D-2-3 New silicone-resin-based integral water repellent for cementitious materials

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ABSTRACT: This paper describes the use of a new emulsion/microencapsulation of a silicone resin as integral water repellent for cement-based matrix and fibre reinforced cement boards. The impact of the new emulsion as a hydrophobic admixture in mortar on water uptake, cement setting time and mechanical properties is given. The impact of adding this emulsion/microencapsulation of silicone resin in mortar or lab made fibre reinforced cement board composition is illustrated. Impact on the water uptake and efflorescence of the modified material was evaluated. Mechanism which can explain the retention of the emulsion into the FRC boards is suggested.

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, scaling due to freeze-thaw cycles, chemical attack and corrosion to reinforcing steel. Post treatment of silane/siloxane water repellent has demonstrated to be a reliable, long lasting solution to minimize water penetration within inorganic construction material [1,2]. In the last 5-10 years, emulsion or powder of silane, siloxane or silicone resin-based additives started to be used as “integral water repellent” in mortar and concrete [3-4]. This is now an established technology, of which benefits are well accepted [5-6]. This document describes a new integral water repellent concept based on a microencapsulated silicone resin. Impact of the new additive is illustrated in mortar and fiber reinforced cement boards (FRC).

Alkoxy silanes and alkoxy silicone resin.
Silanes are molecules based on one silicon atom which bears four substituents. Alkyl trialkoxy silanes (see Fig. 1) are used to formulate water repellents, either for post-treatment or admixture as they have good reactivity towards inorganic, silanol-rich surfaces. Upon hydrolysis and condensation, silanes create a resinous network which can bind covalently to the surface of inorganic materials. The aliphatic chain (i.e. isobutyl or octyl chain) confers the hydrophobic character to the treated substrate and resistance against alkaline environment.

Silicone resins are obtained by a sequence of controlled hydrolysis and condensation reactions of individual or mixtures of silanes. Silicone resin with alkoxy groups and hydrophobic alkyl groups can be designed such as to diffuse within the cement matrix and react with the pore's surface. The reaction leads to a chemical anchorage to the treated materials, while the alkyl group provides the hydrophobic character to the treated surface.

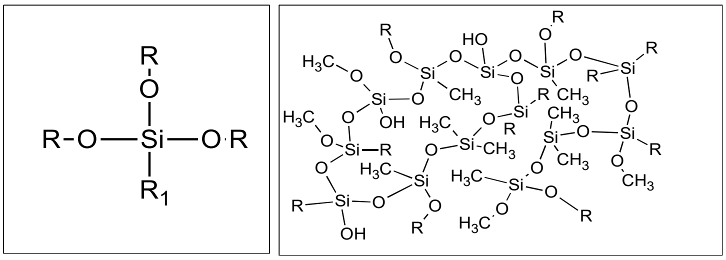

Fig. 1. Structure of an alkyl trialkoxysilane and schematic representation of a silicone resin (R can be ethoxy, methoxy, R1 can be methyl, phenyl or octyl group)

It is often the case that the neat silanes, siloxanes or silicon resins used as water repellent active materials need to be further formulated to enable their effective use. Preparation of oil-in-water emulsion enables their easy incorporation and dispersion in cement, mortar or concrete slurries.

Despite their increased interest as integral water repellent for cement-based materials, conventional silane or silicone resin emulsions cannot be used in a Hatschek process for the making of Fiber reinforced cement board due to the likelihood of having silane droplets being flushed away during the filtration process.

In order to enable the use of integral water repellent for FRC, a new generation of integral water repellent for fibre-reinforced cement board based on a specific silicone resin was developed and which will be named IE 6686 in this document. The silicone resin is emulsified and microencapsulated in a silica-based shell, which leads to the protection of the silicone resin and provides ease of mixing/dispersing into water. This core-shell microencapsulation has been designed to bring additional benefit when used in a cement-based matrix. Being an oil in water emulsion/microencapsulation, it is easy to mix and easy to disperse into cement-based slurry. This new generation of silicone resin micro-encapsulation/emulsion was developed to have low impact on cement hydration processes and to be retained into the cement board when used in Hatschek process. By design, this emulsion is destabilised at high pH, high calcium liquid medium (typical from cement-based slurry) such as droplets of silicone resin are retained into the cement matrix.

The silica-based shell is also designed to delay the delivery of the silicone resin into the cement matrix, which can be very beneficial in some other cement-based material like the foamed or aerated concrete. This document will illustrate the behaviour and 'hydrophobic performance" of the new silicone resin micro encapsulation and/or emulsion in cement matrixes which will be compared with the behaviour of a conventional silane emulsion in a filtration process.

In this document, the phrasing "Hydrophobic performance" will describe the extent to which an additive used as integral water repellent in a cement matrix (mortar for example) or fibre reinforced cement board formulation can decrease significantly the tendency of final material to absorb water by capillary action.

METHODOLOGY, RESULTS AND DISCUSSION

IE 6686 as integral water repellent in mortar

Impact of addition of IE 6686 silicone resin emulsion/microencapsulation in a cement matrix was assessed on mortar.IE 6686 is an emulsion/microencapsulation of a silicone resin which contain 30 wt % of active material. "Hydrophobic performance" is compared with a conventional silane emulsion, IE 6692, which contains 52.5 wt % of active material.Efficiency of IE 6686 as integral water repellent in a cement matrix was assessed by preparing simple mortar modified by the addition of IE 6686 within the slurry.

A set of mortar blocks were prepared according to EN 196-1 Standards using a CEM I 52.5 N cement with a normalised sand/cement ratio of 3/1 and a water/cement ratio = 0.5. Mortars with either no additive (as reference), with IE 6686 (containing 30 wt % silicone resin active content) at 0.1% and 0.5% vs. the overall dry mix weight were prepared. For comparison purposes, a silane emulsion (named IE 6692 containing 52.5% active content), promoted as integral water repellent for concrete, was tested at the same dosage levels (wt %).Mortar blocks were left in a climatic chamber at a minimum of 90% relative humidity (RH). After one day, the samples were demolded and placed back in the climatic chamber at 90% RH. After one-week cure, the samples were tested for mechanical properties. After measurement of mechanical properties, they were further dried at 50°C till constant weight and re-equilibrated at room temperature for one day in the lab.

Values for the compressive strength are plotted as a function of the integral water repellent addition level in Fig. 2. As described in literature [7], overdosing of silane emulsion in a cement matrix can lead to moderate drop of mechanical properties. It can be observed that contrarily to conventional silane emulsion, addition of the new silicone resin emulsion has a minimal impact on mechanical properties of modified mortar specimens.

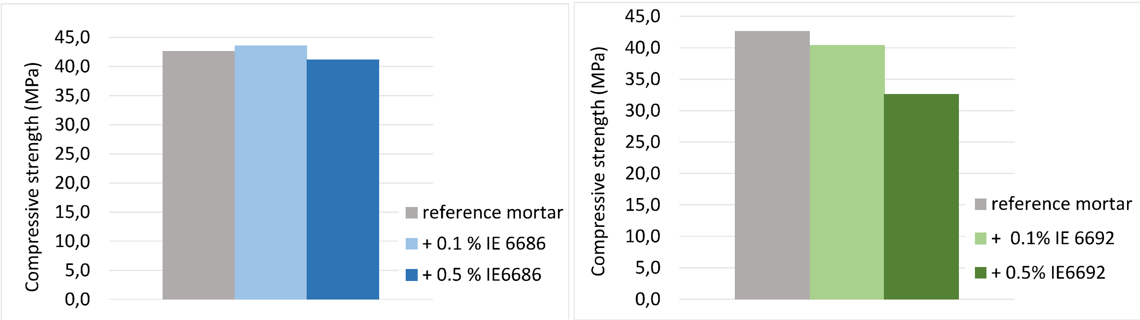

Fig. 2. Compressive strength of reference mortar and mortars modified with 0.1% and 0.5% (vs the weight of dry mortar composition) of IE 6686 and IE 6692 7 days cure).

Impact of IE 6686 addition on cement hydration

Heat of hydration of two reference cements, a Portland cement CEM I 52.5 R LA (called CEM 1 in this text, referred as C1 in the graph) and a blast furnace slag (BFS) cement CEM III/A 42.5 N LA (called CEM 3 in this text, referred as C3 in the graph) were measured. Cement paste were used as such or modified with 1 wt % of the silicone resin emulsion/microencapsulation (IE 6686) or 1 wt % of the silane emulsion (IE 6692). Name of the cement paste has been given as follows: C1 = pure cement; C1E = CEM 1 + 1% IE 6692; C1M = CEM 1 + 1% IE 6686; C3 = pure CEM 3; C3E = CEM 3 + 1% IE 6692; C3M = CEM 3 + 1% IE 6686.

The heat released during the hydration of the cement pastes was followed by isothermal conduction calorimetry (Fig). The experiments were done at a fixed temperature of 20°C. The obtained heat flows are normalized on the mass of cement. All cement pastes showed an initial hydration peak after 10-20 min. This exothermic peak corresponds to the initial hydration reaction of the calcium aluminate phase (C3A) and free lime.

After the initial hydration peak, reactions slow down as shown by a dormant period, which is longer in the pastes with BFS cements (C3, C3E and C3M). This is followed by a period of low hydration activity. The dormant period is longer for the samples with emulsion E (C1E and C3E), on contrary, the admixture M does not modify this hydration step in comparison with the neat paste.

This effect also indicates that the reaction mechanism of the microencapsulated resin and cement is different than the one of the emulsion. The silane monomer from the emulsion attach to the cement grain surface. Due to this, the ability of the water molecules to hydrate the cement is somewhat reduced. Consequently, both the kinetics and the extent of cement hydration are slightly modified. On the contrary, it is hypothesised that the microcapsules delay the resin release long enough so the cement hydration occur as for the cement paste without any additive.

Addition of the silane emulsion IE 6692 in a cement paste lowers the total heat flow for both cements by approximately 7%. Furthermore, it causes a longer dormant period.On the contrary, the new silicone resin emulsion/microencaspulation allows roughly the normal hydration of the cement paste. The total heat released, as shown in Fig. 3 is hardly modified for the cement paste containing the silicone resin emulsion/microencapsulation.

Initial setting time (IST) and final setting time (FST) were measured according to Vicat needle test EN 196-3 and this showed that addition of IE silane emulsion in CEM-1 or CEM-3 retards IST by 30 min and FST by 50 min (data not shown in this paper) as compared to cement paste free of IE 6692 silane emulsion. Addition of the new IE 6686 has very little to no impact on setting time.

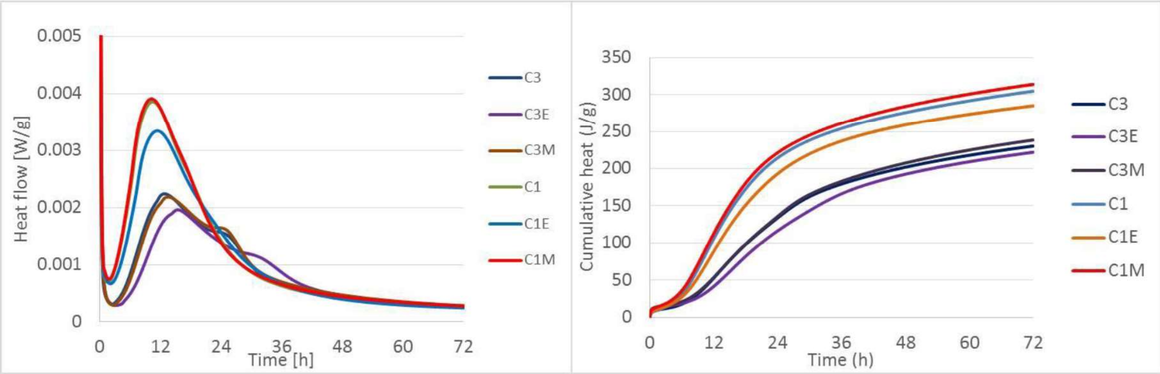

Fig.3. Heat evolution (left hand side) and cumulative heat evolution (right hand side) of cement pastes based on CEM 1 and CEM 3 cements (C1 = pure cement; C1E = CEM 1 + 1% IE 6692; C1M = CEM 1 + 1% IE 6686; C3 = pure CEM 3; C3E = CEM 3 + 1% IE 6692; C3M = CEM 3 + 1% IE 6686).

Resistance to water ingress

Resistance of mortar blocks modified with the new silicone resin emulsion/microencapsulation (IE 6686) and conventional silane emulsion (IE 6692) to water ingress was assessed by capillary absorption. Specimens of reference and modified mortars used for the mechanical properties measurements were placed in a vat so that they protrude from water (see Fig. 4). The base of the blocks is in contact with water in order to enable capillarity absorption.

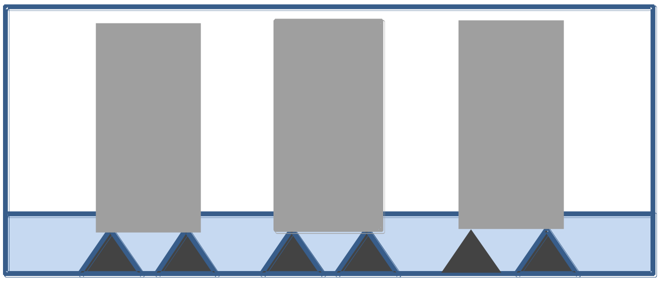

Fig.4. Experimental set up used to measure water uptake by capillarity of reference and modified mortar blocks as a function of time

At fixed times, samples were gently removed from water, quickly towelled, and weighed. The increase of weight (Wx) is reported as wt % of water uptake vs initial dry weight (Wi). The percentage of water uptake is calculated using the following formula:

$$\text{percentage of water uptake} = \frac{W_x - W_i}{W_i} \times 100$$

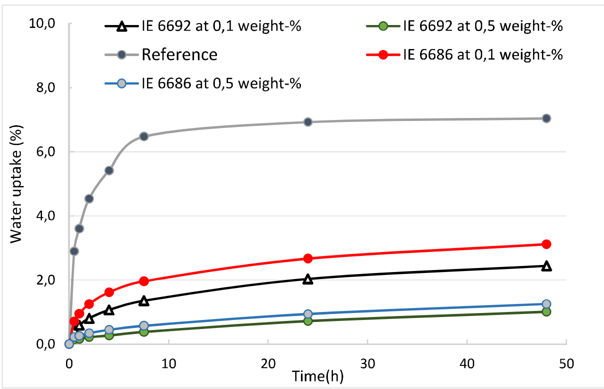

Fig.5. Water uptake by capillarity of reference and modified mortar blocks (modified with a silane emulsion – IE 6692- or the new silicone resin emulsion – IE 6686) as a function of contact time with water.

Fig. 5 is showing the increase of water uptake by the blocks (as % of initial dry blocks) as a function of contact time with water. Mortar modified with either the silane emulsion (IE 6692) or the silicone resin emulsion (IE 6686) are showing much reduced water absorption as compared with the reference mortar.Despite the lower active content of the silicone resin emulsion/microencapsulation, the reduction of water uptake by modifying mortar with IE 6686 is similar if not sometimes better than what is obtained when silane emulsion containing a higher content of active species is used.

Resistance to efflorescence

Impact of admixing IE 6686 in a cement matrix on secondary efflorescence was assessed by placing modified and reference mortar blocks for a couple of days in a saturated sodium chloride solution. The blocks coming from the measurement of the mechanical properties were used, which means they were "pre cracked", in order to make this efflorescence test more challenging. A mortar made with OPC and lime was used for this set of experiments.Migration of water (above the initial level of water in the container) containing dissolved salts through the cement matrix followed by evaporation leads to crystallisation of salts crystals at the surface of the mortar blocks (see Fig. 6). Although simple, this experiment illustrates visually the movement of water within the pores system of a cement matrix.

Addition of IE 6686 as integral water repellent leads to a strong reduction of the efflorescence as limited salt crystallisation is observed at the surface of the modified mortar blocks, even at the lowest IE 6686 addition level. As soon as the IE 6686 addition level reaches 0.25 wt %, almost no crystal formation can be visually observed at the surface of the blocks, above the initial level of the sodium chloride solution.

Table 1. Increase of weight of reference and modified mortar blocks after being in contact with a saturated sodium chloride solution for 3 days.

Salt build up	(g)	Normalized increased of weight due to salt ingress
Reference block	4.87	100%
0.1% IE-6686	1.39	29%
0.25% IE-6686	0.17	3%
0.5% IE-6686	0.15	3%

Mortar blocks were weighed before being placed in contact with salt solution. They were re-weighed after having been in contact for 3 days and dried. Increase of weight due to salt ingress is reported in table 1 showing a strong reduction of salts ingress into the bocks when they are modified with IE 6686.

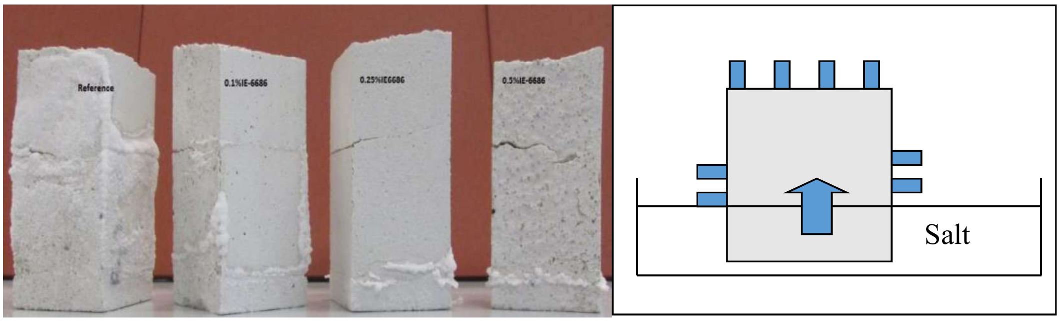

Fig. 6. Picture of set mortar blocks modified with increasing content of IE 6686 (from left to right, 0, 0.1, 0.25 and 0.5% IE 6686 vs dry mortar weight) placed in contact with a saturated sodium chloride solution for several days and further dried before picture is taken. Decreased precipitation of salts at the block surface illustrates the resistance against capillary movement of water and subsequent efflorescence.

Use of IE 6686 as integral water repellent in Fibre Reinforced Cement boards

Fibre reinforced cement (FRC) boards were prepared in the lab to assess the efficiency of IE 6686 as integral water repellent. A simple FRC formulation made of 80% of Ordinary Portland cement, 10% of cellulose fibres and 10% of fine sand was used.

The solid content of the final slurry was set at 20 wt % in order to ease the filtration process at the lab scale.10 g of virgin cellulose fibres sheets were cut into smaller pieces and placed in a 500 mL beaker. 250 mL of water was added and mixed with a lab mixer for 2 min at 700 RPM to obtain a homogenous slurry. 250 mL of water as well as 10 g of sand were added and mixed for 1 min at 500 RPM.Still while stirring, 80 g of cement (CEM II 32.5) were added. Stirring was maintained for additional 3 min.

Integral water repellent was then added and the slurry was further mixed for 2 min. Addition level of IE 6686 was increased from 0.1 wt % up to 2 wt % vs the dry formulation of the FRC boards.The slurry was then filtered on a Büchner funnel of 14 cm in diameter (filtering under vacuum generated with a venturi water pump in order to mimic Hatschek process).The boards were removed from the Büchner funnel, placed between two metallic plates and pressed under a pressure of 1.8 ton for 1 min.The boards were placed in a sealed plastic bag stored at room temperature for 7 days in order to cure the boards in an atmosphere at 100% relative humidity.After 7 days, the boards were, still in the plastic bag, placed in an oven at 50°C for 4 days, then removed from the bags and equilibrated at Room Temperature for one day.

Resistance to water ingress

Reference and modified boards (after setting and drying) were placed on soaked sponge (such as to have 0.5 mm of water in contact with the boards) and were weighed as a function of contact time with water. Water absorption (as % of absorbed water vs initial dry weight) upon time was calculated as explained before and reported as a function of time in Fig. 7.

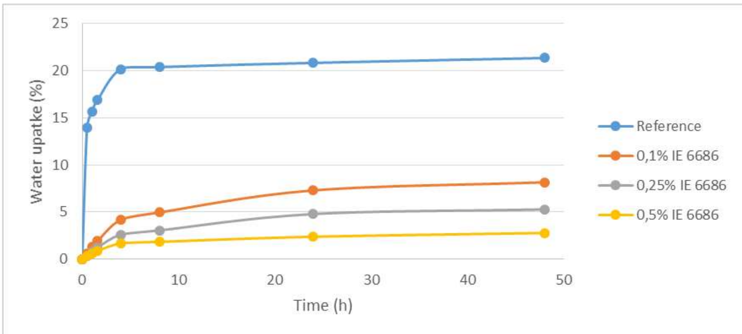

Fig.7. Plot of % of water uptake (as % of initial dry weight of the boards) of lab-made FRC boards modified with increasing content of IE 6686 as a function of contact time with water.

Fig. 7 clearly shows that addition of IE 6686 into the FRC board formulation leads to a strong reduction of water absorption by the boards. The reduction of water uptake tends to level off at higher IE 6686 content.Measurement of contact angle of water droplets at the surface of these lab-made boards is difficult to measure due to the fact that the surface is not flat. Fig. 8 is showing a water droplet placed at the surface of a board modified with 0.25 wt % of the silicone resin emulsion IE 6686.

Mechanism of IE 6686 retention into FRC boards

It is key that an integral water repellent used for making of FRC boards remains trapped into the matrix and is not flushed during the filtration step of the Hatschek process. The mechanism of retention in the boards of the first generation of silicon-based integral water repellent for FRC [6] was based on the extremely low solubility of neat silicone resin (Z-6289) into the cement/cellulose slurry. Experimental results suggest that upon mixing, the finely dispersed silicone resin droplets are adsorbing at the surface of cement particles, where they can react with silanol groups, to provide the integral water repellence. This adsorption fixes the silicone resin droplets and they are not flushed away during the filtration step.

The new IE 6686 silicone resin emulsion/microencapsulation was designed to be destabilised in the high pH, high calcium ions environment which can be found in the cement/cellulose slurry. This was demonstrated by diluting the silicone resin emulsion IE 6686 in high pH solution (pH 12.5) prepared with sodium hydroxide (dilution of IE 6686 at 1%). A slow destabilisation was observed. The turbid mix became slowly clear with a clear phase separation and the presence of an oil phase (coming from the liquid silicone resin) at the top of the flask (Fig. 9). IE 6686 samples were also mixed in high pH solution prepared with calcium hydroxide (Fig. 9c). A quick destabilisation of the colloids was observed with the occurrence of a flocculation process. The mixture sedimented with presence of a floc at the bottom of the flask and a clear aqueous phase in the rest of the flask. The same behaviour is observed when IE 6686 is mixed in a pH 12.5 solution prepared sodium hydroxide but with further addition of calcium chloride to bring calcium ion into the solution (Fig. 9b).

Fig. 8. Picture showing a water droplet placed at the surface of a lab-made FRC boards modified with 0.25 % IE 6686 vs the dry weight of the board formulation.

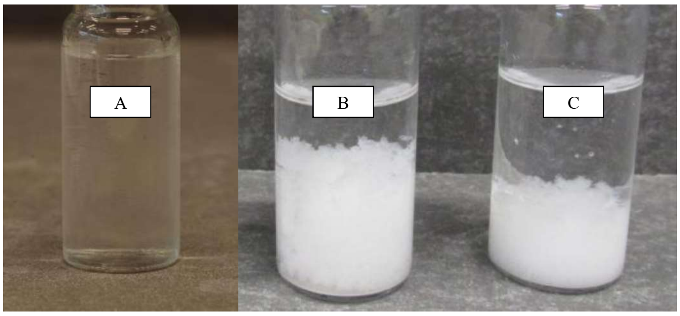

Fig. 9. Pictures showing IE 6686 silicone resin emulsion diluted (1% IE 6686 into the solution) in a pH 12.5 solution prepared with sodium hydroxide (A) with calcium hydroxide with further addition of calcium chloride (B) and calcium hydroxide (C).

It is hypothesised that the silica shell which is protecting the silicone resin is dissolved at high pH in the presence of sodium cations. This can be explained by the formation of the soluble sodium silicate. If the calcium cation is present, the mechanism of the shell dissolution is different. It is hypothesised that formation of water insoluble calcium silicate is formed at the surface of the small core-shell droplets, at high pH, high calcium solution, leading to quick flocculation, and further protection of the silicone resin within the shell. This does not stop the shell dissolution, but significantly reduces its ability to be attacked by the OH^- ions. This flocculation process is used to insure trapping of the silicone resin emulsion into the FRC matrix upon filtration.

Retention of IE 6686 in FRC boards

Lab-made boards were prepared as previously described [6]. One board was modified with nothing (reference board), one with 2 wt % (vs dry weight of FRC components) of IE 6686 and 2% of a conventional silane emulsion, IE 6692. Filtrates were collected and compared. High addition level of the two additives was selected on purpose to be able to visualize transfer of emulsion into the filtrate. Pictures of the flasks collecting the filtrate are reproduced in Fig. 10. Both original IE 6692 and IE 6686 emulsions are conventional milky white liquids (not shown in Fig. 10).

Filtrate obtained upon filtration of the reference slurry (no integral water repellent) is transparent homogenous solution. Filtrate obtained upon filtration of the slurry modified with IE 6686 is very similar, showing that silicone resin droplets are properly retained into the FRC boards structure. Filtrate obtained upon filtration of the slurry modified with IE 6692 silane emulsion is a homogenously turbid dispersion, showing that part of the silane droplets has been transferred during the filtration into the filtrate.

Fig.10. Filtrates obtained upon filtration of reference FRC slurry (no integral water repellent = A) and FRC slurries modified with 2% of IE 6686 (B) or 2% of IE 6692 silane emulsion (C).

CONCLUSIONS

This work illustrates the strong positive impact of adding the new emulsion of silicone resin (IE 6686 in this case) as integral water repellent in a cement matrix and more specifically in a fibre reinforced cement board.This set of experiments clearly demonstrates that adding IE 6686 in a cement matrix decreases the tendency of the matrix to absorb water by capillarity while having little to no impact on cement hydration processes.

The positive impact of admixing IE 6686 in FRC was clearly evidenced by properties such as resistance against efflorescence. The study suggests that the designed instability of IE 6686 at high pH and high Calcium content insures retention of the emulsion into the FRC boards, despite the filtration process used in a Hatscheck process.

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