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Dynamics of early skin formation of tiling mortars investigated by microscopy and diffuse reflectance infrared Fourier transformed spectroscopy

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ABSTRACT

A freshly applied mortar layer is exposed to the environment and forms a skin in the following minutes. Skinning changes significantly the surface properties and therefore limits application procedures. In the case of a tile adhesive, the skin that is formed before the tile is embedded can reduce resulting adhesion properties. Reflected light microscopy reveals that surface "lakes" disappear between 5 and 10 min after mortar application and DRIFTS (diffuse reflectance infrared Fourier transformed spectroscopy) indicates that films of organics and carbonates form simultaneously at the surface.

1. Introduction

A skin is a surface layer with different properties compared to the body underneath. A skin can be very thin, in the range of a micron or tens of microns, but as it coats the material it controls entirely the surface properties.

Skinning describes the generation of a skin, typically of a curing system, the surface of which is exposed to the environment. In the case of a paint, skinning limits the workability time, because the brush will leave marks in the skin which cannot heal anymore. In the case of an adhesive, skinning can occur during the period of exposure, which starts with the application of the adhesive as a relatively thin layer onto the base layer (substrate), and which ends with the laying of the covering layer (e.g., a tile). Such a skin can drastically influence the bond strength between adhesive and covering layer. Therefore, application systems and working techniques with a large variation of the exposure period, and thus, a large variation of the degree of skinning must account for the skinning mechanisms.

A typical example is the laying of ceramic tiles. The tile layer applies the adhesive with a toothed trowel onto the substrate, typically a concrete, screed or render. Thereby, he coats an area of 1–2 m^2 with adhesives before he starts laying a series of tiles. Each single tile is laid, loaded and adjusted in its position in order to generate a regular grout pattern. Thereby easily 10–15 min can pass until the last tile of a series is laid. Thus, at this particular location the applied mortar layer was 15 min exposed to the open environment before it was covered by the tile. During this exposure time, a wicking substrate, hot temperatures and wind can cause the formation of a dry skin at the surface of the applied mortar layer. With a simple finger test, the tile layer can assess the degree of skin formation. He presses a mortar rib and if his finger remains dry, then the mortar formed a skin and lost its ability of wetting. In this situation, the tile layer should stop laying tiles and over-trowel the applied mortar in order to create a new mortar surface with proper wetting properties.

The European Standard EN 1347 proposes a method to measure the "wetting capability" of a tile adhesive. Thereby, the mortar is applied with a 6 mm toothed trowel onto a standardized concrete substrate. After 10, 20 and 30 min a 10 × 10 cm glass plate is laid and loaded for 30 s with 5 kg. The "wetting capability" is estimated as the contact area between the mortar and the glass plate as the percentage of its 100 cm^2 area.

Zurbriggen et al. [1] critically investigated the testing procedure of EN 1347 and concluded the following: The observation through the glass plate gives a measure for the deformability of the mortar ribs, which primarily is a function of the mortar's rheology, namely its yield strength. For a majority of mortar formulations this "degree of deformability" is relatively high and delivers values above

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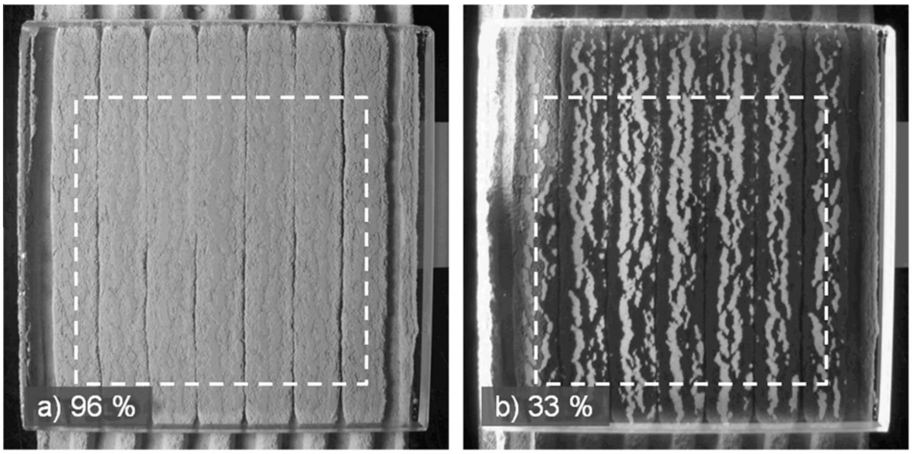

Fig. 1. (a) Photograph of 10 × 10 cm glass plate embedded 30 min after the mortar (formulation F-ref in Table 1) was combed. Sample produced according to EN 1347. Mortar ribs are pressed to a degree of 96 area% (measured within the marked area). (b) Same sample illuminated from the side as described by Zurbriggen et al. [1]. Skin appears dark. Bright wetting area measures 33 area% (measured within the marked area).

90 area%, even after an exposure time of 30 min (Fig. 1a). However, whether or not a deformed mortar rib is capable of wetting the glass plate cannot be observed by EN 1347. This explains, why the results of this particular test are of little relevancy to measure the real capability of a mortar to wet the tile.

However, Zurbriggen et al. [1] demonstrate that a slight modification of the experimental setup of EN 1347 allows one to observe the area of skin at the interface between mortar and glass plate, which correlates with adhesion properties as measured by EN 1346. The modification of the testing setup is a simple change of the angle of illumination by 90°. If the glass plate is illuminated from the side, then the light travels parallel to the interface and due to total reflectance at sites where mortar is in direct contact to the glass, these locations appear bright (Fig. 1b).

Jenni et al. [2] investigated the mechanisms of tile adhesion and found that skinning is a strongly limiting factor. Their work revealed that both, organic (mortar additives) and inorganic (carbonates) substances compose the skin (p. 46 in Jenni et al. [2]). However, their investigations were limited to microscopy on cross-sections of cured samples. The same authors provide electron microscopic evidence for a thin skin at the surface of a cured mortar – so thin it is transparent for back-scattered electrons but can well be seen in the secondary electron mode (Fig. 8 in Jenni et al. [3]).

Bentz et al. [4] investigated the drying of cementitious tile adhesive mortars by X-ray absorption. They confirmed earlier studies (see references therein), which describe a drying front migrating from the surface inwards. In addition, their data indicate a densification front occurring immediately adjacent to the retreating drying front, which is interpreted in relation to the migration of mortar water and therein dissolved and dispersed cellulose ether and small cement particles, respectively.

The exact composition of the skin and the dynamics of its formation under defined environmental conditions is not yet studied, and was therefore, taken to be the goal for this paper. The following key question was asked: How do the surface characteristics, in terms of chemical composition, microstructures and physical properties change within the first 30 min of exposure? A number of analytical methods had to be evaluated and adapted to answer this key question. Because skin forms as a thin coating layer within a relatively short period of time, the priority was given to analytical methods which deliver surface characteristics in (i) a spatial resolution of a few microns and (ii) a time resolution of minutes, as described in the following section.

2. Materials and methods

2.1. Materials

For this study very simple mortar formulations were used (Table 1). "F-ref" is a test formulation from a larger screening program where the influence of different mortar ingredients and environmental parameters were studied.

Formulation *F*1 is similarly composed and represents the reference for formulations *F*2 (contains a liquid dispersion instead of a redispersible polymer powder), *F*3 (contains cellulose ether as its only additive) and *F*4 (contains no additives). This mortar series (*F*1–*F*4) was employed for kinetic studies.

For all experiments, dry mortar ingredients were homogenized before the liquids (liquid polymer dispersion and water) were added. After intense mixing with a propeller stirrer for 1 min, the mortar was let to mature for at least 3 min. Then, it was mixed with a spatula for another 15 s before it was combed with a toothed trowel (6 × 6 × 6 mm) according to EN 1348.

2.2. Methods

2.2.1. Wetting capability of tile adhesives according to a modified EN 1347

The samples are produced according to EN 1347. Thereby, the adhesive mortar is applied with a 6 × 6 × 6 mm toothed trowel onto a standardized concrete substrate. After 10 min of exposure the first glass plate (measuring 10 × 10 cm) is laid and loaded for 30 s with 5 kg. A second and third glass plate is laid after 20 and 30 min of exposure time, respectively. According to EN 1347 one has to estimate the contact area between mortar and glass plate as a percentage of the size of the glass plate (100 cm^2).

The modification of EN 1347 exists in the way the cured samples are illuminated from the side. This allows an optical discrimination between mortar and skin (including entrapped air voids and hollows) which is related to the phenomenon of internal total reflection. Divergent light from the lamp comes in by the flank of the glass plate and is reflected at its boundaries. At locations where the mortar is in good contact to the glass a large proportion of the incident light is reflected because the critical angle for total reflection is nearly 90° (critical angle = arc sin n_{mortar}/n_{glass}, where n_{mortar}, the refraction index of the mortar is assumed to be similar to $n_{glass} \approx 1.5$). At locations where a skin formed, and, therefore, a thin layer of air is enclosed between mortar and glass, much less

Table 1
Mortar formulations.

Ingredient (producer)	Formulations				
	F-ref	*F*1	*F*2	*F*3	*F*4
Portland cement CEM I 42.5R (Heidelbergcement)	40.0				
Portland cement CEM I 42.5 N (Jura cement)		35.0	35.0	35.0	35.0
Quartz sand 0.1–0.3 mm (Carlo Bernasconi AG)	57.5				
Quartz sand 0.1–0.5 mm, H33 (Quarzwerke Frechen)		62.5	62.5	62.5	62.5
Cellulose ether, Culminal C 8564 (Ashland Aqualon)	0.5				
Cellulose ether, MHS 15000 P6 (SETylose)		0.5	0.5	0.5	
Redispersible polymer powder, MP2100 (Elotex AG)	2.0	2.0			
Solids of emulsion, base for MP2100 (Elotex AG)			2.0		
Added water (incl. water from liquid dispersion; F2)	22.0	22.0	22.0	22.0	16.0

of the incident light is reflected, because the critical angle is only *c*. 42° (arc sin n_{air}/n_{glass}, and n_{air}. ≈1). Therefore the skin (in fact, the air inclusion between skin and glass) appears significantly darker.

A detailed description of the analytical setup can be found in Zurbriggen et al. [1].

2.2.2. Open Time of tile adhesives according to EN 1346

After different exposure times (5, 10, 20, 30 min), semi-vitrified tiles (5 × 5 cm) are laid and loaded for 30 s with 2 kg. After 28 days (23 °C/50% rel. humidity), adhesion strength is measured. The longest exposure time with a resulting adhesion strength >0.5 MPa is referred to as the Open Time.

2.2.3. Polarized light microscopy of thin sections

Cured mortar samples are cut. A vacuum impregnation with epoxy resin stabilizes the delicate pore structure during polishing of a face of the sample. The polished face is glued onto a glass slide. When hard, the sample is cut near to the glass slide and the remaining slice is polished down to a thickness of 20–25 μm. Seen through a polarized light microscope, most mortar components in such a thin section are transparent and can be investigated by their optical characteristics.

2.2.4. Surface gloss measured with a "Zehntner Gloss 75°"

Two 4 mm high metal bars were placed in parallel with a spacing distance of 4 cm onto a plastic foil. The fresh mortar was placed in between and trowelled to a thickness of 4 mm. The gloss meter was placed readily over the mortar layer to start measurement at the standard angle of 75°. During a measurement the device was not moved. The reflection values were read from the display and plotted in a diagram.

2.2.5. Reflected confocal light microscopy with an Olympus LEXT

The freshly mixed mortar was filled between two 4 mm high metal bars, which were placed with a spacing distance of 4 cm onto the rear side of a non-porous tile. Then, the mortar was trowelled with a spatula in a 45° angle to produce a 4 mm evenly thick layer. The ready sample was placed under an Olympus LEXT OLS3000 3D laser measuring confocal microscope, which is equipped with a 408 nm violet opto-system to realize a planar resolution of 0.12 μm. A pinhole is provided in a position optically conjugated to a focused position (confocal plane) to eliminate excess light coming from non-focused positions. The acquisition interval for each 3D image was 3 min.

2.2.6. DRIFTS (Diffuse Reflectance Infrared Fourier Transformed Spectroscopy)

The freshly mixed mortar was filled into a polyvinylidene fluoride cup of 12 mm diameter and 4 mm depth and trowelled with a metal spatula in a 45° angle. The sample was mounted into the DRIFTS sample chamber, which was constantly purged by nitrogen. Freshly milled potassium bromide was used as the background.

The spectra were recorded with a Digilab FTS 7000 spectrometer equipped with a DRIFTS accessory from SPECTRA-TECH baseline 1-395.

Generally, DRIFTS is used for the analysis of powders and solids having a rough surface. However we found that DRIFTS is suitable to analyze the composition of an early curing mortar surface. A set of mirrors focuses infrared radiation onto the rough mortar surface from where it is diffusely reflected. An ellipsoidal mirror collects the radiation and sends it to the detector. The signals are converted by the Kubelka–Munk relation into an absorption spectra. The Kubelka–Munk relation is based on a one dimensional model wherein the optical properties on the sample are given by two relevant constants, the absorption and the scattering coefficient [5]. Advantages of DRIFTS are early measurements (immediately after mortar preparation), short acquisition times of about 20 s, and spectral information from 4000 cm^{-1} down to 600 cm^{-1}.

3. Results

Fig. 2 illustrates that a skin at the surface of a mortar (here a self-leveling underlayment; formulation Pc-c in Table 1 of De Gasparo et al. [6]) can be as thin as 1 μm. Under polarized light (Fig. 2b done with crossed nicols) the skin disappears because it is composed of an isotropic material with no birefringence, an indication for its organic composition. This organic skin is confirmed by laser scanning microscopy of similar mortar samples in which different organic additives (which were previously stained by a fluorescent dye) show significant enrichments towards the surface [6].

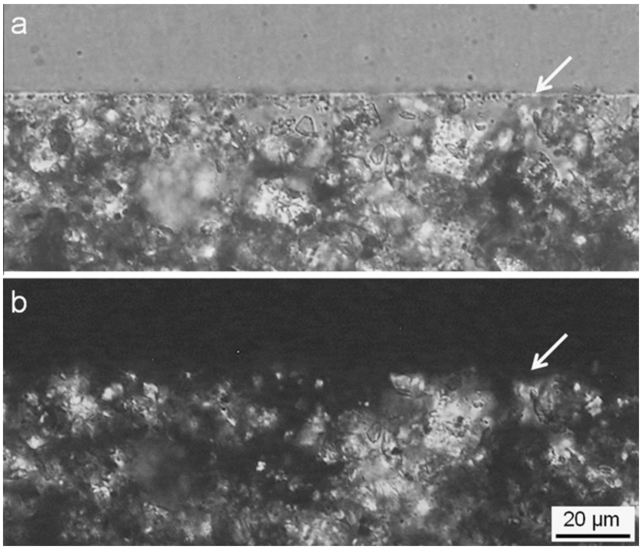

Fig. 2. (a) Transmitted light micrographs of mortar skin (indicated by arrow) of self-leveling flooring compound. (b) Same with crossed nicols.

A skin can also be composed of inorganic substances. Fig. 3 holds microstructural evidence that carbonation can generate a 10 μm thick layer of newly formed calcite within the first 30 min of exposure. Carbonation is a well known neutralization reaction where alkaline cement phases (typically $Ca(OH)_2$) are converted to calcite. Usually, carbonation is described as a long-term process at and near the surface of cementitious materials like concrete, where substantial amounts of cementitious phases are converted. However, to form a micron-thin skin at the surface of a freshly applied cementitious mortar, only minutes are required. The carbonation reaction requires the presence of water and is therefore only active as long as the mortar is wet. With continued drying of the surface, the carbonation reaction is slowed down. As the evaporation front retreats underneath the mortar surface, the carbonation front is migrating too. The micrograph of Fig. 3 shows a cutting mark which was created with a sharp knife 30 min after the mortar (formulation *F*2, Table 1) was applied. After curing the mortar was sampled for thin-section preparation. The polarized light microscope reveals that the carbonate skin (3–4 μm) along the original mortar surface (indicated by arrow in Fig. 3b) is clearly more intense compared to the surface along the V-shaped mark (indicated by arrow in Fig. 3c) which was created 30 min after. Thus, the 30-min mark clearly truncates a surface which was already carbonated to a certain extent. After the creation of the mark, enough water was present at the newly formed surface to allow a weak carbonation reaction to take place. This can also be observed at the surface of marks created 3 h after application, but later marks show no carbonation at their surfaces anymore (data not shown here).

Fig. 4 demonstrates how the wetting area of transparent glass tiles is significantly reduced due to skinning during the first 30 min after application. Under laboratory conditions of 23 °C and 50% relative humidity the wetting area is reduced after 10 min of exposure time (period between mortar application and the moment when the tile or glass plate is laid) to 80 area%. If exposure time is prolonged to 20 and 30 min, the wetting area is reduced to 55 and 33 area%, respectively. The complementary area corresponds to the skin which prevents wetting of the glass interface. Thus, the skin area grows from 20 to 45 and 67 area% as exposure time goes from 10 to 20 and 30 min, respectively. If the measurements are repeated under cold and high humidity conditions (5 °C/80% rel. humidity) then the wetting percentage is significantly improved to values of 90%, 87% and 65%, thus the skinning rate is significantly reduced to 10, 13 and 35 area% (Fig. 4, lower row).

Besides the area percentage, the fracture pattern of the skin is also quite different. Under 23 °C/50% rel. humidity the skin breaks up after 20 min of exposure time along the former edges of the mortar rips (indicated by small arrows in the upper row of Fig. 4). Under 5 °C/80% rel. humidity the skin breaks up in a much more irregular manner, even after an exposure time of 30 min (lower row of Fig. 4).

From a large screening program where different mortar formulations, application techniques, types of substrates and climatic conditions were tested with respect to their influence on the rate of skin formation, the following observations could be made (see Table 2).

As shown in Fig. 4, the climatic conditions have a strong influence on the rate of skin formation. The lower the temperature and higher the humidity, the slower skinning is. The same can be observed in terms of failure modes (Fig. 5) generated by pull-out tests according to EN 1346. In analogy to the test series according to the modified EN 1347 (Fig. 4), the upper sample series of Fig. 5 was laid under 23 °C/50% rel. humidity and the lower series under 5 °C/80% rel. humidity. In both series, the adhesion strength and percentage of cohesive failure decrease with increasing exposure time. But at lower temperature and increased humidity (lower series in Fig. 5), the quality of adhesion is significantly better in terms of both, strength and failure mode.

By naked eye, one can observe how a freshly combed mortar has a glossy surface in the first 5–10 min. A closer look with a confocal reflected light microscope reveals that the macroscopic gloss corresponds to the presence of microscopic "lakes" at the mortar surface (Fig. 6a), which continuously disappear, typically between 4 to 8 min after the mortar was combed (Fig. 6b and c).

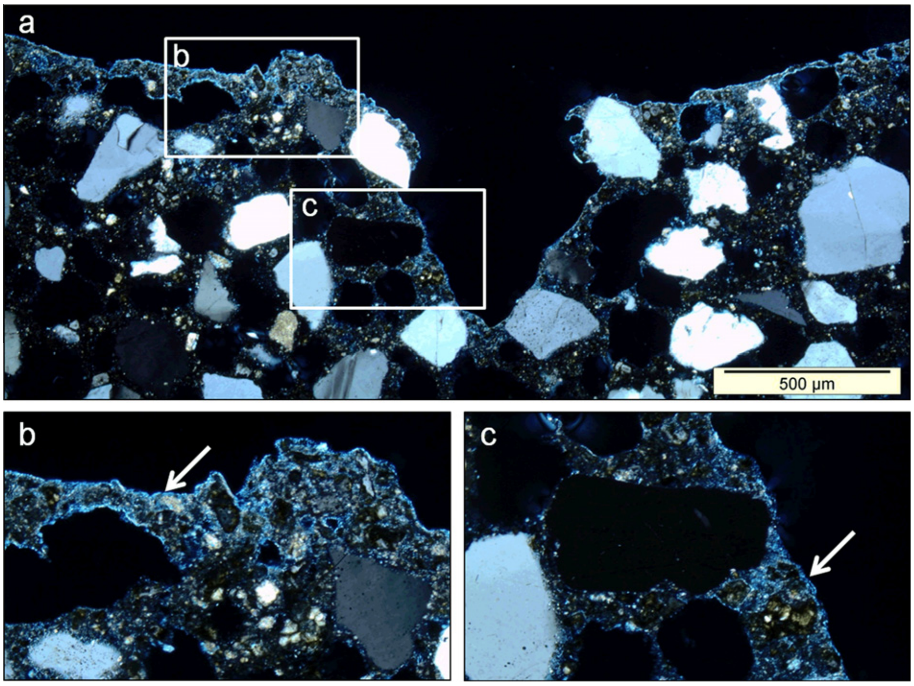

Fig. 3. (a) Carbonate skin truncated by mark, which was created 30 min after application of mortar. (b) Details of carbonated skin (indicated by arrow) at original surface of mortar layer, and (c) at the surface of the 30-min mark (indicated by arrow).

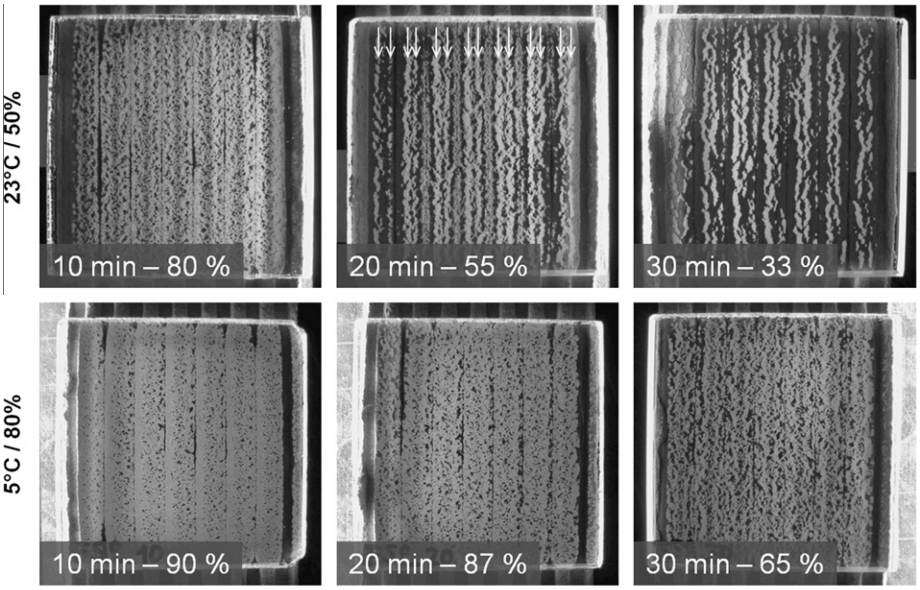

Fig. 4. Wetting capability of mortar (formulation F-ref, Table 1) according to Zurbriggen et al. [1] as a function of exposure time (from left to right 10, 20, 30 min) and climatic conditions as indicated. Glass plates measure 10 × 10 cm.

Table 2
Overview of parameters influencing the dynamics of skin formation.

Parameters	Influence on skin formation
Application	
Larger toothed trowel	Skinning is retarded ☺
Environment	
More load on tile	Skin is more sheared ☺
Higher temperature	Skinning is accelerated ☹
Higher humidity	Skinning is retarded ☺
More wind	Skinning is accelerated ☹
Formulation	
More or finer cement	Skinning is accelerated ☹
Add retarder	Skinning is retarded ☺
Add accelerator	Skinning is accelerated ☹
More limestone powder	Skinning is accelerated ☹
More sand	Skinning is not influenced 😐
Add cellulose ether	Influence according to type 😐
Add redispersible powder	Influence according to type 😐
Add more water	Skinning is retarded ☺
Substrate	
Higher porosity	Skinning is accelerated ☹

The degree of reflectivity can also be measured by the help of a surface reflectance meter. Fig. 7 shows two reflectance curves. The difference between the two formulations is that *F*3 contains no polymer emulsion. Therefore, the higher reflectance of *F*2 might originate partially from a water film which disappears and partially from reflecting polymer films which form simultaneously. However, in both cases (*F*2 and *F*3) the relative intensity of reflectance is highest in the first couple of minutes (1–4 min.) and the decrease in signal is fastest at about 8 min.

To get a clearer view of the original chemical composition of the mortar surface and how it changes as the skin is formed, Diffuse Reflectance Fourier Transformed Infrared Spectroscopy (DRIFTS) was applied. It must be said at this point, that DRIFTS is not a straight forward method for the analysis of a wet mortar surface, because it was primarily developed to analyze dry and fine powders. In contrast, strongly reflecting particles and wet films cause dominant artifacts and do not allow the collection of a DRIFT spectra. However, the dynamic scenario of a wet mortar surface which continuously dries and successively exposes a porous composite material containing organic and mineral particles can nicely be portrayed by DRIFTS (Fig. 8). In comparing the DRIFT spectra of different mortars free of organic additives (formulation *F*4, Table 1), with cellulose ether (formulation *F*3), with cellulose ether and polymer emulsion (formulation *F*2), and with cellulose ether and redispersible polymer powder (formulation *F*1), characteristic absorption bands for each ingredient could be identified. With this information, the DRIFT spectra could be interpreted. To study the changes in chemical composition, DRIFTS was applied in the kinetic mode, which allowed for the extraction of spectra at any time. Fig. 8 shows the data of two DRIFTS experiments. In the first experiment, the dry mortar ingredients of formulation *F*1 were mixed with normal water (Fig. 8a) and in the second experiment the same dry mortar formulation was mixed with deuterated water (Fig. 8b). The comparison of the two diagrams confirms that the "artifacts" caused by a strongly reflecting water film, which disappears at about 10 min, shows up by "strange absorption bands" at about 3400 cm^{-1} and 2500 cm^{-1} in case of H_2O and D_2O mixing water, respectively. In fact, these "strange absorption bands" migrate with time from 3650 to 3450 cm^{-1} in case of H_2O mixing water (Fig. 8a). In the case of D_2O mixing water, analogous bands shift from c. 2700 to 2500 cm^{-1} (Fig. 8b).

Complementary to the continuous disappearance of these reflecting water films, characteristic absorption bands for aliphates (C–H at 2939 cm^{-1}), carbonyl groups (C–O at 1740 cm^{-1}) and carbonates (CO_3 at 2517 cm^{-1}) develop, which can be attributed to the deposition of cellulose ether, latex (main component of redispersible polymer powder and polymer emulsions) and the formation of carbonates, respectively.

Another interesting detail can be seen in Fig. 8b. By using D_2O to prepare the fresh mortar, the signals of the mixing water shift to 2500 cm^{-1} and other types of water absorption bands show up at 3400 cm^{-1}. These could represent chemically bound water of cement hydrate phases. The fact that their signal intensity decreases might be related to the ongoing carbonation at the mortar surface, on account of such early formed hydrate phases. These hydrate phases could also have their origin in the pre-hydration of the dry mix during its shelf life.

Once the characteristic absorption bands are identified, the kinetic measuring mode allows one to extract intensity curves with a time resolution on the order of 30 s. Fig. 9 shows such kinetic data

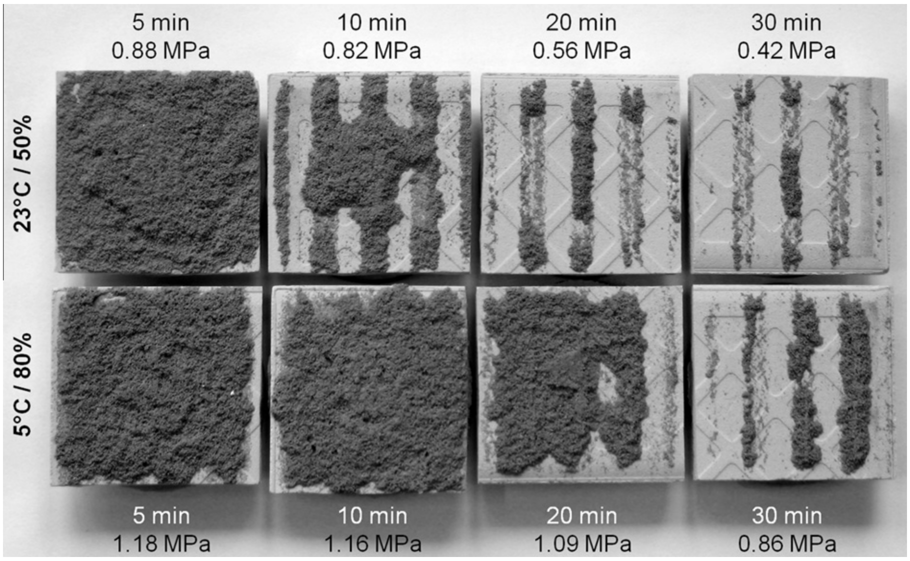

Fig. 5. Fracture patterns after pull-out test according to EN 1346 (so-called "Open Time test"). The tiles were laid 5, 10, 20 and 30 min after application of the adhesive mortar (formulation F-ref, Table 1) under normal climate (23 °C/50% rel. humidity, upper row) and cold and humid conditions (lower row, 5 °C/80% rel. humidity).

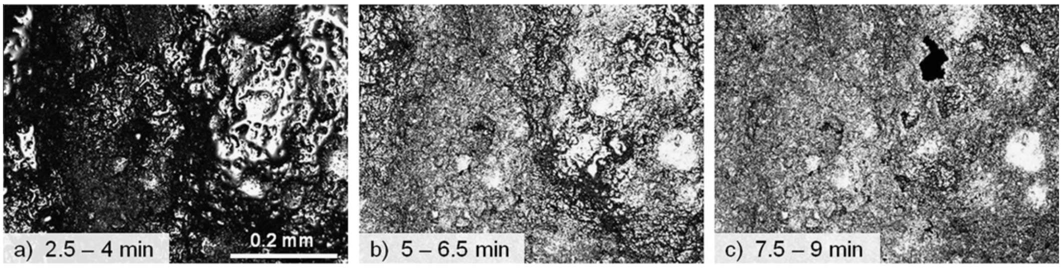

Fig. 6. Series of reflected light micrographs which show the disappearance of "water lakes" at the mortar surface (formulation *F*1, Table 1). Noted time intervals indicate acquisition times.

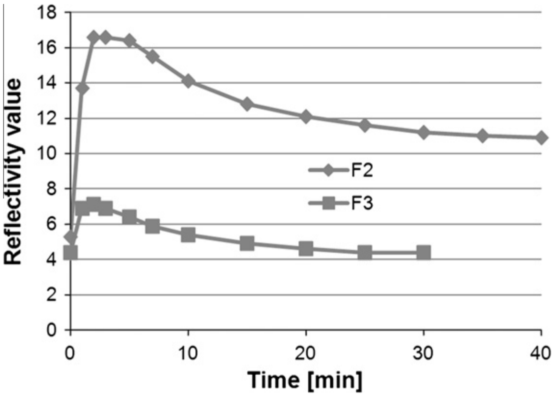

Fig. 7. Relative surface reflectivity measured by a "Zehntner Gloss 75°" for two formulations, *F*2 and *F*3 (Table 1).

for four formulations (*F*1–*F*4). The shift of the OH–band from 3630 cm^{-1} to 3420 cm^{-1} (Fig. 9a) allows one to trace the disappearance of the "water lakes" at the mortar surface. This shift occurs mainly within the first 10 min. Formulation *F*4 (without any additives; see Table 1) shows a completely different curve. It is a simple sand-cement mixture containing no cellulose ether or other additives. Therefore, *F*4 has no water retention ability and does not show the "surface lakes" at all. In fact, *F*4 represents no thin-bed tile adhesive, because its lack of cellulose ether does not permit its application with a toothed trowel. Furthermore, the lack of cellulose ether causes a very reduced water demand of only 16% (Table 1).

The aliphate absorption band (Fig. 9b) is mainly caused by the polymer emulsion (*F*2) or redispersible polymer powder (*F*1) and partially by the cellulose ether (*F*3 which contains no polymer emulsion or redispersible polymer powder). However, all aliphate absorption curves show a maximum during the first 4 min. The decrease in signal between 4 and 10 min before the curves slightly increase in intensity is not understood yet.

The carbonyl absorption bands (Fig. 9c) are only seen in formulations *F*1 and *F*2 which contain polymer emulsion or redispersible polymer powder. Their intensities increase mainly during the first 10 min and then reach a stable plateau.

Preliminary measurements with pure carbonate powders revealed the absorption band at 2517 cm^{-1} to be a characteristic signal for $CaCO_3$ which is not overlaid by any of the absorption bands of the other mortar phases. However, for the carbonate absorption curves (Fig. 9d), only formulation *F*4 (without any organic additives) shows an initial strong increase of the signal followed by a pseudo-plateau. The curves of the other formulations (*F*1–*F*3) reach a small maximum at 3 min and decrease to zero by 10 min.

4. Discussion

DRIFTS, in the continuously measuring kinetic mode, delivers a method (i) with a spatial resolution of a few microns (given by the strongly limited depth of the signal, which is on the order of a few

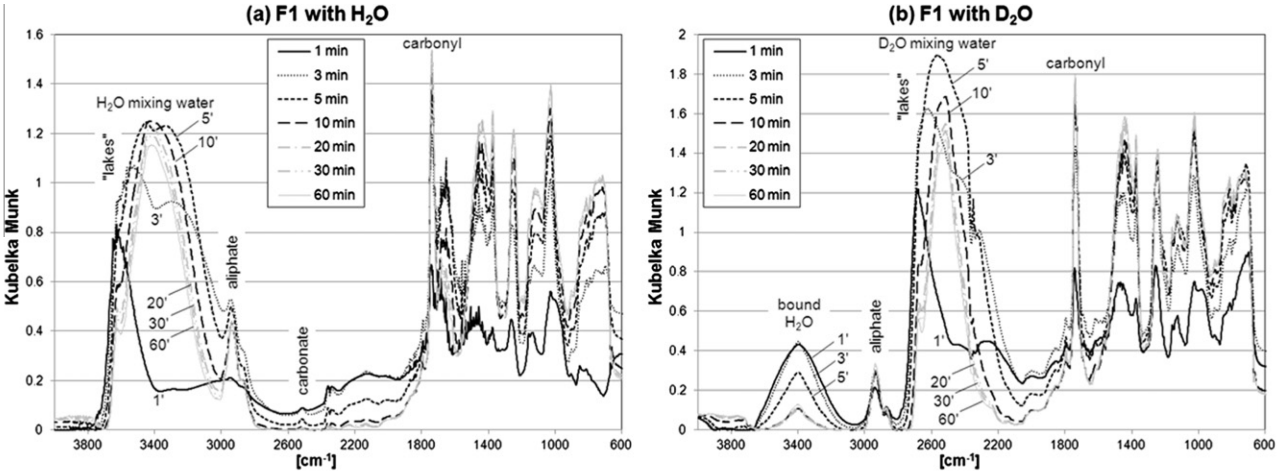

Fig. 8. DRIFT spectra taken at 1, 3, 5, 10, 20, 30 and 60 min. after application of (a) mortar (formulation *F*1, Table 1) mixed with normal water and (b) mixed with deuterated water (D_2O).

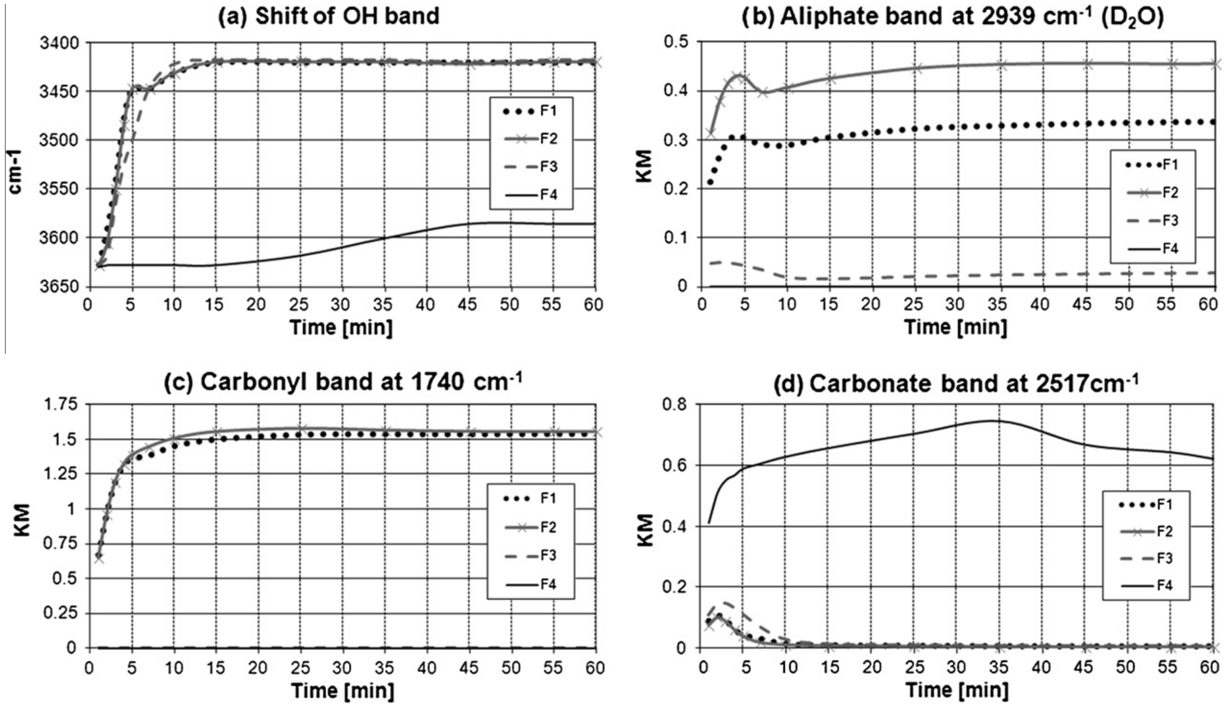

Fig. 9. Intensity of absorption bands versus time for (a) shift of OH bands, (b) aliphates (2939 cm^{-1}), (c) carbonyl (1740 cm^{-1}) and (d) carbonate (2517 cm^{-1}). Mortars were mixed with H_2O, except for measurement of the aliphate curves (b) D_2O was taken as mixing water.

microns, but which can also change during drying of the mortar surface) and (ii) a time resolution on the order of a minute. Thus, from the resolution point of view, DRIFTS is an ideal method to analyze skin structures which can be as thin as a micron and form within a few minutes. In addition, DRIFTS is a non-invasive method and allows in situ kinetic measurements of exactly the same surface location over the entire experiment time of 1 h or even longer.

But as mentioned above, DRIFTS is primarily designed for the analysis of fine-grained powders, and the application of this method to wet mortar surfaces is unusual and has to deal with a number of artifacts such as spectral reflectance (caused by the strongly reflecting water films) and distortion of absorption bands. Therefore, comparing experiments with (a) ATR (Attenuated Total Reflectance) FTIR and (b) reference samples had to be done, and (c) confirmation of the DRIFTS results by other analytical methods was required.

(a) The DRIFTS sample chamber is purged with nitrogen. This could accelerate drying. On the other side, a defined gas flow improves the reproducibility of the measurements. However, in the ATR setup the samples are not purged. On the other hand, ATR requires one to press the ATR-Germanium-crystal onto the mortar surface. This may crack the surface structures and one is forced to change the location from every single measurement to the next. Furthermore, when the mortar surface begins to dry (after 10 min) it is difficult to achieve good contact between the mortar surface and the ATR Germanium-crystal, and reproducibility is lost.

(b) The strong distortions of DRIFT spectra makes it difficult, and in many cases impossible, to interpret the quantified intensity of the absorption bands into a concentration of the corresponding substance. However, the comparison of signals over a series of different formulations, where key ingredients were left out systematically, allowed for identification of characteristic absorption bands. The most prominent signals around 3400 cm^{-1} produced by spectral reflectance of surface water films could be (1) nicely reproduced by repeated measurements, (2) confirmed by analogous signals shifted to 2500 cm^{-1} when D_2O was taken as mixing water, and (3) regenerated when dried mortar surfaces were rewetted and redried again. Also the repeated wetting, drying and rewetting of inert quartz powder or pumice allowed for reproduction of these spectral reflectance signals. Richard et al. [7] did similar DRIFTS studies on the evaporation of free, capillary and confined/adsorbed water in fine mineral powders. They found that the OH-stretching band is shifted towards shorter wave numbers than in bulk water.

(c) Over all, the most important point was to confirm DRIFTS data with data from other microscopic methods and macroscopic observations. The disappearance of the spectral reflectance at about 10 min is simultaneous with the disappearance of surface "water lakes" observed by confocal reflected light microscopy. Furthermore, the loss in surface gloss as it can be observed by a reflectance meter or even by the naked eye occurs during the same time interval, typically between 4 and 8 min.

With the disappearance of the "water lakes" the polymers show up in the DRIFT spectra, indicating the formation of films. The corresponding carbonyl absorption bands develop within the first 5–10 min and persist (Fig. 9c). The formation of polymer films would also explain why the water absorption bands at 3400 cm^{-1} (Fig. 8b, experiments with D_2O as mixing water), which are either related to early formed hydrates or hydrates formed during aging of the dry mix (so-called pre-hydration), constantly disappear within the first 10 min. It could be due to a coating with organic films and/or the formation of a carbonate skin. The latter might even grow on account of existing hydrates.

The carbonation curves (Fig. 9d) of formulations *F*1–*F*3 reach a small maximum at 3 min and decrease to zero by 10 min. In the cases of formulations *F*1 and *F*2, this could be explained again by the formation of polymer films on top of the carbonated mineral surface. But for formulation *F*3, this cannot be the case because it contains no polymer emulsion nor redispersible polymer powder.

However, all significant dynamics in the DRIFTS absorption bands (Fig. 9a–d) appear within the first 10 min after application. This is a clear indication that any chemical changes in the topmost few microns of a freshly applied mortar, thus, the formation of the skin, is a matter of at most 10 min.

This major finding would fit the observed evolution of the failure modes. In fact, the failure surfaces of Fig. 5 represent an overlay of two basic patterns: (i) a set of alternating adhesive and cohesive stripes parallel to the trowelling direction and (ii) a concentric pattern with a tendency for adhesive failure at the rim and cohesive failure in the center. These two patterns indicate two different mechanisms. The parallel set of stripes is related to skin formation on top of the mortar ribs, where the interface to the tile develops poor adhesion. The concentric pattern is related to continuous drying from the rim towards the center. For a majority of formulations, the characteristic stripe pattern already shows up after 5 or 10 min of exposure. This confirms the DRIFTS data, which indicate that skin formation occurs within the first 10 min. As a result, the first 50 area% of wetting generally is already lost within 5 to 10 min. However, with respect to final adhesion, this is in most cases not yet problematic because an adhesive strength of 0.5 MPa is still reached when tested according to EN 1346.

As can be seen in Figs. 4 and 5, the climatic conditions have a large influence on the rate of skin formation. Drying rate measurements have shown that under a controlled climate (23 °C/50% relative humidity), the mortar layer (formulation F-ref applied on a non-absorbing porcelain tile) lost 18 wt.% of the initially added amount of water within the first 30 min of exposure. At climatic conditions of 5 °C and 80% relative humidity, the drying rate is only half of that (8 wt.% within 30 min.). On the other hand, this implies that higher temperatures and lower relative humidity accelerate skin formation because the evaporation rate is increased. Thus, wind, as it occurs in the exterior or even in the interior of bare building constructions where the windows are not yet installed, can also accelerate skinning rate because it accelerates the evaporation rate.

5. Conclusions

Three major observations can be made within the first 10 min on a freshly applied mortar surface: (i) the surface dries, (ii) organic and (iii) inorganic phases (carbonates) show up.

All of the applied methods only provide information from the surface (reflected light microscopy) or from a very thin surface layer corresponding to the limited depth of signal (DRIFTS).

(i) The by eye macroscopically observable loss of gloss can also be measured by gloss meters and corresponds to the microscopically observable disappearance of free water at the surface (so-called "lakes"). The high reflectivity of these "lakes" causes a dominant artifact in the DRIFT spectra, which is referred to as "spectral reflectance". In the dynamic measuring mode of DRIFTS, the disappearance of this artifact is another confirmation for the drying surface within the first 10 min.

(ii) Simultaneously, absorption bands for aliphates (C–H at 2939 cm^{-1}) generated by cellulose ether, polyvinyl alcohol and vinyl acetate–ethylene copolymers, and absorption bands for carbonyl groups (C–O at 1740 cm^{-1}) generated by polyvinyl alcohol and vinyl acetate–ethylene copolymers (both components of polymer emulsions and redispersible polymer powders) appear.

(iii) Polarized microscopy indicates that the top 3–4 μm of the mortar surface become carbonated. Carbonation is driven by the activity of CO_2 and Ca in the water films. Thus drying stops carbonation, and in fact, the rate of carbonation decelerates at the mortar surface. The dependency of carbonation on the activities of CO_2 and Ca ions in the mixing water also explains why the amount and quality of Portland cement and the addition of accelerators or retarders, which all influence the early concentration of Ca-ions in the mixing water have a direct influence on the rate of carbonation, and by that an influence on the rate of skinning.

Conclusively, the generation of a skin can be explained by drying of the mortar surface and related mechanisms of formation of organic and inorganic films composed of cellulose ether, polymers, carbonates and minor hydrates.

How can skinning be influenced? Having the list of influencing parameters (Table 2), the discussion of data and the scheme of Fig. 10 in mind, one can think about several influencing parameters/mechanisms such as (a) evaporation rate, (b) flow rate of mortar water, (c) passive transportation of dissolved ingredients with the flowing mortar water, (d) active enrichment of surface active ingredients and (e) rate of carbonation at the surface.

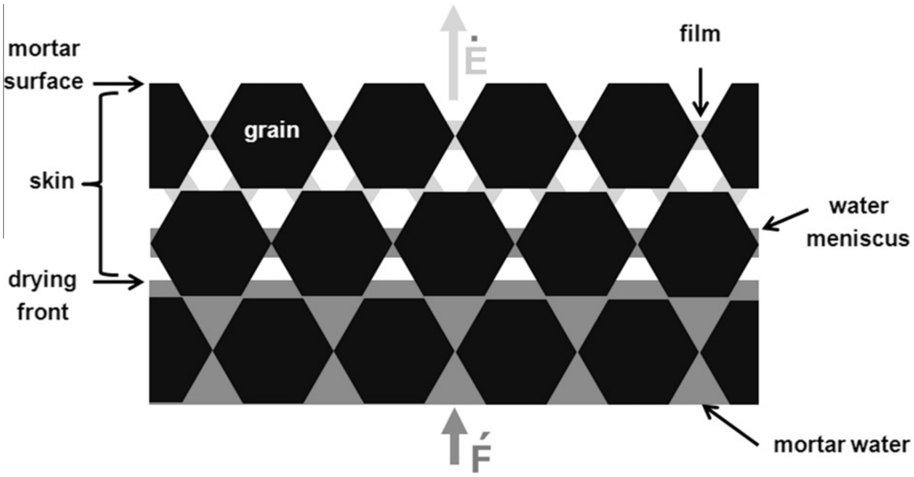

Fig. 10. Scheme for illustrating skinning mechanism. Abbreviations: $\dot{E}$, evaporation rate; $\acute{F}$, flow rate of mortar water.

(a) The evaporation rate is largely dependent on the climatic conditions which are given by the specific environment on the construction site. Thus, it is up to the workman to take influence on it and shield the working place from direct sunlight and wind, and to control skinning by the finger test, in order to adjust the maximum exposure time of the combed mortar layer until the last tile of a series can still be laid before skinning is too strong.

(b) The flow rate of the mortar water can be influenced by a corresponding pretreatment of the substrate done by the workman (e.g., reduce capillary wicking of a porous substrate by cautious pre-wetting or application of a primer) or by adjusting the mortar formulation. With respect to the latter, each ingredient which influences distribution and binding of water must be regarded. Because, on one hand, the mortar water must be retained against capillary wicking of the substrate, but on the other hand, it should be able to flow towards the evaporation front in order to keep it as long as possible at the mortar surface in order to retard drying and related skinning. Jenni et al. [2] conclude that the free water in a freshly applied tile adhesive flows towards the porous substrate and towards the mortar surface (see their Fig. 12). The water flux towards the substrate creates specific enrichments of cellulose ether and polyvinyl alcohol (a component of redispersible powders) at the interface, where the small sized porosity of the concrete substrate acts as a filter. Such interfacial enrichments of cellulose ether build up a flow barrier and provide water retention. Recently, Bülichen et al. [8] have investigated water retention mechanisms of methyl hydroxyethyl cellulose (same type of cellulose ether as used for this study) and identified two separate effects. Firstly, water sorption, and secondly, the formation of a hydrocolloidal associated 3D polymer network, which corresponds to the above mentioned enrichments of cellulose ether at the boundary to porous substrates. Fig. 13 of Jenni et al. [2] shows that the same polymers are also enriched at the mortar surface (and form a skin) indicating water transport in the opposite direction, related to drying. De Gasparo et al. [6] did similar investigations on self-leveling flooring compounds which were applied onto low-porous substrates and let to cure uncovered. Thus, the majority of unbound mortar water can leave the curing mortar layer only by drying and related flow of free mortar water towards the evaporation front. In 4 mm thin mortar layers, cellulose ether could be enriched towards the surface by a factor of five. In 20 mm thick mortar layers, which take much longer to dry, the corresponding factors of enrichment were well above 10. These authors conclude, that evaporation causes two aspects: An upwards directed flow of mortar water, and, as soon as the capillary flow rate decreases below the evaporation rate, a retreating of the drying front inwards, into the mortar layer. By the retreating drying front, they explain the strong hydrations gradients of those fast-setting flooring compounds.

However, the same mechanisms of a retreating evaporation front can also explain the build-up of a dry surface layer in a much earlier phase, which we refer to as skin. Fig. 10 illustrates that drying of the surface results when the evaporation rate ($\dot{E}$) is larger than the flow rate of the mortar water ($\acute{F}$). Then, the free water films at the surface disappear and the drying front further retreats inwards. At contact points between mineral grains, water is left and forms menisci. With ongoing drying of these water menisci, organic and inorganic solids increase in concentration and begin to form films which over-bridge neighboring grains. These interlocked grains form together the structure of the skin.

Not considered in this scheme is the compaction of the pasty mortar layer as a result of water drainage by wicking and drying. Thus, the build-up of a dry surface layer (skin) is regarded as a relative movement between the surface of the mortar (which itself retreats by compaction) and the evaporation front which relatively retreats from the mortar surface.

(c) The flow of mortar water towards the evaporation front will not only transport organics, as described above, but also cementitious ions which will enrich at the evaporation front and cause locally early precipitation as hydrates and carbonates.

(d) Additives (or chemical modifiers therein) with an affinity to air–water interfaces will actively occupy the interface of entrained air and enrich at the mortar surface.

(e) From the mineral side, the high ionic strength, which is established very early, has a major influence on the hydration and carbonation reactions. The latter are very critical as carbonation is pinned to the evaporation front. This also explains why the type and amount of cement (incl. mixed binders) and the addition of retarding or accelerating additives usually have a strong influence on the rate of skinning, especially in cases where a high adhesion strength is required and therefore elevated levels of cement and/or

> the use of highly reactive cements or cement mixtures are needed. The use of retarders can help to reduce the rate of skinning, but the resulting retardation of setting and early strength build-up can be a limiting drawback.

However, all observations point to a very early formation of the skin within the first 10 min of exposure. But from test series where the adhesion strength is measured as a function of exposure time (according to EN 1346), we know that for a majority of mortars, the adhesion strength becomes critically low between 20 and 30 min, thus, well after the first 10 min. Therefore, dynamic mechanisms must occur below the skin, which cannot be seen at the surface.

Coming from this point back to the key question which was raised in the introduction part: How do the surface characteristics, in terms of chemical composition, microstructures and physical properties change within the first 30 min of exposure? This question could largely be answered from a top-view perspective. Reflected light microscopy and DRIFTS allowed us to observe the very surface of the mortar. But, with respect to a cross-sectional perspective, we only got information from thin-sections (Figs. 2 and 3) made from hardened mortar samples.

Thus, it is still an open question how the skin grows in the third dimension (thickness) and at which point it gets critically thick with respect to adhesion strength, as it is measured by the Open Time test (EN 1346) – the key question for the follow-up study.

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