SILICONE RESIN HYDROPHOBER AS INTEGRAL WATER REPELLENT FOR FIBRE REINFORCED CEMENT BOARDS.

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ABSTRACT

Protecting Fibre reinforced cement boards against water absorption is key to protect the boards against water-induced physical change or freeze thaw degradation.

A silicone resin hydrophober was tested as integral water repellent in simple mortar and in FRC boards prepared on a pilot plant.

Deeper analysis of the impact of the silicone resin hydrophober on the cement matrix properties was studied on mortar samples while impact on the FRC process was study on a mini Hatschek pilot plant.

Samples of Autoclaved and Natural Cured Fibre Cement with variations of mix formulations were produced on a Mini Hatcheck machine. For every alternative mix formulation the silicone resin hydrophober was added. The samples were tested for flexural strength and physical characteristics. Water absorption was tested with different methods. The results demonstrated significant reduction of water compared with the standard formulations.

INTRODUCTION

The porous structure of construction materials based on Ordinary Portland Cement leads to high sensitivity to capillary water absorption. Control of water absorption is therefore key to reduce various kinds of water-induced damages such as efflorescence, staining, spalling due to freeze-thaw cycles, chemical attack and corrosion to reinforcing steel. A number of solutions have been used in the past to decrease water absorption such as the post-treatment of water repellents or the use of so-called "hydrophobic admixtures" within the cement matrix itself to provide integral water repellency. Siloxane and alkoxysilanes have now become a well-known class of materials used both for post-treatment water repellents [1,2], admixtures in non load bearing concrete [3] or as post-treatment or admixture in Fiber reinforced cement boards [4].

SILANES AND SILICONE RESINS

Silanes are molecules based on one silicon atom which bears four substituents. Alkyl trialkoxy silanes (see Figure 1) are used in hydrophobic additives, either for post-treatment or admixture as they have good reactivity towards inorganic, silanol-rich surfaces. The aliphatic chain (i.e. octyl chain) confers the hydrophobic character to the treated substrate. Upon hydrolysis and condensation, silanes create a resinous network which bonds covalently to the surface of treated materials leading to outstanding water resistance durability.

Silicone resins are obtained by a sequence of controlled hydrolysis and condensation reactions of individual or mixtures of silanes (see figure 1). They are highly branched polysiloxanes of higher molecular weight. Their structure consists of hydrophobic alkyl chains and reactive SiOR groups (with R = methyl or ethyl) [5]. The hydrophobicity comes from the presence of the alkyl groups. Longer alkyl chains provide good resistance in alkaline environment. When applied to (or in) a substrate, the alkoxysilyl groups react with water to form a labile silanol intermediate which will condense with other silanol (from another resin or from the substrate/matrix).

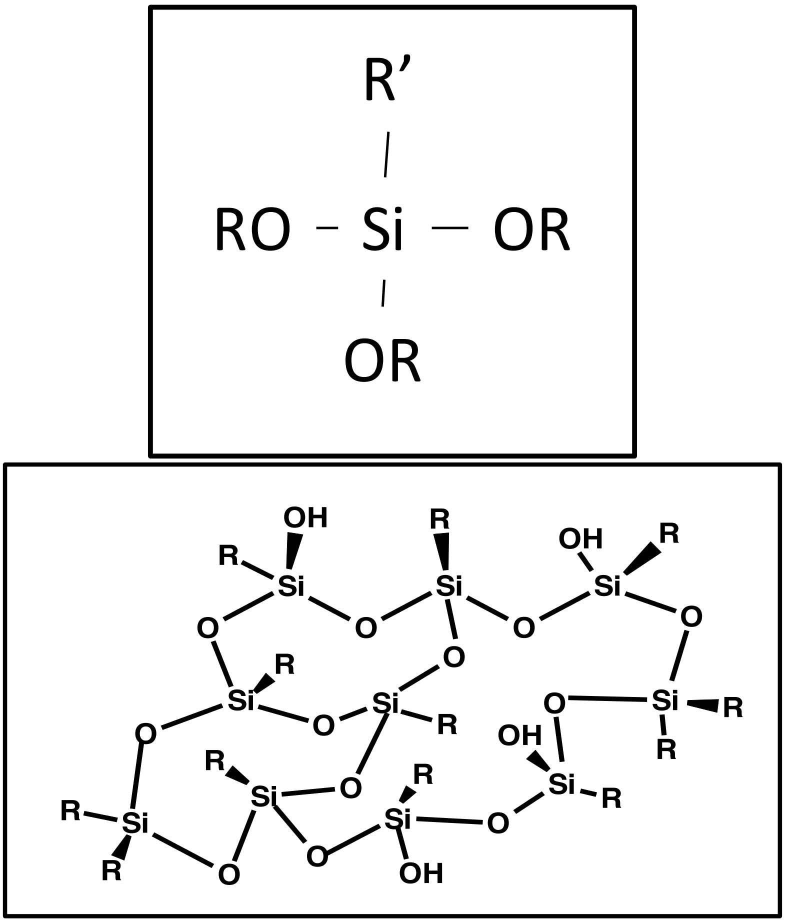


Figure 1 – structure of alkyl trialkoxysilane and schematic representation of a silicone resin (R can be ethoxy, methoxy, methyl, phenyl or octyl group)

These kind of silicone-resin networks bestow water repellency on the pores and in some cases strengthen the pore structure, depending on the substrate and the concentration of silicone based products [7]. In construction applications the inorganic constituents spread out across the surface of the material, with the organic side groups projecting outwards and presenting a barrier to impinging water, Figure 2 [6].

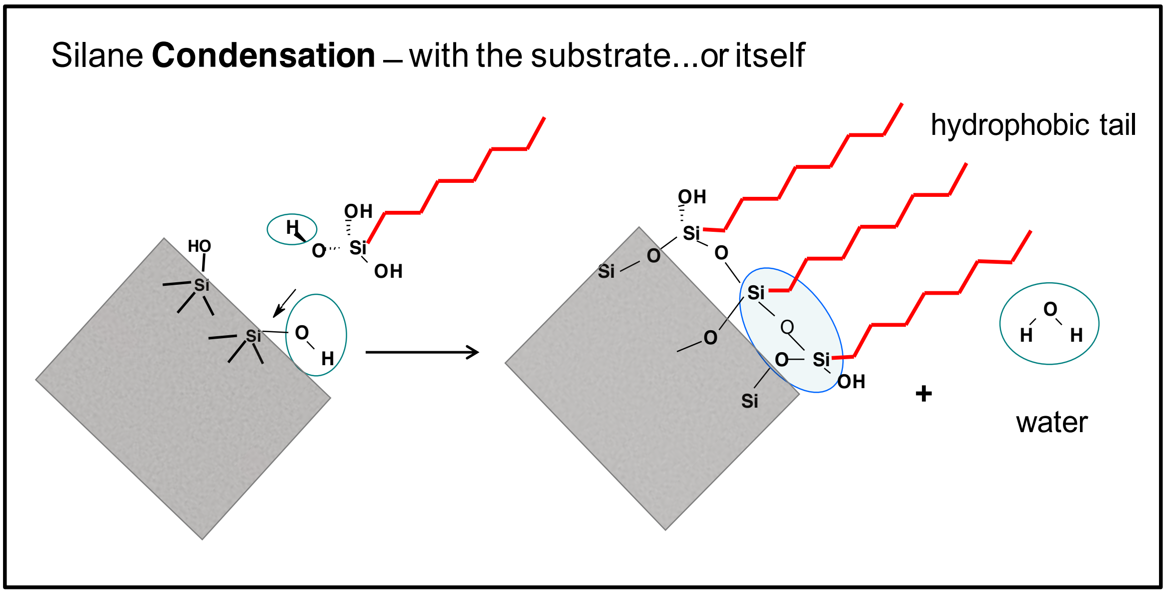


Figure 2 – reaction of alkoxysilane with silanol-rich surface.

By treatment with silicone compounds the building material becomes hydrophobised as a result of a chemical modification and newly formed bonds (Figure 2). The performance and durability of the water repellent treatment rely on the reaction of the silicon-based additive with the treated construction material.

This paper concentrates on the use of silicone resin as "integral water repellent" for Fibre Reinforced Cement (FRC) boards. In this treatment method, the silicone resin will become an integral component of the board as it cures and therefore forms a water barrier throughout the entire board. One advantage of this approach would be that the FRC products would be protected from water absorption from the time they are initially produced and would not depend on a post-treatment or protective coating to provide improved water resistance.

This paper describes the efficiency of a specific silicone resin named Z-6289 as hydrophobic admixture for cement matrixes and as admixture for fibre reinforced cement boards in particular. This specific silicone resin has been used as integral water repellent for FRC boards prepared on a mini Hatschek pilot plant. The study concentrates on the impact of the silicone resin addition on the process parameters, boards mechanical properties and impact of resin addition on boards water absorption.

IMPACT OF SILICONE RESIN ON CEMENT MATRIX

Impact of Z-6289 silicone resin on cement matrix mechanical properties

Impact of the Z-6289 silicone resin on a cement matrix was assessed by measuring mechanical properties of mortar prepared according to guidelines given in norm EN 196-1, although mechanical properties were measured after only 7 days cure. CEM I 52.5 N cement was used. Reference mortar (with no additive) and mortars modified with 0.25%, 0.5% and 1.0% (vs dry mortar weight) of Z-6289 were prepared. Mechanical properties were measured after 7 days cure. Values for the compressive strengths were 49.1 MPa for the unmodified mortar and 47.8 MPa, 44.0 MPa and

42.6MPa for mortar modified with respectively 0.25%, 0.5% and 1.0% of Z-6289 silicone resin. Only a limited impact of addition of (too) large amount of the silicone resin is observed.

Impact of Z-6289 silicone resin on water absorption of cement matrix

The same mortars samples (as prepared for the mechanical properties) were used to assess impact of Z-6289 silicone resin on capillary water absorption of modified mortars.

Mortar blocks of a 4cm*4cm section were placed vertically on a water container. 1 cm of the blocks is immerged, the rest of the bocks protruding from water. Blocks were cured for 7 days, dried at 50°C for one day, weighed and then placed in the water container. Blocks were removed after 1 day, towelled and weighed. They were replaced in the container and the same measurements were repeated after 7 days partial immersion.

Increase weight due to capillary water absorption is reported as % of the dry mortar blocks. Table below gives the % of increase of blocks weight due to capillary water absorption.

The table shows a strong reduction of capillary water absorption due to the addition of Z-6289 into the mortar formulation. The same experiment was carried out, using an emulsion of the silicone resin instead. The same amplitude of water absorption reduction was observed, suggesting the silicone resin is properly dispersed into the cement matrix, although it is at start, not water soluble or easily water-dispersible.

Mortar specimens	Z-6289 active content (% of mortar weight)	**Water absorption after different contact time with water**	
		t=24h	***t=7 days***
	(%)	*(%)*	*(%)*
Reference CEM I	0	3,84	6,16
Mortar modified with Z 6289	0,1	3,6	4,82
	0,25	1,91	3,33
	0,5	1,52	2,63
	1	1,01	2,07

Table 1 - capillary water absorption (as % of dry mortar blocks) after 1 and 7 days contact time with water of reference and mortar blocks modified by addition of different % of Z-6289 silicone resin.

MINI HATSCHEK TRIAL

Method

Two trial runs were done on the Mini Hatschek Machine at Everite, the first was for Autoclave mix formulations and the other for Natural Cure mix formulations. The trial started with a Standard formulation and once the process was stable the samples were produced. Process measurements were done at constant intervals and corrections to the process was minimised to ensure comparative results. To ensure that there would be no contamination of the process water the trial run of the standard mix formulations were completed before the formulations with the hydrophober additive was done. The addition of the quantity of hydrophober (0.3% vs the dry board components weight) was kept constant for all the mix formulations. Samples of 250x250x6mm were produced. The Autoclaved samples underwent a 12 hour hydration period before being autoclaved at 900kPa for 12 hours. The Natural Cured samples were wrapped after production and only opened at the required test intervals of 7, 14, 21 and 28 days.

Process

The raw materials are pre-batched and added into a turbo mixer. Once the mix has a homogeneous consistency it is transferred to a holding stirrer. A constant flow of mix is then delivered to a pre-mixer that reduces the consistency of the mix before it feeds into the Mini Hatschek machine that has one vat and runs at a nominal speed of 15m/min. Four Samples are produced at a time and the Sheet Moisture Content and Wet Density are measured with regular intervals. Other measurements include Solid Loss, Vat Efficiency and Flocculent Dose Rate. The process and machine running parameters are kept constant for the duration of the trial. The mix formulations were numbered AM for Autoclave (sample A to D) and NC for Natural Cure (sample A to B), the suffix D indicates the Dow Corning hydrophober additive.

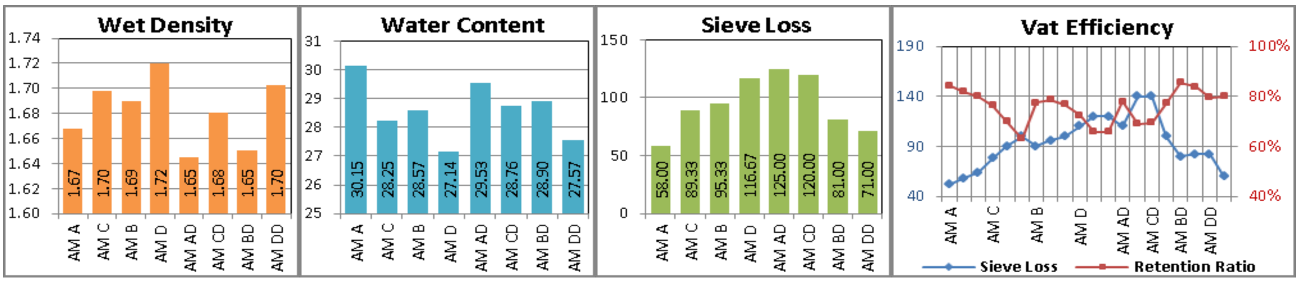


Figure 3 – Graphs of Process data recorded during production of Autoclaved boards

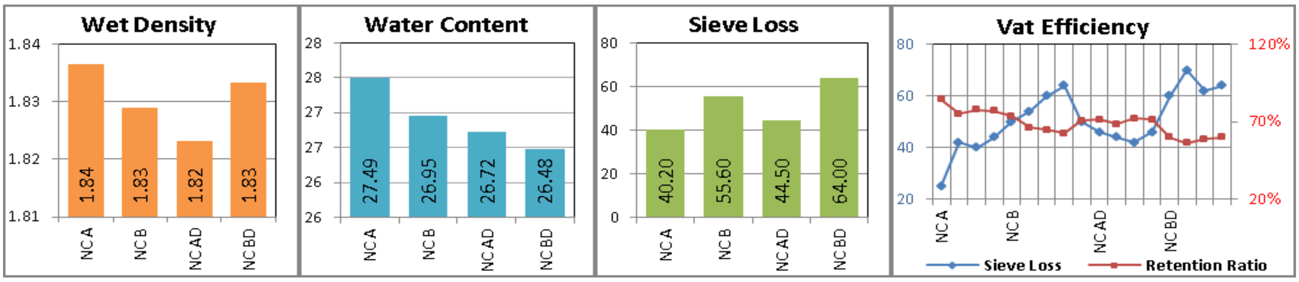


Figure 4 – Graph of Process data recorded during production of Natural Cured boards

Figure 3 and Figure 4 reflects the process data for the different trials. From the data it is clear the the process parameters were well under control for the duration of the trials and that no significant changes were observed with the addition of the hydrophober additive.

Results

All the samples were tested for flexural strength in both grain directions on a 230mm load bearing span with a constant linear pressure and a speed of 1mm/s.

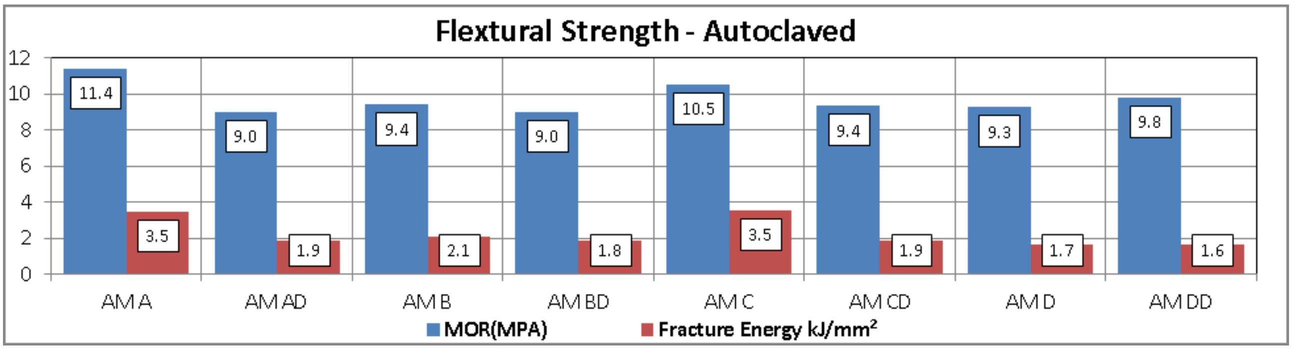


Figure 5 – Flexural Strength of Autoclaved boards

The break strength results in Figure 5 were very even and no signifficant difference was noticed on the results of the Modulus of Rupture but the Average Flextural Regdidity of AM A and AM C was much higher than that of the other samples. This indicates that the samples that contained the hydrophober additive changed the matrix and that resulted in the increase in embrittlement. To illustrate the difference between the results of the break strengths the stress curves, as the sample was tested, has to be examined. The Stress curves of samples AM A and AM AD is displayed in Figure 6 to illustrate the embrittlement. The maximum point of failure is much higher on average for the samples of the AM A formulation if compared to the AM AD formulation but there is a high variance in the AM A results. The AM AD formulation produced more uniform results but with a lower (Modulus of Rupture) MOR. Although the difference between the averege 11.4 MPa and 9.0 MPa might not seem much different the deflection of the samples plays a substancial role in the calculation of the Fracture Energy results. Fracture Energy measured in kJ/mm² is an indication of sheet thoughness. The extention or deflection for the AM A samples are about 10mm more than that of the AM AD.

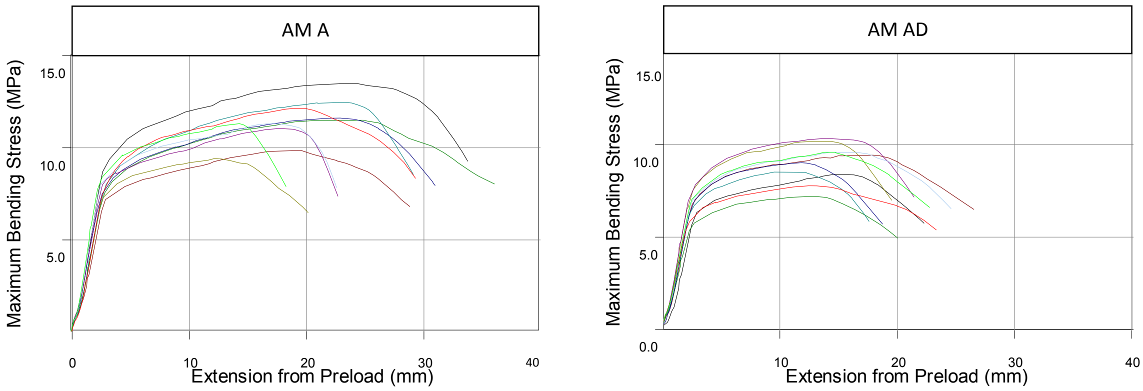


Figure 6 – Stress Curves of the autoclaved boards: AM A and AM AD

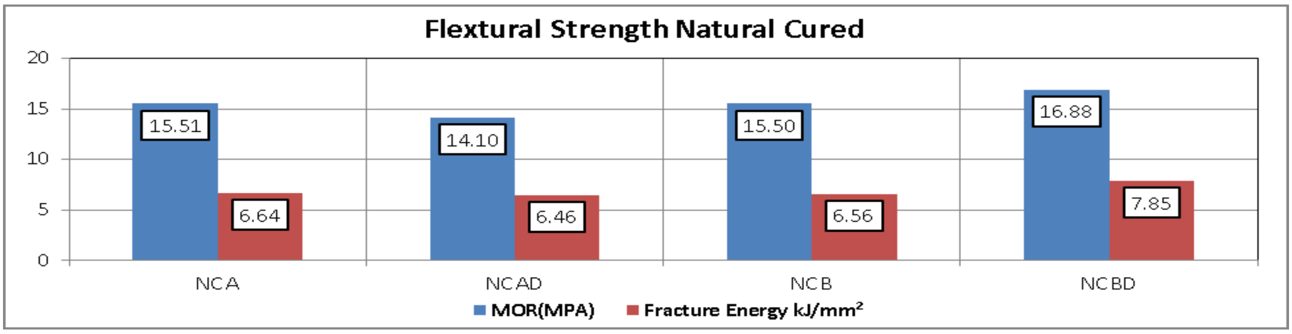
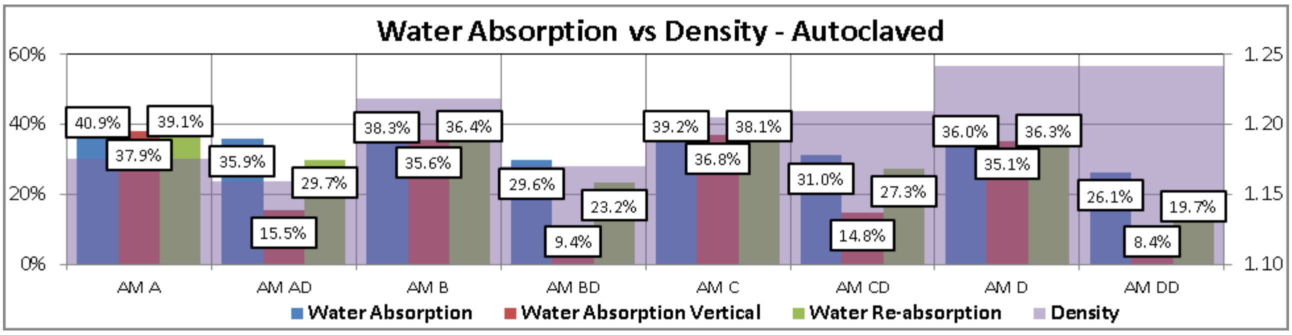


Figure 7 – Flexural Strength Natural Cured boards

The strength characteristics in Figure 7 of the Natural Cured samples were almost uniform throughout the curing period. No significant correlation could be made because the values for the different formulations hence the hydrophober additive had no influence on the final strength.

Water Absorption

The test for Water Absorption is normally done by drying the sample for 24 hours. Weigh the sample and record the weight. The sample is then soaked in water for 24 hours and then weighed again. So called Water Absorption in this document is the difference of weight between the two samples (soaked and dry) divided by the weight of the dry sample. Water Absorption is related to the porosity of the matrix and reflects the maximum absorption of water from the board dry state. Any Fibre Cement product has a natural moisture content and that is determined by the ambient humidity and the ability of the matrix to absorb water. When the surface pore structure is rendered without changing the porosity, the ability of the matrix to absorb water is changed.



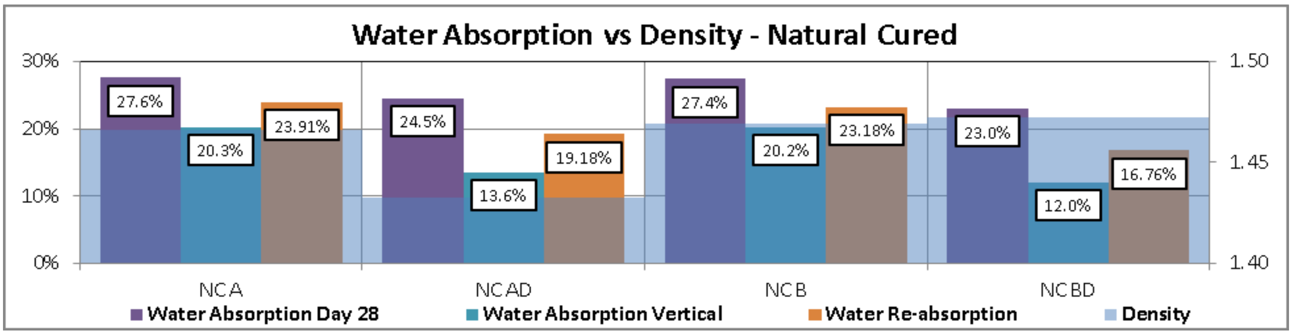


Figure 8 – Water Absorption vs Density

The measurements for Water Absorption of both Autoclaved and Natural Cured mix formulations are displayed in Figure 8. The first noticeable difference is that the formulations that contained the hydrophober additive produced samples with a lower Water Absorption than that of the standard formulations. Some samples had a higher density but that did not influence the magnitude of the absorption significantly. Although the samples with higher density had a somewhat lower Water Absorption but difference is only 1 – 3%. Reaction of the hydrophober with the cement matrix (in the bulk of the boards) is therefore reducing the affinity of the pores for water, decreasing the capillary water absorption of the boards. The result is the reduction in the ability for water to be absorbed into the matrix.

Vertical Water Absorption

To test the surface pore structure a test was devised to verify the resistance of the matrix to absorb water only on one surface of the sample. An open ended square frame of 200x200x20mm is placed on the pre-cut sample. This sample is dried for 24 hours and the weight is recorded before the test starts. The contact edges between the sample and the frame is sealed with petroleum jelly to prevent water from leaking from the enclosed area. The frame is then filled with water. Pictures are taken at this time to assist with the visual data collected for this test. The water is left in the frame for 24 hours. Before the water is removed pictures are taken and visual observations recorded. The sample is then padded dry and the excess petroleum jelly removed. The sample is then weighed and the values recorded. The Vertical Water Absorption is then calculated by the difference between the wet and dried weights divided by the dried weight.

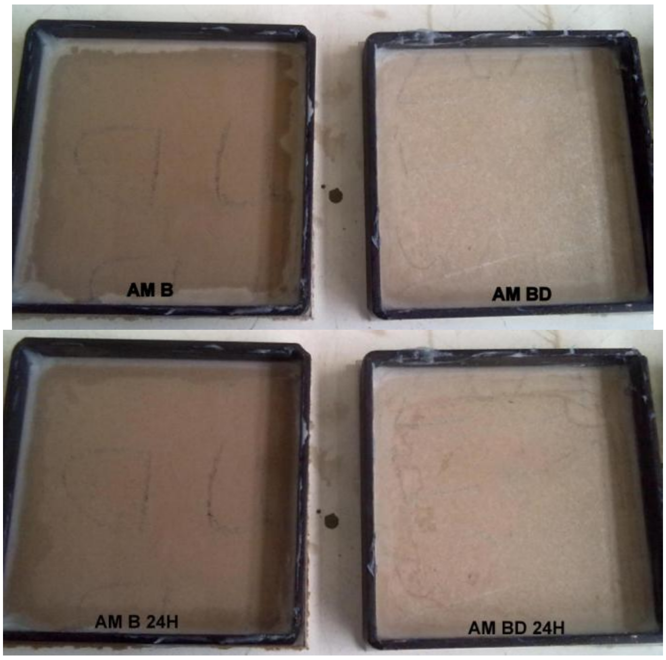


Figure 9 – Vertical Water Absorption Test

Figure 9 displays the samples at the start of the Vertical Water Absorption test AM B and AM BD and also after 24 hours AM B 24H and AM BD 24H. At the start of the test it is already evident on visual inspection that the initial water absorption between the two samples is different. The sample that does not contain the hydrophober additive immediately discolours. After 24 hours the colour of the AM B has darkened around the edges but the AM BD sample hardly changed colour as a result of absorption. The Water Re-absorption is basically the repeat of the normal Water Absorption test with the same samples used in the Vertical Water Absorption test.

Reduction of water absorption

The first noticeable improvement in Figure 10 is difference of Water Absorption for the same mix formulations. A reduction of up to 9.9% was measured for the Autoclave formulation with the hydrphober additive. The reduction of absorption for the Natural Cured Formulations was only up to 4.4%. The test for Vertical Absorption yielded excellent results up to 26.7% better than the Standard Mix formulation for Autoclaved and up to 8.2% for Natural Cured. The final test result confirms that the pore structure of the matrix closes up for the Natural Cured Samples in Figure 10 but the Samples with the hydrophober additive showed even a higher resilience to absorption. Autoclaved products have a very low reactivity with re-absorbed water because the reactivity of the hydration products is saturated and completed in the Autoclave process. The re-absorption of water is therefore almost identical to the initial Water Absorption result for all the standard formulations. The samples that contained the hydrophober all showed reduced values of re-absorption. The absorption of water is greatly reduced with samples that contained the hydrophober additive.

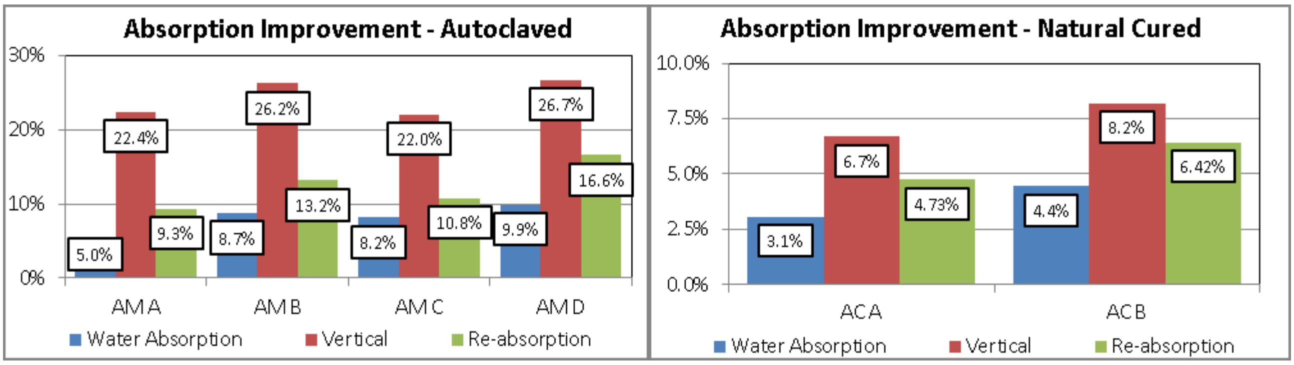


Figure 10 – Water Absorption Improvement

MINI HATSCHEK TRIAL CONCLUSION

The addition of the Silicone Resin Hydrophober to the mix formulations did not have any impact on the Hatschek process. The results of the measurements of the process parameters during the trials were normal and the running parameters of the machine did not need any readjustment to compensate for the addition. This indicates minimal or no upset to the process on a production scale. The results and parameters of the Mini Hatschek machine are attuned to the production process and render a high degree of correlation. The confidence level of how the trial formulation would perform on production scale has been proven with historical data and numerous successful implementations. The strength and integrity testing of the samples revealed that all the samples passed the requirements for a seamless and smooth inclusion to any Fibre Cement production process irrespective of the formulation or curing technology selected.

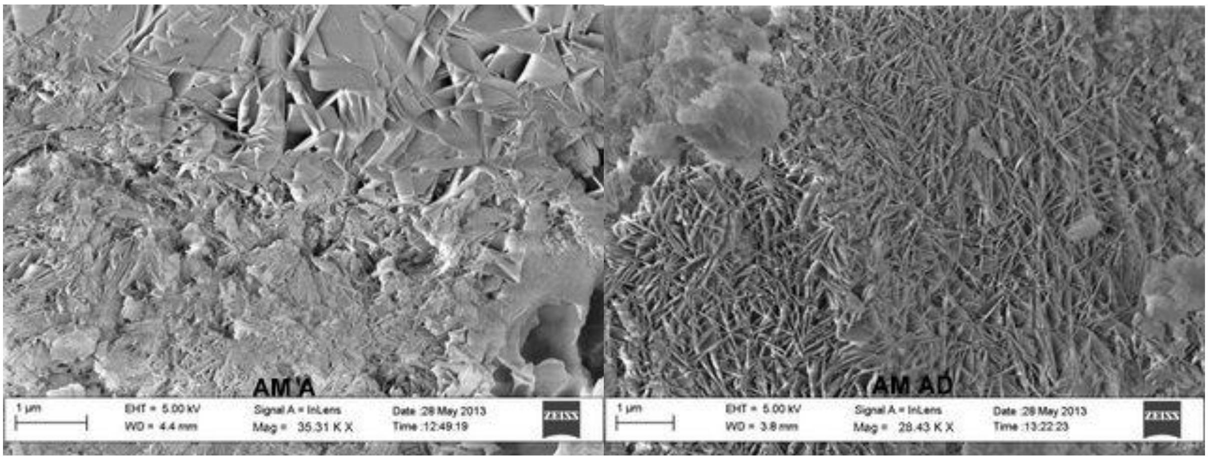


Figure 11 – Electron Microscope images of AM A – and AM AD

The benefit resides with the reduction in the Water Absorption of Fibre Cement. Water is inherently necessary for the cement hydration but once the matrix is formed the influence of water in the matrix creates various problems for manufacturers. The only way to overcome tendency of the matrix to absorb water was to manufacture at a higher density or to stack press the product. This hydrophober additive reduces the ability of the matrix to absorb water without changing the porosity. The results for Water Absorption measured in the conventional method clearly indicate the value of which the matrix repels the water therefore reducing the absorption. This repelling characteristic of the Silicone Resin is visible in the Vertical Absorption test where the surface of the pore structure resists the penetration of water. The surface of the pores has to be different from that of the standard. Figure 11 shows the SEM analysis, Electron Microscope pictures of unmodified and admixture board. The crystal formation of the standard formulation (not admixtured) is not uniform and varies in density. Whereas the crystal formation on the sample that contains the hydrophober is well distributed and creates many small pores. It is suggested that the observed pores structure further reduce the water penetration in the boards. Further studies are on going to better understand the impact of the silicone resin in the cement hydration processes. This will hopefully helps to understand the difference observed in Figure 9.

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