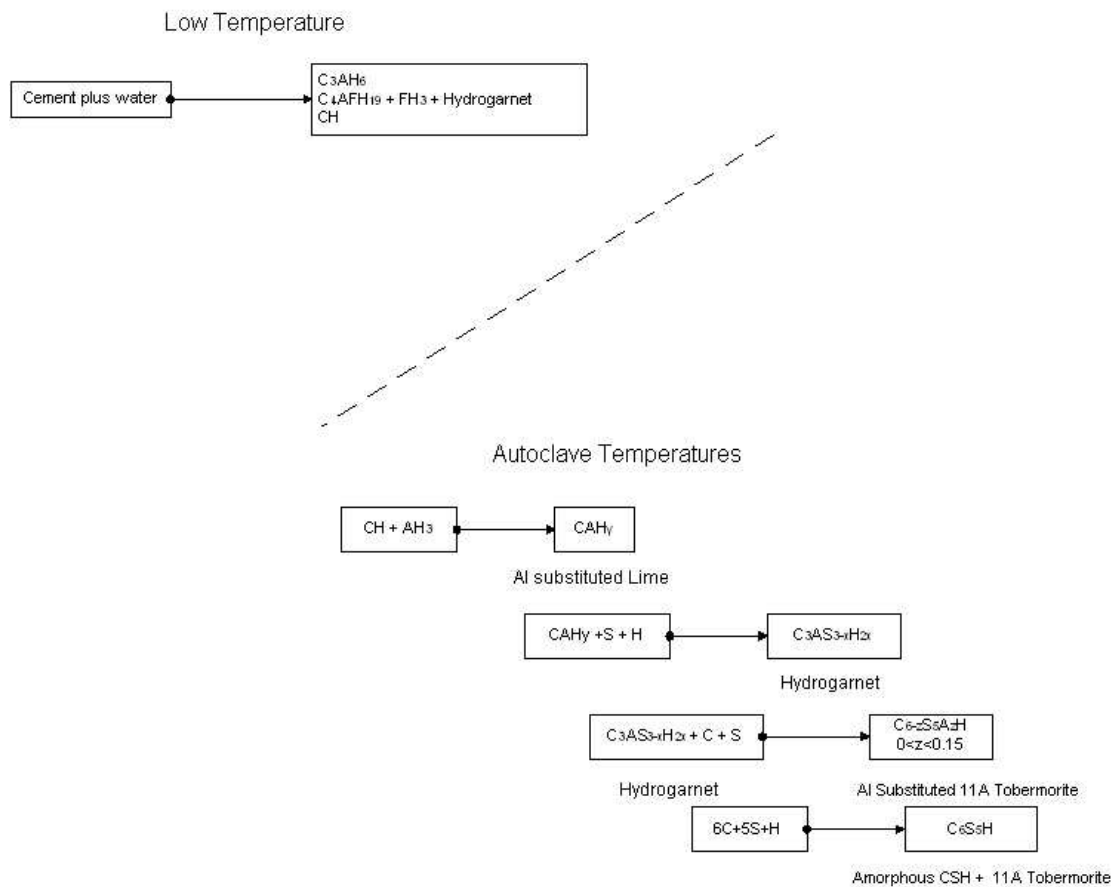


Figure 16: Reactions taking place in precuring and during autoclaving

### Conclusions

The presence of compounds containing easily available octahedrally coordinated Al is necessary for the formation of crystalline Al substituted Tobermorite and this material determines the final properties of the ACFC.

## 3 Practical Implementation

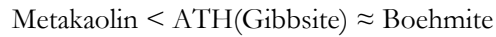
Our main objective will be to achieve a durable ACFC that is reasonably ductile without being too weak and that will withstand the usual environmental conditions in which it will serve. Some of these conditions have been outlined previously<sup>xv</sup> and a combination of low moisture and carbonation movement with high ductility and strain to failure with sufficient strength to survive fixing is necessary for whatever conditions to which the ACFC will be exposed. National standards will also have to be considered so that the product at least meets minimum acceptable standards for strength and other properties. In general standards however will be silent on long term properties because of the difficulty of measuring them or predicting their requirements on the basis of accelerated tests.

In order to achieve these objectives and taking into account the practical implication of the findings above we need to consider the following

- the types of additives necessary
- the amount of additive
- the proportions of the materials other than additives in the mix and

- the curing cycle (including low temperature precuring and autoclaving)

It is clear from the discussion above that only compounds containing easily available octahedrally coordinated Al will be effective in reducing moisture and carbonation movement and that they do this by promoting the formation of crystalline Tobermorite in its pure or Al substituted forms. Thus the use of Alumina (anhydrous) or Kaolin, which have limited availability of this form of Al, is of little value.<sup>11</sup> We are therefore left with the following options arranged in order of their reactivity in the mix.



The decision on which one and amount to use will therefore be based on their availability and their cost in relation to their effectiveness. This will also depend on the other materials that are being used in the mix particularly the composition of the cement and it is not possible to be prescriptive in a paper such as this. It has been the author's experience that the amount to be used can be related directly to the amount of ATH equivalent contained in the additive. Thus Bauxite which contains Gibbsite mixed with other hydrated oxides such as Haematite must be added so that the equivalent amount of Gibbsite is added as pure ATH to achieve the same result. Of course other effects may be introduced e.g. colouration of the ACFC so this may rule out an otherwise attractive raw material.

The proportions of other materials and particularly the Cement:Silica ratio also affect the ACFC properties. In general reducing the cement:silica ratio reduces moisture movement but has little effect on the carbonation resistance or carbonation movement. So it is likely that a reduction in cement content could achieve the same effective moisture and carbonation resistance with a lesser introduction of aluminous additive. To the author's knowledge there is no complete published information on the effect of aluminous admixtures on the practical range of Cement:Silica ratios although it has been found that at 70:30 cement silica ratio, aluminous admixtures have no effect on moisture and carbonation movement. Thus it is not possible to prescribe effective formulations at other than what has been revealed above.

The ACFC must be precured to develop a significant amount of free CH. This is necessary to provide large amounts of reactive alkali that will react with both the aluminous admixture and the free silica. Too early introduction of unreacted cement into autoclave also results in the formation of  $\alpha$ -C<sub>2</sub>S hydrate which is a high temperature hydrate. This forms tabular crystals which because of their shape can form only few bonds between adjacent crystals and a weak matrix results. It is generally recommended that precuring be continued for at least 12 hours as this produces the maximum amount of free CH.

The autoclave cycle needs to be adjusted to the raw materials for best effect and this will be dependent not only on their chemical composition but also on their treatment. Thus very fine materials will not require as much curing as coarser materials.

The temperature of autoclaving must also be sufficient to trigger the formation of the high temperature forms of CSH but not so high that it produces forms of CSH other than Tobermorite. For example it is found that at temperatures above 190°C Xonotlite may be formed which is weaker than Tobermorite probably because it is more crystalline in a like manner to  $\alpha$ -C<sub>2</sub>S hydrate.

Although it is desirable for minimum moisture movement to convert as much of the amorphous CSH to tobermorite as possible, the autoclave cycle must not be continued for too long as this can be detrimental to strength.

Duration and temperature of autoclaving need to be optimized for two important reasons:-

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<sup>11</sup> Kaolin can be used in conjunction with ATH but the evidence shows that it has limited effect and may act in this circumstance as a process aid only.

- i. The strength in ACFC as was shown above is determined principally from amorphous CSH rather than crystalline material and over autoclaving may therefore reduce the strength and
- ii. Over autoclaving will damage the cellulose reinforcement.

Thus autoclaving that is too protracted or at too high a temperature, will result in loss of strength and lower strain to failure in the ACFC.

The curing cycle should therefore be adjusted to produce adequate precure and adequate but not overextended autoclaving. However the choice of specific cycles will depend on the available raw materials.

## **4 Future research**

There are obvious gaps in the published literature on aluminous admixtures for use in ACFC and there appears to be scope for significant advances.

There is a significant gap in the information on the effectiveness of aluminous admixtures at cement:silica ratios outside of a narrow range and a systematic investigation would be most useful.

The effect of the cellulose in the products of curing at low and high temperatures has been excluded from the research conducted to date presumably because it adds a further level of complexity to the system. However the components of the fibre certainly affect the early curing of the cement and it is known that they can be deleterious to the final properties of the ACFC so their inclusion in future research may reveal much of interest.

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