EFFLORESCENCE - MECHANISM OF OCCURRENCE AND POSSIBILITIES OF PREVENTION

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Summary

Taking concrete paving blocks into special account, the author discusses the mechanism of th formation of primary and secondary efflorescence and presents test methods of reproducing th phenomena on laboratory scale. All possibilities of reducing efflorescence practically boil dow to the production of a compacted as possible, waterrepellent concrete, the cement/sand ratio, th water/cement ratio and the curing conditions playing some role. The use of additives as a reliabl means of obtaining a concrete stable to efflorescence is regarded with great scepticism. Only th impregnation of the concrete surface with a plastic resin emulsion has proved a certain success The paper concludes by explaining how efflorescence disappears in the course of exposure t weathering.

1 Chemical principles

Efflorescence is an unpleasant phenomenon familiar to any concrete expert, but to a lot of laymen as well: hazy whitish layers to thick white crusts, spoiling concrete surfaces. From the purely optical point of view, they become increasingly visible against darker backgrounds. Which is why they are a particular problem on coloured concrete; on the other hand, they are unnoticeable in white concrete.

The chemism behind the occurrence of efflorescence can be described in only a few words: as the cement sets, free calcium hydroxide is formed, this being soluble in water, even if only to a slight extent. Consequently, it can migrate to the concrete surface either after already being dissolved in the mixing water of the fresh concrete, or through the hardened concrete when exposed to the effects of rain or dew. Having reached the surface of the concrete, the calcium hydroxide reacts with carbon dioxide in the air to form water-insoluble calcium carbonate. The following equation represents this mechanism:

$$Ca(OH)_2 + CO_2 \quad CaCO_3 + H_2O$$

It is not the water in the concrete which migrates to the surface and entrains the calcium hydroxide; rather, the calcium hydroxide diffuses up through the water-filled capillary system of the concrete to the surface, where it reacts in accordance with the above equation. The precipitation of the calcium carbonate reduces the calcium hydroxide concentration, thus creating a concentration difference in relation to the interior of the capillary system. New $Ca(OH)_2$ is supplied to the surface. Efflorescence occurring during the hardening of the concrete will be referred to as "primary efflorescence", that resulting from the weathering of the hardened concrete being referred to as "secondary efflorescence".

2 Test methods

Investigations of efflorescence on concret are made more difficult by the fact tha there were for a long time no reproducibl test methods. Today, efflorescence unde natural weathering conditions can easily b detected by brightness measurements on th concrete surface, using an electric reflec tance photometer. Flat, extruded concret slabs are best suited to this purpose. The are best coloured with iron oxide black i order to increase the contrast. Carbon blac pigments are not resistant to weathering an would falsify the results.

Outdoor weathering, which primarily cause secondary effloresence, is time-consuming Consequently, there has been no lack of at tempts to simulate these natural occurrence in the laboratory. Primary efflorescenc during the initial phase of hardening can b reproduced well, for example by compressin a slightly moist mixture of cement and sili ca flour into specimens and allowing thes to harden under different atmospheric condi tions. In this case, the resultant efflores cence can again be determined quantitativel by way of brightness measurements.

The puddle test can be carried out on bot fresh and hardened concrete, as will b shown later on. In principle, it involves ap plying a puddle of distilled water to th surface of the concrete. The surface is sub sequently assessed in relation to the forma tion of efflorescence after the water ha evaporated. We have recently started t surround the area to be tested with a perma nently elastic sealing compound.

Efforts to simulate natural weathering phenc mena in the laboratory probably failed fc the most part through doing too much of good thing: if concrete samples are constant ly sprayed with water, the calcium hydroxid appearing at their surface is immediatel washed off and cannot settle in the form of

calcium carbonate. Exposure to dew is, therefore, a far more suitable method. In this case, concrete samples are stored in a very damp atmosphere and cooled, so that the water condenses on their surface. It first penetrates the capillaries of the concrete, eventually forming a film of moisture on the surface. Since the calcium hydroxide migrating to the surface is not washed off, efflorescence occurs after only a few days under such conditions (Fig. 1).

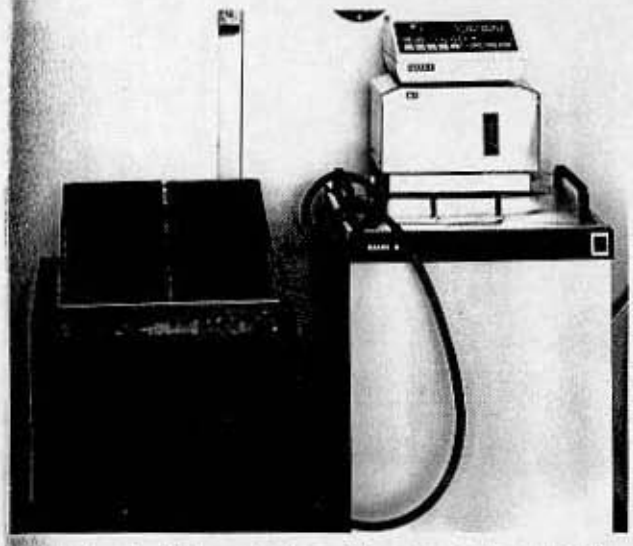


Fig. 1: Cooling plate with concrete roofing tiles and thermostat

The principle of producing efflorescence with the minimum possible amount of water is also taken into account in the other method developed by us. In this case, a stack of concrete pavers is sprayed with distilled water for 20 minutes every day, once in the morning and again in the evening. The water penetrates into the stack and is active between the concrete layers virtually all day long. The top layer, on the other hand, layer, on the other hand, dries out very rapidly, consequently always displaying far less efflorescence than the layers below (cf. Fig. 2). The test duration should be between 9 and 14 days. The method simulates practical conditions very well, since most problems with efflorescence on concrete pavers probably occur during storage of the pallets in the yard or on the building site.

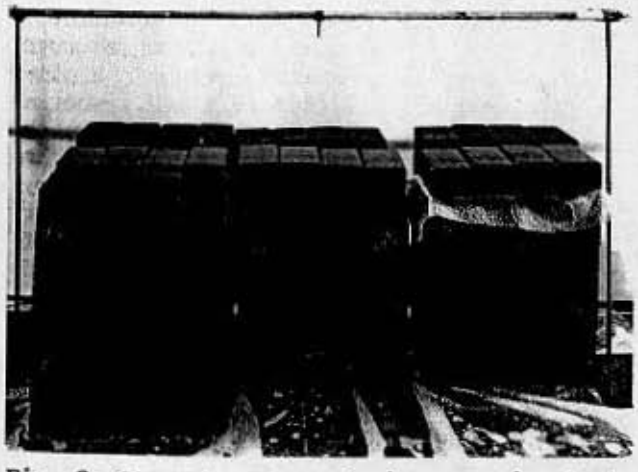
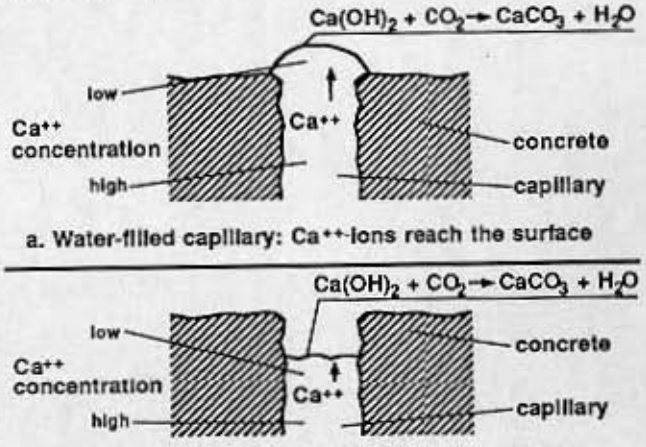


Fig. 2: Concrete pavers during spraying test

3 Primary efflorescence

We shall now turn to primary efflorscence. It is always true that visible efflorescence can only occur if the capillaries in the concrete are filled with water to the very top. Only then can calcium hydroxide reach the surface.

This applies equally for both fresh and hardened concrete. However, if the concrete dries out near the surface, with the result that the capillaries are only filled with water to a level below the surface of the concrete, a reaction will take place inside the concrete between the calcium hydroxide and the carbon dioxide in the air. A light zone below the surface can occasionally be seen on fractured concrete surfaces. Figure 3 describes the aforementioned situation in schematic form.



a. Water-filled capillary: Ca^{++}-ions reach the surface

b. Reduced water level in the capillary (drying-out of concrete): transport of Ca^{++} ions to the surface is inhibited

Fig. 3: Formation of primary efflorescence on concrete surfaces

Therefore, since primary efflorescence can only occur if the capillaries are full to the brim with water during the initial phase of hardening, gradual drying will promote efflorescence. In contrast, a climate leading to rapid drying of the concrete is unlikely to cause efflorescence. The decisive factors in this context are not only the relative humidity and temperature, but also air movement. The test specimens of cement and silica flour described earlier on were made here every day for 1 1/2 years and allowed to harden in the open. The difference in brightness in comparison with the reference samples without efflorescence was subsequently measured. Figure 4 shows the results: particularly great brightness differences, i. e. primary efflorescence, in the Autumn months.

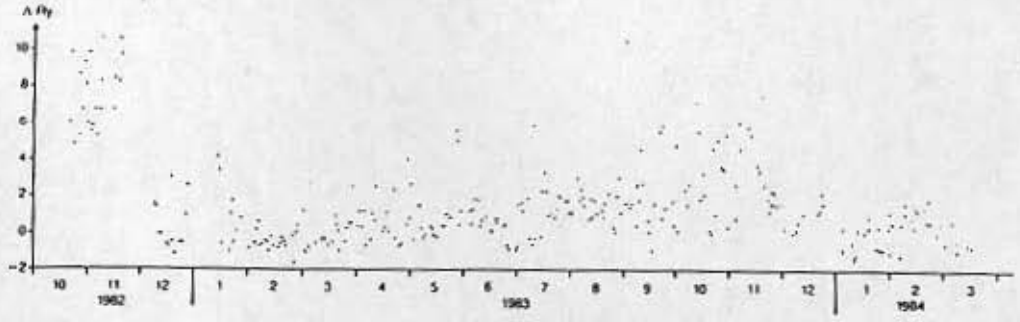


Fig. 4: Prinary efflorescence and weather conditions (the higher Ry, the higher the degree of efflorescence)

How long does primary efflorescence occur on concrete? To find this out, the puddle test was performed every hour on two series of specimens under different hardening conditions. Figure 5 shows the results: irrespective of whether hardening took place at 28 °C and 95 % relative humidity or 20 °C and 50 % relative humidity - virtually no more efflorescence occurred in the puddle test after 8 hours. We obtained similar results with concrete roofing tiles. Is this

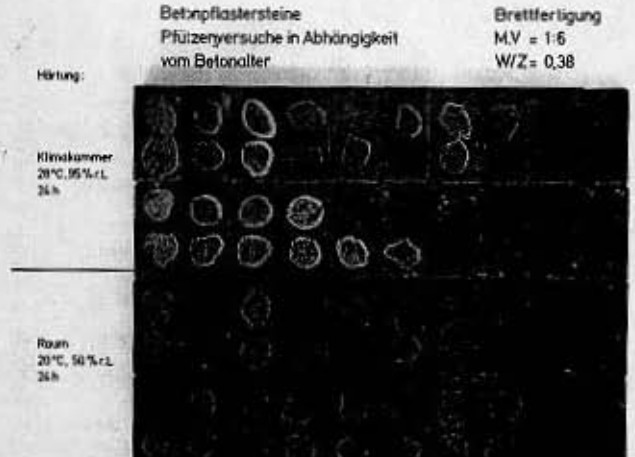


Fig. 5: Puddle tests as function of concrete age

cessation of efflorescence in the puddle test after more than 8 hours due solely to progressive hardening, or does carbon dioxide react with the calcium hydroxide on the surface during this time that the capillaries of the concrete are sealed off at the surface? To answer this question, we allowed the pavers to harden in nitrogen, i.e. without CO_2. The puddle test then proved positive even after several days. The amount of carbon dioxide required to seal off the capillaries can be determined. To do so, we allowed concrete pavers to harden in sealed crates containing a weighed quantitiy of solid carbon dioxide. It was found that as little as 0,5 g CO_2 per paver, corresponding to 270 ml, suffice largely to prevent efflorescence (cf. Fig. 6).

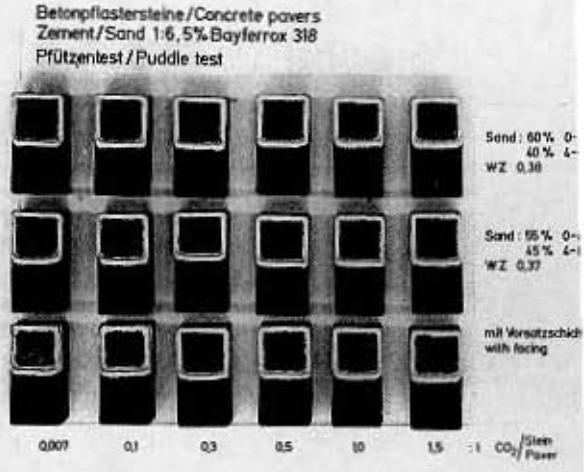


Fig. 6: Puddle test as function of CO_2 presence during curing

The results obtained to date are paradoxical: while CO_2 is necessary for efflorescence, it also does its best to prevent If there is a film of water on the fresh concrete, meaning that calcium hydroxide escape from the mouths of the capillar and react with carbon dioxide over the tire surface of the concrete, primary efflorescence occurs; however, if the react takes place in the mouths of the capillaries, they are rapidly clogged by the calcium carbonate formed and the formation of primary efflorescence comes to a halt. This be visualized when concrete is cured in presence of CO_2, i. e. in air, and in the sence of CO_2, i. e. in a pure nitrogen mosphere. Figure 7 shows the electron micrograph of the surface of an extruded concre roofing tile which underwent curing in a climatic chamber at 60 °C and 98 % r.h., whe as Figure 8 shows a tile from the same ba which set at room temperature in a nitro atmosphere. Apart from a few larger pore the surface of Figure 7 is much smooth than that of Figure 8, where the mouths the capillaries are obviously not clogg due to the absence of CO_2. Therefore, wh ther primary efflorescence is caused prevented depends on the quantity and t of occurrence of the two agents required efflorescence, CO_2 and water.

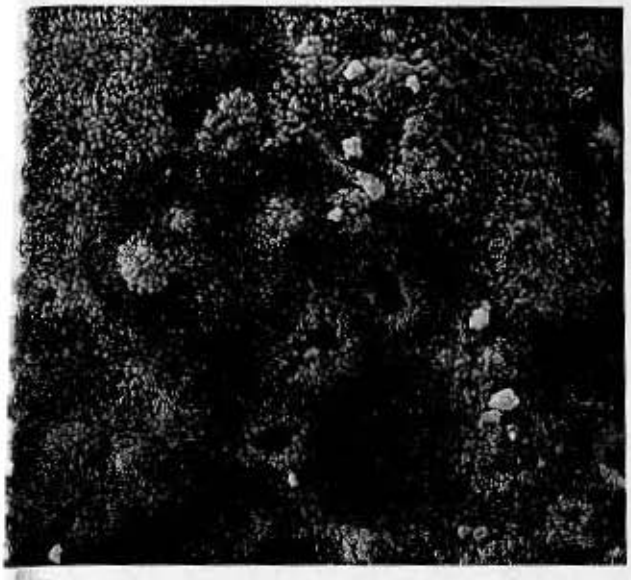


Fig. 7: Electron micrograph of a concrete surface, cured under access of CO_2 contained in the air



Fig. 8: Electron micrograph of a concrete surface, cured in absence of CO_2

But this is not the only apparent contradiction observed in relation to primary efflorescence: Figure 3 showed that calcium carbonate is formed inside the concrete if the surface of the latter dries out rapidly. In this case, however, the capillaries are not sealed off at the surface, but at lower layers of the concrete, meaning that extraneous water occuring later on can cause primary efflorescence. The calcium hydroxide required then comes from the upper layer or incompletely hardened concrete. This happens if the concrete hardens in a strong wind or while the relative humidity is very low. Concrete pavers allowed to harden in the climatic chamber at 95 % relative humidity do not react to the puddle test after hardening.

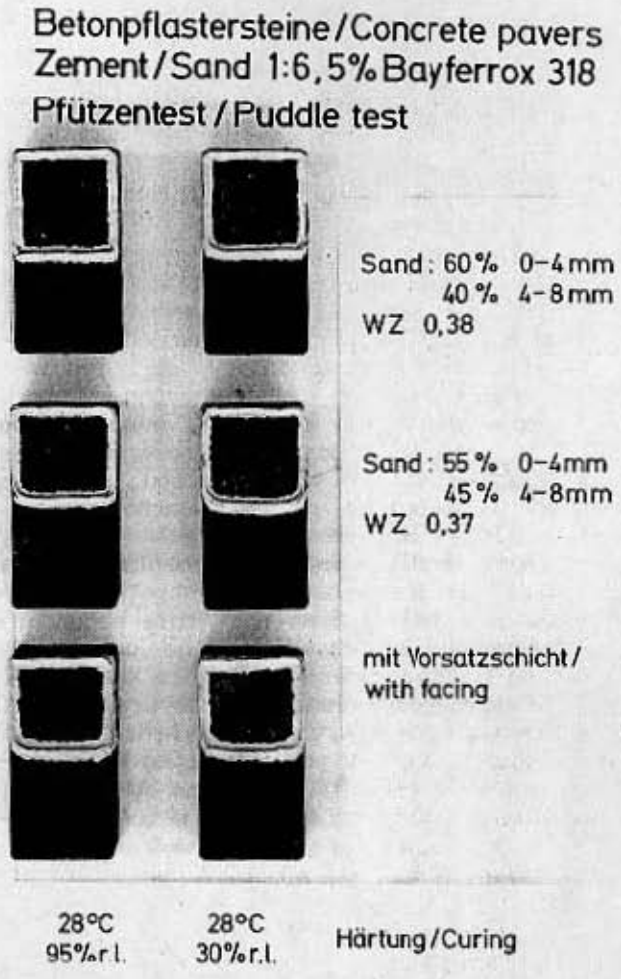


Fig. 9: Puddle test as function of curing conditions

However, the same pavers do react if allowed to harden in the laboratory atmosphere with 35 % relative humidity (cf. Fig. 9). A higher relative humidity, but in the prescence of a strong draught, generated by a fan for example, can lead to the same result. The pavers pigmented with iron oxide black then look particularly black at the start, since there is no calcium carbonate in the mouths of the capillaries, this otherwise having a certain lightening effect. However, they become all the lighter when exposed to the puddle or dew test. In other words, preventing primary efflorescence can cause an increased level of secondary efflorescence.

4 Secondary efflorescence

One reason for the occurrence of secondary efflorescence has already been mentioned: the drying out of the concrete at the surface. A second cause can also be described in very few words: if the concrete is poorly compacted to start with, meaning that extraneous water is rapidly absorbed after hardening, this water can also dissolve calcium hydroxide and cause efflorescence. Water in concrete with very coarse pores can dissolve large quantities of calcium hydroxide, this resulting in sintering. On the other hand, if the capillaries are narrower, meaning

that the water can penetrate into the concrete but not flow through it freely, efflorescence will occur over the entire surface. In the case of poorly compacted, porous concrete, there is little point in making a distinction between primary and secondary efflorescence, since the mechanism of formation is virtually identical.

A more difficult fact to explain is that any highly compacted concrete, such as that in concrete roofing tiles, which reacts negatively to the puddle test after hardening, subsequently displays secondary efflorescence after several months of weathering. It occurs irrespective of location, even in the desert climate of Arizona. The maximum is always reached within a year, and it takes another year before it is weathered away again. After that time, it is virtually never seen again, as measurements over a period of six years have demonstrated. There are numerous indications that this secondary efflorescence is caused by the continuing hardening of the cement, which is know still to be in progress even after several month. During this process, calcium hydroxide is formed all the time, then reacting with carbon dioxide in the air. This theory at least correlates with the fact that secondary efflorescence is no longer observed after two years, that is tc say, after the setting process of the cement has probably come to an end. The fact that severe secondary efflorescence even occurs in Arizona indicates that dew suffices for its formation, although not for subsequently weathering it away. Figure 10 again summarizes the occurrence of efflorescence as a function of the water and carbon dioxide supply.

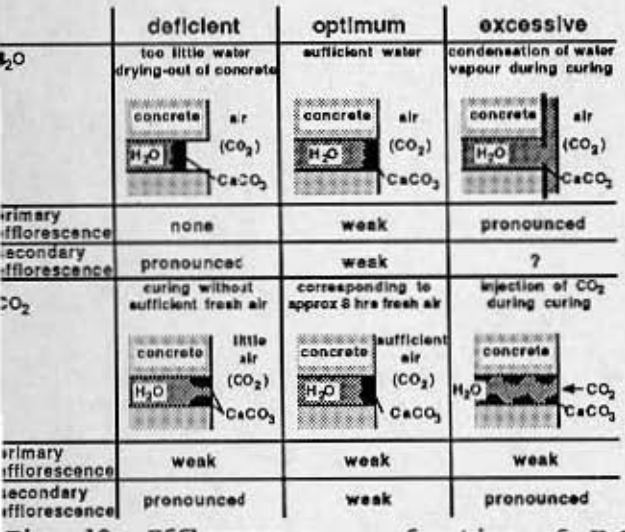


Fig. 10: Efflorescence as function of H_2O and CO_2 supply during curing of the concrete

5 Countermeasures

The mechanism of occurrence of primary and secondary efflorescence has been described in such detail because it can in itself provide information on how extensive prevention can be achieved. If caused by the subsequent hardening of the concrete, there is so far virtually no way at all of preventing secondary efflorescence. The greater part of our attention must concentrate on preventing primary efflorescence.

5.1 Concrete formulation

Everything which impairs the permeability of the concrete, that is to say, favours the penetration of water into the hardened concrete, must be avoided. Concrete consists of the aggregate and the hardened cement paste which binds it. In the fresh concrete, the latter, in turn, consists of cement, the very fine particles of the aggregate, possible pigments, water and a certain amount of air voids. If the volume of this paste is insufficient to fill completely the cavities left by the aggregate after compaction, the concrete is certain to have a high water absorption capacity later on. If the cement/aggregate ratio of the concrete is changed from very rich to very poor in cement, efflorescence increases with declining cement content. Figure 11 shows a series of concrete pavers with cement/aggregate ratios of 1 : 5 to 1 : 10, the W/C ratio also having to be changed for processing reasons. The ef-

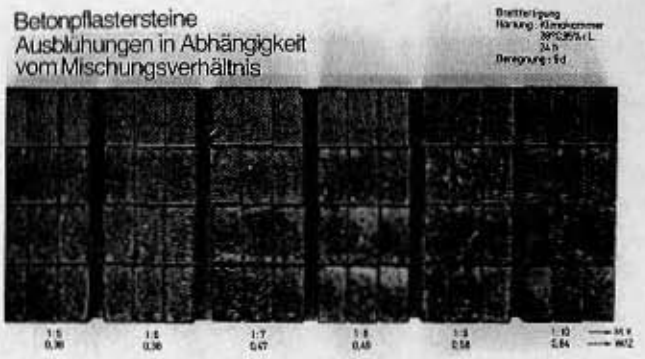


Fig. 11: Efflorescence as function of mixing ratio (= M. V.)

florescence increased with decreasing cement content, although this no longer applies for the 1 : 10 mixing ratio. This concrete is so porous that, when sprayed with water, the water drained through, washing the dissolved calcium hydroxide down and out. This picture and the next clearly illustrate that the top row of pavers in the spraying test, which is also at the top in the pictures, shows less efflorescence than the pavers lower down in the stack. This test lasted 9 days.

Fig. 12 shows concrete pavers with a constant cement/aggregate ratio of 1 : 6, but three different gradings of the aggregates and W/C ratios ranging between 0.24 and 0.38. At the very low W/C ratios, the volume of the hardened cement paste was obviously not enough to fill out the aggregate structure completely.

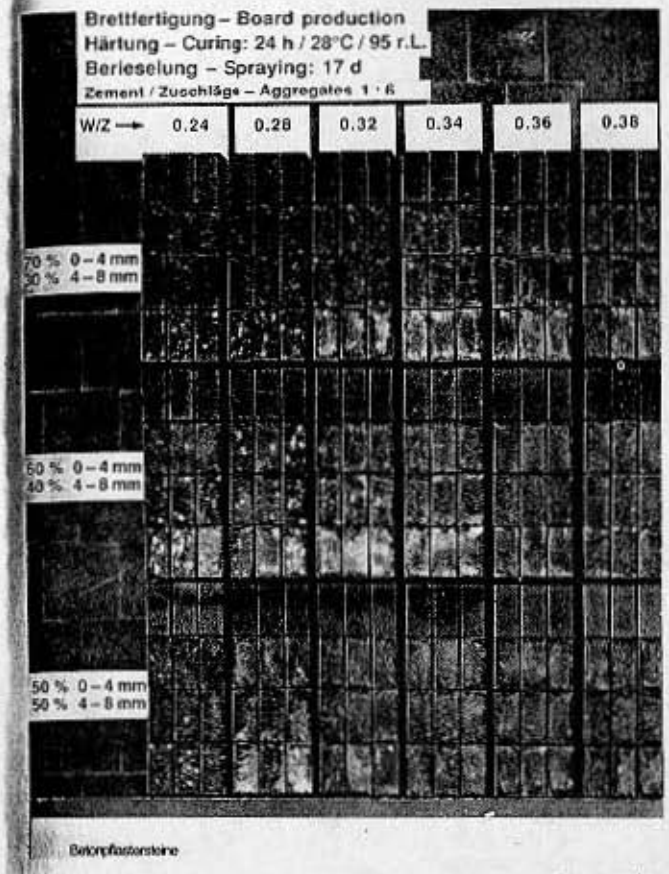


Fig. 12: Concrete pavers with increasing W/C ratio and three different gradings of aggregates after spraying test.

In addition, the compactability of these mixtures is very poor. In case of W/C 0.24, the concrete is so porous that water drains through very easily, thus leaching soluble calcium hydroxide downwards so that these pavers seem to have little efflorescence. It is the same phenomenon as with mixing ratio 1 : 10 in the previous picture. Apart from these far too dry mixtures, the pavers absorb, with increasing W/C, smaller quantities of extraneous water and display correspondingly less efflorescence in the spraying test. The addition of concrete plasticizers may be beneficial, if they produce a denser concrete. In general, however, such agents cannot be expected to have any positive effect.

5.2 Compaction, hardening and storage

Good mechanical compaction is essential, particularly at the surface. It can frequently be improved with the aid of a fine facing layer.

Mention has already been made of the risk of the surface of the concrete drying out during hardening. Although this prevents the occurrence of primary efflorescence and yields particularly brilliant colours, it also increases the likelihood of secondary efflorescence. Figure 13 shows the influence of various types of hardening in mixtures with ratios of 1 : 5 and 1 : 6. Very high atmospheric humidity during hardening produces the best results in the spraying test. Fur-

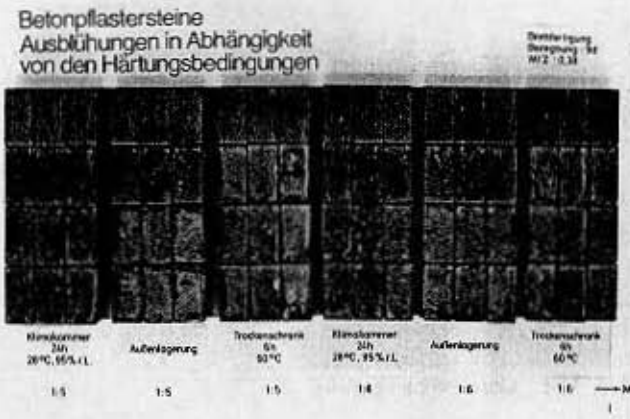


Fig. 13: Efflorescence as function of curing conditions

ther investigations were aimed at establishing whether indoor storage of the pavers for as long as possible has any effect on subsequent efflorescence. Hardening was carried out at 24 °C and 50 % relative humidity, in one case, and at 28 °C and 95 % relative humidity, in the other. The pavers were subjected to the spraying test after 1, 3, 7, 14 and 28 days, the results showing that the different pre-storage periods had no effect (Fig. 14). This contradicts the old



Fig. 14: Efflorescence as function of storage time

belief that exposure to rain, particularly during the first few days of hardening, is a prime cause of efflorescence. Rather, the pavers should be protected against extraneous water for as long as they are stacked since, once water had penetrated into the paver stacks, it hardly evaporates at all. It is doubtful whether shrink-wrapping of pallets is the best solution, since condensed water can reamin under the wrapping for a considerable time. A sheet of plastic or strong paper placed below the first layer of pavers could prove better, since it not only affords the palleted stack mechanical stability, but also prevents the penetration of water into the stack, while at the same time promoting drying (Fig. 15).

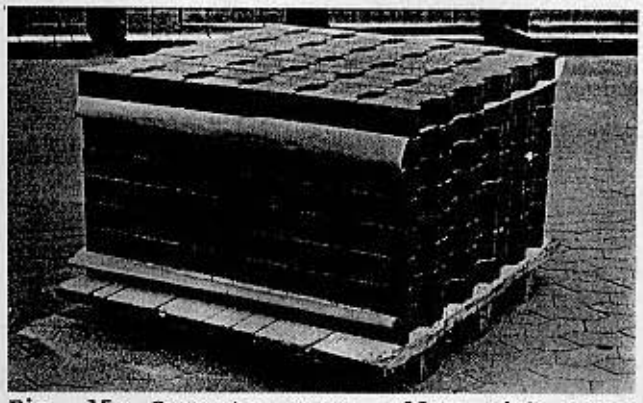


Fig. 15: Concrete paver pallet with paper below top course

5.3 Cement type

Our experience to date has shown that the type of cement is relatively unimportant in relation to the occurrence of efflorescence. The cement in 1 m³ of concrete should contain up to 100 kg lime, this acting as a reservoir to supply $Ca(OH)_2$. In view of this figure, it is surprising that efflorescence does not occur far more frequently; after all, a mere 0.1 mg $CaCO_3/cm^2$ is sufficient to cause visible efflorescence. That is equivalent to only 6 g, referred to the surface of 1 m³ of concrete! However, this also shows that minor fluctuations in the cement composition should be irrelevant in relation to the occurrence of efflorescence.

5.4 Chemical additives

The dream of every concrete manufacturer is an additive which reliably prevents efflorescence when added to the concrete. What could the effective principle of such a substance be? In view of the aforementioned vast quantity of calcium hydroxide potentially available for efflorescence, an additive capable of binding this calcium hydroxide would be inconceivable.

Impregnation of the concrete with silicones or stearates also holds no promise of success, since they only prevent penetration of water in its liquid state. These agents have no effect on the condensation of water vapour in the capillaries and pores of the concrete. On the other hand, the condensation of water vapour on and in the surface of the concrete is of considerable importance for secondary efflorescence, in particular.

5.5 Spray-coating with plastic dispersions

Sealing of the concrete surface with transparent, unpigmented plastic dispersions, based on acrylics for example, was more successful. The sealant film thickness should be so thin that the film coating is hardly coherent. Between 10 and 20 m² of concrete paver can be sealed with 1 kg of a commercially available dispersion. The thin film thickness ensures that the concrete surface does not remain sticky. Nor does it gather dust and dirt, and costs are reduced as well. The dispersion should be mixed with water at a ratio of 1 : 1 for spraying. On the other hand, a sealing coat such as that shown in Fig. 16 can only be applied in mono-layer presses.

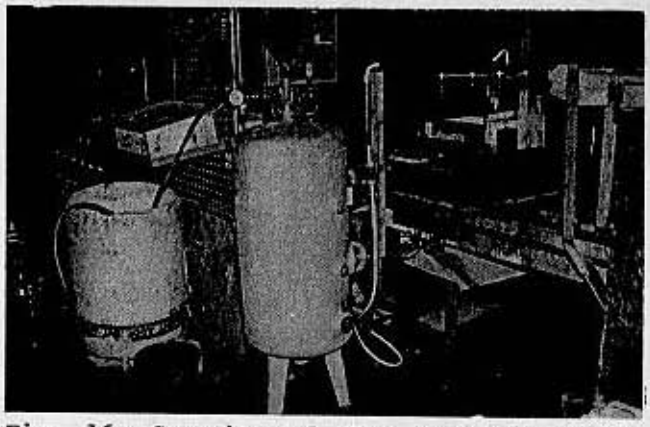


Fig. 16: Spraying of flat concrete pavers with an aqueous acrylic emulsion

The results are illustrated in Fig. 17. The right-hand side of the photograph shows unsealed blocks after a short spraying test, the sealed blocks being on the left. The efflorescence-preventing effect is obvious. Inadequacies of the concrete manufacturing process, however, cannot be made good by sealing. The best it can do is prevent secondary efflorescence, not that caused by poor compaction of the concrete.

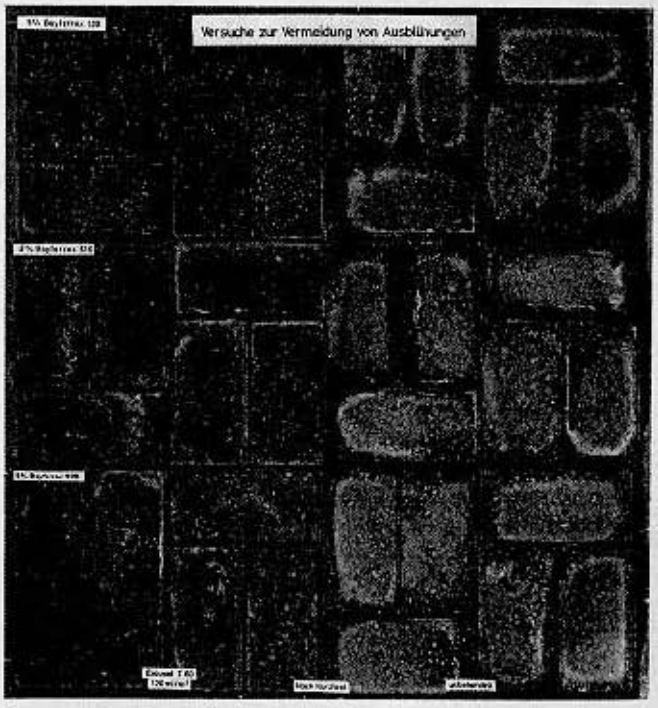


Fig. 17: Spraying test: Influence of the impregnation with aqueous acrylic emulsion

6 Weathering away of efflorescence

Once efflorescence has occurred, it can only be removed by acid washing. This should be done with diluted acid, such as 3 % hydrochloric acid. Aqueous solutions of organic acids are commercially available, and these are less risky to handle. It is recommend-

able to soak the concrete in water beforehand, since this will prevent the acid penetrating too deep into the concrete. Acid washing should be followed by washing with water. Concrete pavers can be cleaned of efflorescence fairly well by such post-treatment.

If there is no hurry, natural weathering will do just the same as acid washing. Calcium carbonate reacts with the carbon dioxide in the air, gradually forming calcium hydrogencarbonate, a water-soluble product. This reaction means that efflorescence disappears again after a certain time (cf. Equation 2):

(2) $CaCO_3 + CO_2 + H_2O \quad Ca(HCO_3)_2$

Figure 18 shows concrete pavers which had shown severe efflorescence after the spraying test. They regained their original, much deeper colour shade after 12 months of weathering.



Fig. 18: Weathering away of efflorescence

Efflorescence needs only be expected to survive longer in areas with very little rainfall, as in Arizona, for example. At all other exposure sites used for our weathering tests in the Federal Republic of Germany, the Netherlands, Belgium, Italy, France, Sweden, England, Florida and South Africa, the efflorescence always disappeared within a period of two years. Numerous trials have also shown that secondary efflorescence only occurs once.

7 Conclusions

The primary efflorescence occuring during hardening may be attributable to the concrete formulation, compaction or the hardening conditions. The first prerequisite for minimizing efflorescence is a dense concrete which absorbs as little water as possible after hardening. It must also be ensured that the fresh concrete does not dry out on the surface, but also that no water condenses which could drip onto the surface of the concrete during the first few hours of hardening. We achieved this by heating the ceiling in our hardening chamber to prevent condensation of water vapour at that point. Furthermore, free access of air and, thus, carbon dioxide should also be ensured during initial hardening. These conditions help also to reduce subsequent secondary efflorescence. However, since it is probably also attributable to the setting of the cement, a process which takes several months, it cannot be avoided entirely. The only limited chance is to apply a transparent plastic coating as soon as the blocks come out of the press. Penetration of water into the stack of pavers during storage of the blocks before laying should be avoided if at all possible.