

## Internal water-repellent treatment – a novel strategy for mitigating alkali-aggregate reaction in concrete pavements

Frank Weise <sup>(1)</sup>, Matthias Fladt <sup>(2)</sup>, Marko Wieland <sup>(3)</sup>

(1) Federal Institute for Materials Research and Testing, Berlin, Germany, [frank.weise@bam.de](mailto:frank.weise@bam.de)

(2) Federal Institute for Materials Research and Testing, Berlin, Germany, [matthias.fladt@bam.de](mailto:matthias.fladt@bam.de)

(3) Federal Highway Research Institute, Bergisch Gladbach, Germany, [wieland@bast.de](mailto:wieland@bast.de)

### Abstract

To prevent future alkali-aggregate reaction (AAR) damage, which has occurred frequently in the German highway network in recent years, a new regulation has been drafted. This regulation severely limits the use of alkali-sensitive aggregates by requiring that their suitability be verified by certified inspectors using newly developed AAR concrete tests that involve the external supply of alkali. This has led to a significant limitation in the number of aggregates usable for concrete pavements. A novel AAR avoidance strategy is now being pursued, which aims to enable the use of borderline alkali-sensitive aggregates through the application of an internal water-repellent treatment. The addition of water repellents during concrete production should significantly reduce the ingress of water and external de-icing salts into the concrete pavement, thus reducing the potential for AAR damage.

This paper presents the results of laboratory tests to assess the suitability of this new AAR prevention strategy. Representative, highly AAR-susceptible road paving concrete made with an alkali-sensitive greywacke and various water repellents were used as the basis for these experiments. The tests for concrete suitability included determining the conventional fresh and hardened concrete properties as well as concrete prism tests with external alkaline supply. Building on these results, laser-induced breakdown spectroscopy (LIBS) analyses of de-icing-salt intrusion as well as microscopic examinations for verification of the AAR characteristics were carried out.

The results of the AAR concrete tests with external alkaline supply support the conclusion that, when hydrophobic agents containing a suitable active ingredient are used, the AAR damage process in road paving concrete can be sufficiently prevented.

**Keywords:** concrete pavements; internal water-repellent treatment; preventive measures; testing for potential AAR

## 1. INTRODUCTION

Increased amounts of damage to concrete pavement linked to the AAR have occurred in recent years in sections of the German highway network built before 2005. For example, after a Germany-wide inspection by the Federal Highway Research Institute (BAST) in 2012, 1,500 km carriageway were suspected of AAR [1]. The often-drastic AAR-linked reduction in the useful life of concrete pavement led to greatly intensified research in this field. In this context, the General Circular on Road Construction ARS 04/2013 was among the regulations issued in Germany [2]. This excludes to a great extent the use of alkali-sensitive aggregates in new construction and renovation of heavily used concrete pavement, through evidence of suitability provided by recognized AAR experts using newly developed concrete tests with external application of alkalis. This in turn led to a significant restriction in the range of aggregates that may be used. The novel AAR prevention strategy now aims to make borderline alkali-sensitive aggregates usable for this purpose by internal hydrophobic treatment. The addition of hydrophobic agents when preparing the concrete should significantly reduce the penetration of water and external de-icing salt into the concrete pavement, thus adequately reducing potential AAR damage. Against this background, in the context of a research project commissioned by the BAST, the performance of internal hydrophobic treatment in preventing AAR damage in concrete pavement was thoroughly researched at the Federal Institute for Materials Research and Testing. Starting with the current state of technology in this area, the following paper gives an insight into the current state of this research.

## 2. STATE OF THE ART

Previously, both in Germany and elsewhere, hydrophobic agents were applied almost exclusively to the surface of concrete pavements to reduce and prevent damaging AAR [among other sources, see 3-7]. Experience in Germany shows that early application of silane-based hydrophobic agents can delay the AAR damage process in highway concrete pavement by approx. six years. However, it was also determined that moisture sometimes entered via the joints. The resulting infiltration of the waterproofed concrete boundary zone then caused increased AAR damage potential in the joint area. Internal hydrophobic treatment aims to prevent this. An added advantage is that even when the outer concrete surface is weathered away by the effects of climate and traffic load, an effective water-repellent treatment over the entire cross-section is ensured.

Unlike the surface application of hydrophobic agents, internal application has not yet been applied in concrete road building, despite initial approaches by Schäffel [8]. On the contrary, so far it is restricted to special applications in solid construction unrelated to AAR. For example, internal water-repellent treatment has already been used in individual cases for exposed concrete and concrete products (paving stones and roof tiles).

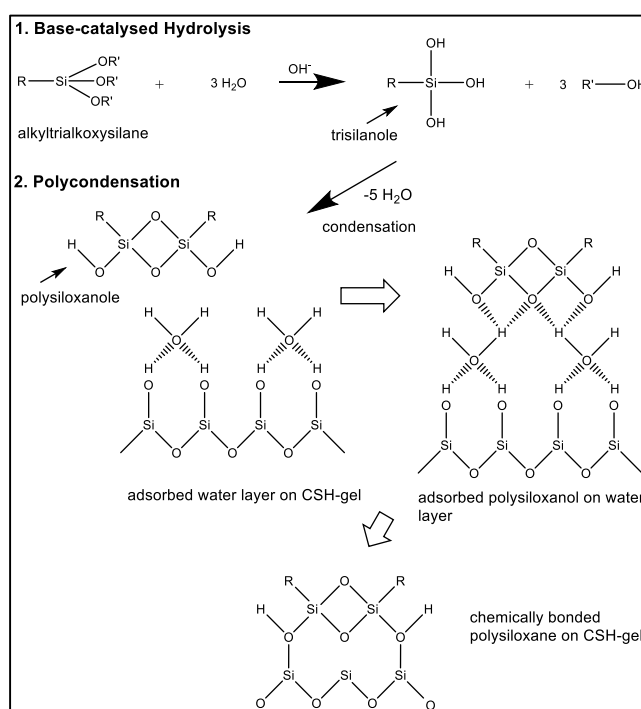


Figure 2.1: Schematic sketch of hydrolysis and condensation reactions of silanes in cement-based materials. Modified after [9,10].

Organosilicon compounds are often used as internally applied hydrophobic agents. They can be added to fresh concrete during the mixing process in the form of liquid (active component emulsified in liquid) or powder (active component applied to a carrier substance). Figure 2.1 shows an example of the multi-stage reaction mechanism of silane-based hydrophobic agents in cement-bound mineral construction materials. Here, in the first stage, the alkoxy groups of the alkyl trialkoxy silane are separated by means of an alkali-catalysed hydrolyzing reaction creating trisilanole, a reactive interim product. In the second stage, the trisilanole condensation reaction produces polysiloxanol molecules that are then bound to the silanol groups of the CSH gel. While the polysiloxan part of the molecule is responsible for binding to the capillary pore walls, the remaining alkylalkoxy (R) extends into the capillary pore space, increasing surface tension between pore solution and cement stone surface. This increases the contact angle to over 90°. The resulting hydrophobic surfaces of the capillary pore space reduce capillary transport of pore solution and external moisture, with the ions it contains, into the concrete [11, 12]. In this way, numerous tests carried out in the context of reinforcement corrosion proved that the penetration depth of chloride ions is significantly reduced by internal hydrophobic treatment of concrete [13,14]. Further

tests showed that contrary to expectations, silane-based internal hydrophobic agents significantly reduce concrete's resistance to freeze-thaw with de-icing salt. The reason for this has not yet been adequately researched [15, 16]. However, mechanical properties also deteriorated on application of silane-based hydrophobic agents to concrete. In particular, for example, the concrete's compressive strength was significantly reduced. We suspect that this is due to the hydration process being influenced by the hydrophobic agent [17, 18].

Based on this state of technology, the evaluation of the performance of internal hydrophobic treatment as a novel AAR prevention strategy in concrete road construction requires a thorough, systematic examination of fresh and set concrete properties. In addition to AAR damage potential and hygric parameters, the latter must also include the mechanical properties and resistance to freeze-thaw with de-icing salt of the concrete pavement without and with internal hydrophobic treatment.

### 3. TEST PROGRAM, MATERIALS AND TEST METHODS

#### 3.1 Test program

This research project focused on the holistic evaluation of the performance of internal hydrophobic treatment as a novel AAR preventive strategy following the multi-level test programme presented in Figure 3.1. This paper presents as an example the performance of one of the three hydrophobic agents tested in exposed aggregate concrete. In principle, each hydrophobic agent was tested with one metal soap, one silane/siloxane emulsion and one silane as the active ingredient. This paper presents the tests with the silane-based hydrophobic agent because it yielded the most promising results. The exact composition is subjected to a confidentiality agreement. The reason for selecting exposed aggregate concrete was that, due to its high cement content and smaller maximum grain size, it has higher potential for AAR damage in comparison to top course concrete and subconcrete that were also tested.

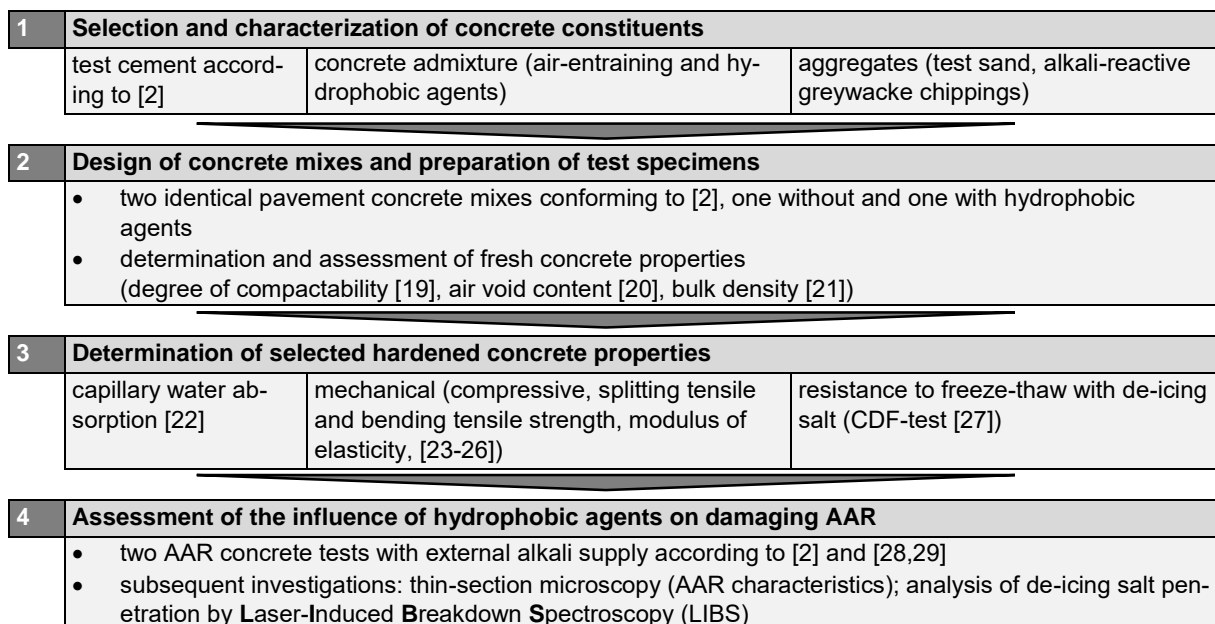


Figure 3.1: Test program of the research project.

#### 3.2 Materials

##### 3.2.1 Concrete constituents

The test cement according to [2] was a CEM I 42,5 N with a Na<sub>2</sub>O-equivalent of 0,76 wt.-%. For air entrainment a resin soap-based agent was used. The hydrophobic agent, which is a proprietary product, was a greyish powder that was premixed in dry form with cement. Figure 2.1 illustrates the reaction scheme for commonly used silane-based products.

A test sand of grain-size 0/2 mm according to [2] was used for the fine-grained aggregate. It consists mainly of quartz with small amounts of feldspar. It has a borderline sensitivity to alkalis. In addition, a strongly alkali-reactive greywacke aggregate was used (grain-size 2/5 mm und 5/8 mm). It consists mainly of the following minerals: quartz, feldspar, white mica and clay minerals. Some greywacke grains occasionally contain large grains of calcite. The binding matrix is often constituted of siliceous and/or argillaceous materials.

### 3.2.2 Concrete mixes

The precise composition of the exposed aggregate concrete without and with the hydrophobic agent can be seen in Table 3.1. It is striking that the dosage of air entraining agent was significantly increased for hydrophobic treated concrete. This is due to the contrary effect of the hydrophobic agent and the air entraining agent on the surface tension of the cement paste. The mixing process included 1 minute dry mixing of cement or cement/hydrophobic agent compound, sand and aggregates; 2 minutes mixing with 90 % mixing water and another 1 minute mixing with air entraining agent dispersed with the remaining 10 % mixing water.

The exposed aggregate concrete mixtures, one with and one without hydrophobic agent, were mixed in two batches each in a 250 l mixer. The first batch (approx. 200 l) was used to produce the test specimens for the determination of selected hardened concrete properties. The second batch (approx. 140 l) was used to produce test specimens for the various AAR concrete tests. The concrete test specimens with the dimensions required by the respective standards were cast between 10 and 54 minutes after addition of the mixing water. The fresh concrete was taken from the mixer and processed in 2-3 portions. The fresh concrete remaining in the mixer was protected from drying out. For each further removal, the fresh concrete was mixed a few seconds and then cast into the moulds in two layers and compacted on a vibrating table. The surface of the test specimens was then screeded with a straightedge. All test specimens were left in the moulds with foil covering for one day at a temperature of  $(20 \pm 2) ^\circ\text{C}$ . The test specimens for determining compressive strength and modulus of elasticity were cured under water for six days, and then in a standard climate ( $(20 \pm 2) ^\circ\text{C}$  and  $(65 \pm 5) \% \text{RH}$ ). The test specimens for the CDF test were preconditioned in the same way. However, after water storage, the plate-shaped test specimens for the CDF test were obtained from the cubes by sawing, then prepared and stored at standard climate.

After demoulding, the test specimens for determining bending and splitting tensile strength were cured under water at a temperature of  $(20 \pm 2) ^\circ\text{C}$  until the test. In the same way, the test specimens for determining capillary water absorption were preconditioned up to a concrete age of 42 days. After 28 days' water storage, however, they were dried at  $40 ^\circ\text{C}$  until constant mass and cooled down in sealed plastic boxes with silica gel to a temperature of  $(20 \pm 2) ^\circ\text{C}$  to avoid moisture absorption from air humidity. Then the lateral surface was sealed with an epoxy resin to ensure unidimensional moisture transport during the capillary absorption tests.

The test specimens for the  $60 ^\circ\text{C}$  concrete test with alkali supply were subjected to preconditioning in accordance with RILEM AAR-12 [30]. The test specimens for the cyclic climatic storage test were packed airtight in foil after demoulding and stored up to an age of five days. Afterwards, the test specimens were prepared and further stored at standard climate until testing began after seven days.

Table 3.1: Mix design of exposed aggregate concrete without and with hydrophobic agents.

type of exposed aggregate concrete	component								
	cement [kg/m <sup>3</sup> ]	water-cement ratio	air entrainment agent	hydrophobic agent	aggregates				
					sand			greywacke	
			[wt.-%] related to cement mass				[wt.-%] related to entire aggregates		
				0,1/0,5	0,5/1,0	1,0/2,0	2/5	5/8	
reference	430	0,45	0,18	-	12	10	8	40	30
hydrophobic	430	0,45	1,10	2	12	10	8	40	30

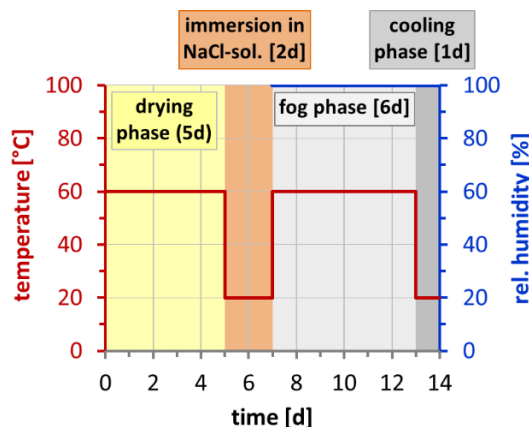
### 3.3 Description of selected test methods

#### 3.3.1 AAR concrete tests with external alkali supply

To evaluate the influence of internal hydrophobic treatment of exposed aggregate concrete on the AAR damage process, both of the two alternative test processes with external alkali application envisaged in the national standard [ARS] were applied. These AAR concrete tests are briefly described below. For comparison purposes, exposed aggregate concretes both without and with internal hydrophobic treatment were tested.

##### 60°C concrete prism test with external alkali supply

In this test, six defined preconditioned prismatic test blocks (75 mm x 75 mm x 280 mm) aged 28 days after the reference measurement were subjected to ten cycles of storage under changing climatic conditions (Figure 3.2). Each cycle comprises a five-day drying phase at a temperature of  $(60 \pm 2)^\circ\text{C}$ , a two-day immersion phase in the test solution (three test blocks each in a 10% and a 3% NaCl solution) at a temperature of  $(20 \pm 2)^\circ\text{C}$ , a six-day storage phase out of water at a temperature of  $(60 \pm 2)^\circ\text{C}$  (relative humidity at least 98%) and a one-day cooling phase at a temperature of  $(20 \pm 2)^\circ\text{C}$ . After this, the test blocks were removed for a maximum of two minutes from the closed stainless-steel containers to determine their length and mass. Linear expansion is taken as the AAR damage indicator. Its threshold value after 10 storage cycles under changing conditions is 0.5 mm/m when using a 10% NaCl solution and 0.3 mm/m when using a 3% NaCl solution. A more detailed description of the test procedure can be found in [28] and in RILEM AAR-12 [29,30].



(a) Schematic depiction of hygrothermic impact on the specimens during 1 cycle

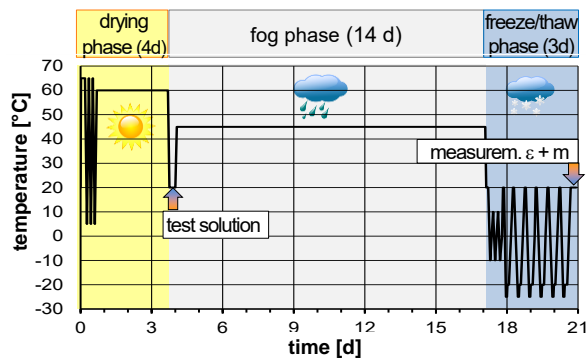


(b) Practical realisation

Figure 3.2: Description of 60°C concrete prism test with external alkali supply.

##### Cyclic climate storage test

For this test six prismatic samples (100 x 100 x 400 mm) of each concrete type were cast in two layers and compacted for 15 s each on a vibrating table. After one day in the moulds, concrete beams, covered with plastic foil, were cured for 7 days in a climate chamber (20 °C, 65 % RH). On the fifth day a 50 mm wide stripe of neoprene was glued around the upper surface of the concrete prism, protruding 25 mm above the later testing surface. After preconditioning and preparing, the samples were subjected to twelve cycles of cyclic climate storage test. Each cycle consists of three phases: four days drying, fourteen days fog storage and a three-day freeze-thaw-cycle phase (Figure 3.3). After each drying phase the NaCl test solution (3.6 M.-%) was applied to three specimens of each test series while demineralized water was applied to the other three. The linear expansion of the specimen determined after each freeze-thaw cycle phase is used as a damage indicator. To perform the measurement, the test solution on the surface of the test specimen was removed and reapplied after measurement. If the expansion exceeds a threshold of 0.5 mm/m or 0.4 mm/m (NaCl solution or water application) after twelve cycles, AAR damage potential is high. A detailed description of the test method is shown in [28].



(a) Schematic depiction of hygrothermic impact on the specimens during 1 cycle

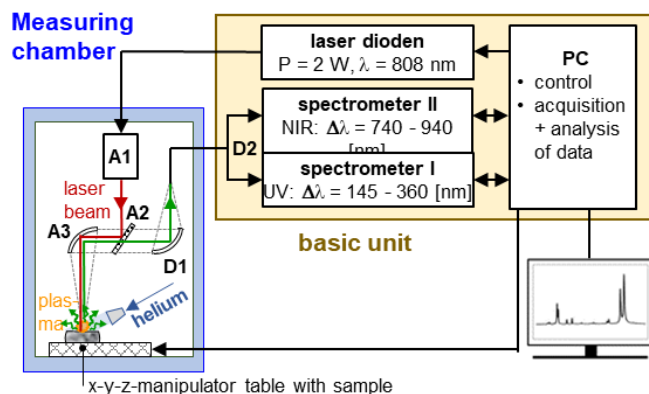


(b) Practical realisation

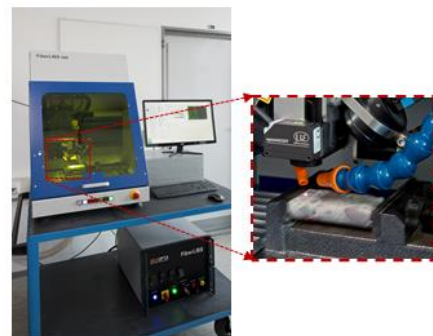
Figure 3.3: Description of the cyclic climate storage test.

### 3.3.2 Analysis of de-icing salt penetration in concrete using LIBS

The effect of hydrophobic agents in exposed aggregate concrete on alkali and chlorine penetration after both AAR concrete tests with external alkali supply were verified using LIBS [32-34]. For this purpose, after accelerated AAR storage, one test specimen each was cut, when dry, perpendicular to the test surface to obtain a  $100 \times 100 \text{ mm}^2$  cross sectional area. The Na and Cl distribution on the cut faces were determined by imaging using LIBS. The measuring principle of this method is shown in Figure 3.4: a pulsed, focused laser beam is applied to the surface of the building material. The high-power density of the laser beam leads to vaporization of a small near-surface area, generating plasma. As it cools, the plasma decomposes and emits element-specific radiation. The different elements can be identified by spectroscopic analysis of the radiation. They can also be quantified by additional calibration. In the present case the distribution of sodium, chlorine and calcium in particular was analysed by LIBS in vertical cross sections of specimens before and after AAR concrete tests. The determination of the calcium distribution is used to distinguish between the cement stone, which was of primary interest, and the aggregates. In this context it should be noted that the local resolution of LIBS is only sufficient to detect aggregates with a diameter bigger than 0.5 mm. In the present case, therefore, the amount of sodium and chlorine is related to the fine mortar content.



(a) Schematic depiction (A1: NdCr:YAG microchip-Laser, A2: dichroitic mirror, A3/D1: parabolic mirror, D2: optical Y-fibre)



(b) Overview and detail photographs of the equipment used

Figure 3.4: Measurement set-up of LIBS according to [32].

## 4. RESULTS AND DISCUSSION

### 4.1 Fresh concrete properties

The relevant fresh concrete properties of exposed aggregate concrete are shown in Table 4.1. It can be seen, that the significantly increased dosage of air entraining agent ensures the normative required air void content in the hydrophobic concrete. The bulk density and the degree of compactability does not differ significantly in the presence of an internal hydrophobic agent compared to mixtures without hydrophobic treatment.

Table 4.1: Fresh concrete properties of exposed aggregate concrete with and without hydrophobic agents.

fresh concrete properties			limit value	reference	hydrophobic
bulk density	[kg/m <sup>3</sup> ]	10 min	2000 .. 2600 (normal concrete)	2241	2245
		54 min		2254	2242
air void content	[Vol.-%]	10 min	5.5 ≤ x ≤ 6.5 (ref. to TL Beton Stb 07)	6,4	6,5
		54 min		5,9	6,0
degree of compactability	[-]	10 min	C1: 1.45..1.26 C2: 1,25..1,11	1,17	1,16
		54 min		1,22	1,22

### 4.2 Mechanical properties, capillary water absorption and resistance to freeze-thaw with de-icing salt of hardened concrete

As it can be seen in Table 4.2, the hydrophobic agent has a significant influence on mechanical and capillary water absorption as well as on resistance to freeze-thaw with de-icing salt. The different strengths are lowered significantly, resulting in measured values some of which are below the lower limit values. The measurement of static elastic modulus shows that concrete stiffness is also reduced.

On the other hand, capillary water absorption, the most important feature for verifying the hydrophobic nature of concrete, is significantly reduced. Consequently, the capillary transport mechanism of moisture, sodium and chloride ions is inhibited effectively. Thus, improvement of durability aspects should be expected.

In contrast to what the hypothesis suggests, the resistance to freeze-thaw with de-icing salt of exposed aggregate concrete with hydrophobic treatment was significantly reduced, despite the reduced absorption of test solution during preliminary storage and cyclic freeze-thaw with de-icing salt storage in the CDF test (Figure 4.1). The weathering of concrete treated with hydrophobic agent increased during the CDF test from 227 to 1346 g/m<sup>2</sup>. However, the threshold value of 1500 g/m<sup>2</sup> was not exceeded. More detailed tests show that pore structure is probably not the cause of this effect. The pore spacing factor (AF) and the micro air pore content (A<sub>300</sub>) referring to DIN EN 480-11 [35] for exposed aggregate concrete without and with hydrophobic agent were in accordance with the normative threshold values given by ZTV concrete StB [36]. To further examine the freeze-induced damage mechanism in concrete with hydrophobic agent, measurements with in-depth resolution of moisture and de-icing salt penetration during the CDF test are currently being carried out, among other tests. Furthermore, the holistic analysis of frost-induced damage mechanisms requires us to take into account the reduction of the concrete's mechanical properties by the hydrophobic agent.



Table 4.1: Mechanical properties of hardened concrete with and without internal hydrophobic treatment.

properties of hardened concrete			limit value	reference		hydrophobic	
				mean	standard deviation	mean	standard deviation
bulk density DIN EN 12390-7[21]	[kg/m <sup>3</sup> ]	7 d	-	2273	13	2253	8
		28 d		2225	9	2220	13
compressive strength DIN EN 12390-3 [23]	[N/mm <sup>2</sup> ]	7 d	- ≥ 37 <sup>12</sup>	37,7	2,4	27,1	1,6
		28 d		40,0	0,9	30,3	0,3
		180 d		44,7	0,5	37,7	1,1
bending tensile strength DIN EN 12390-5 [24]	[N/mm <sup>2</sup> ]	28 d	≥ 4,5 <sup>3</sup>	5,4	0,1	3,9	0,1
splitting tensile strength (lower cylindrical slices 50 mm height, 100 mm diameter) <sup>4</sup>	[N/mm <sup>2</sup> ]	28 d	≥ 3,3	4,4	0,2	3,7	0,3
static elastic modulus DIN EN 12390-13 [26]	[GPa]	28 d	-	28,9	0,3	21,4	0,2
capillary water absorption coefficient, based on DAfStb 422 [22]	[kg/(m <sup>2</sup> *h <sup>0,5</sup> )]	24h	-	0,41	0,02	0,11	0,08

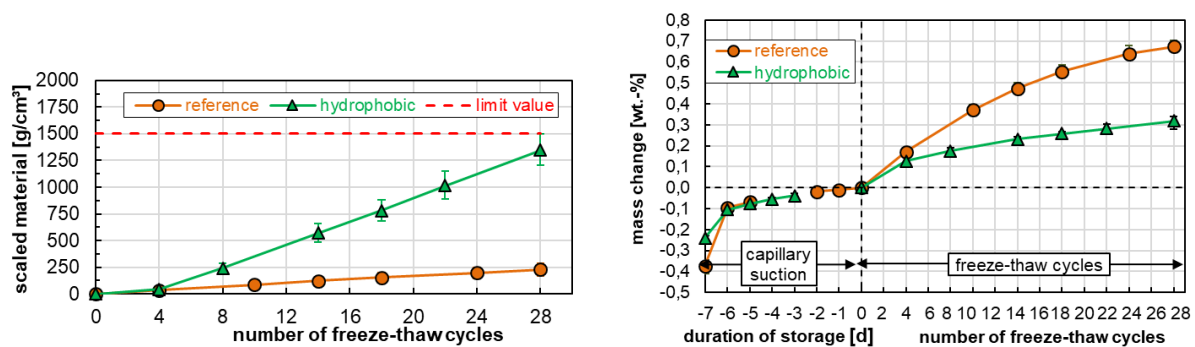


Figure 4.1: Temporal course of scaled material and mass change of samples made from concrete with and without hydrophobing agent during CDF-test.

### 4.3 AAR damage potential

#### 4.3.1 60°C concrete prism test with external alkali supply

Figure 4.2 gives a comparative presentation of the temporal development of the expansion and mass change of exposed aggregate concrete without and with hydrophobic agent in the 60°C concrete test with external alkali supply. It shows that the addition of hydrophobic agent to exposed aggregate concrete results in a significant reduction in expansion, regardless of the concentration of the NaCl solution. Here the expansion value actually shows negative values even for acceptance criterion of 10 cycles (concrete age: 168 days). The additionally recorded temporal development of the mass change leads to the conclusion that this is due to the drying shrinkage of concrete with hydrophobic treatment. The test sample's moisture release during individual cycles is obviously greater than its moisture absorption during the submersion and fog phases in each cycle. To sum up, it can be stated that the hydrophobic

1 characteristic compressive strength ( $f_{ck,cube}$ ); limit value referring to TL Beton-StB 07

2 calculation referring to DIN EN 12390-3 Anhang NA for dry storage at 20 °C, 65 % RH;  $f_{c,cube}=0,92*f_{c,dry}$

3 limit value referring to TL Beton-StB 07

4 test method and limit value referring to FGSV AL Sp-Beton – 2016 Blatt 1 [25]



agent in this AAR concrete test more-or-less completely cancels out the AAR damage potential of the exposed aggregate concrete.

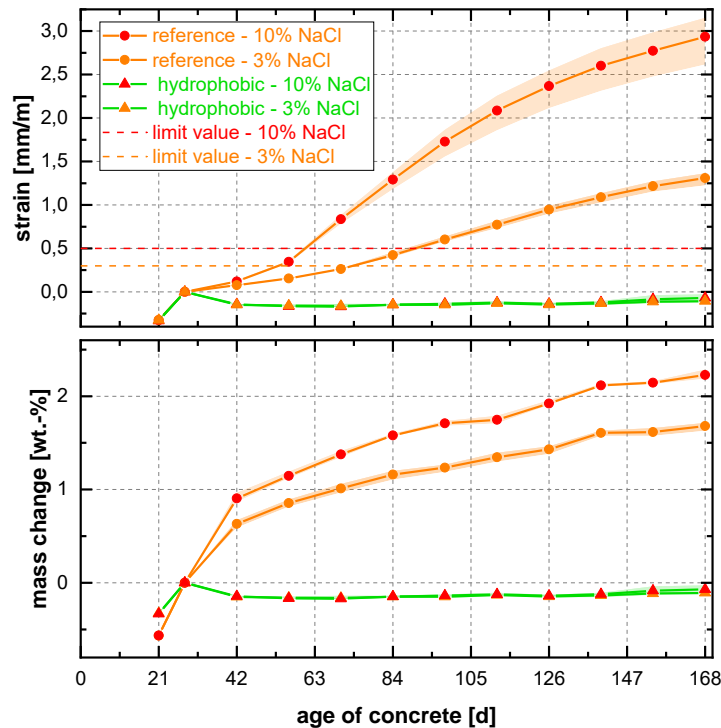


Figure 4.2: Temporal course of strain and mass change of samples made from concrete with and without hydrophobic agent during 60°C concrete prism test with external alkali supply.

#### 4.3.2 Cyclic climate storage test and subsequent investigations

The expansion of the test blocks during cyclic climate storage test is also significantly reduced by the addition of hydrophobic agent to exposed aggregate concrete. The average expansion of the test blocks even with the application of the 3.6% NaCl solution is reduced by 3.82 mm/m to 0.32 mm/m after 12 cycles, well below the threshold value of 0.5 mm/m (Figure 4.3). However, it is clear that from approx. the 8th cycle onwards, the average expansion of the concrete with hydrophobic treatment with NaCl solution application shows a continuous slight increase. This is not considered critical, however, because even after two additional cycles the expansion is still well below the threshold value.

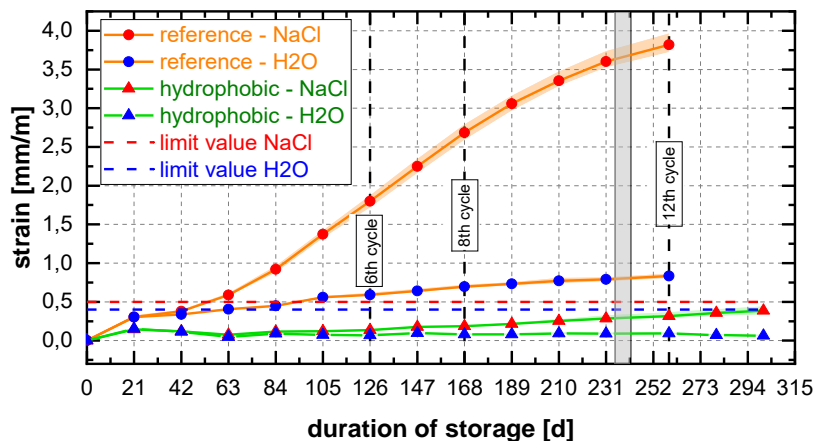


Figure 4.3: Temporal course of strain of samples made from concrete with and without hydrophobic agent during cyclic climate storage test (grey marked area: interruption of test due to device error).

Figure 4.4 and Figure 4.5 give detailed information about the occurrence of AAR characteristics and de-icing salt penetration in exposed aggregate concrete without and with hydrophobic treatment after 12 cycles of cyclic climate storage test with the application of 3.6% NaCl solution. Figure 4.5 gives a comparative presentation of the petrographic microscopy findings in vertical cross section of one test block without and one with hydrophobic treatment. The cracks and AAR-characteristics are highlighted in red in the overview micrograph.

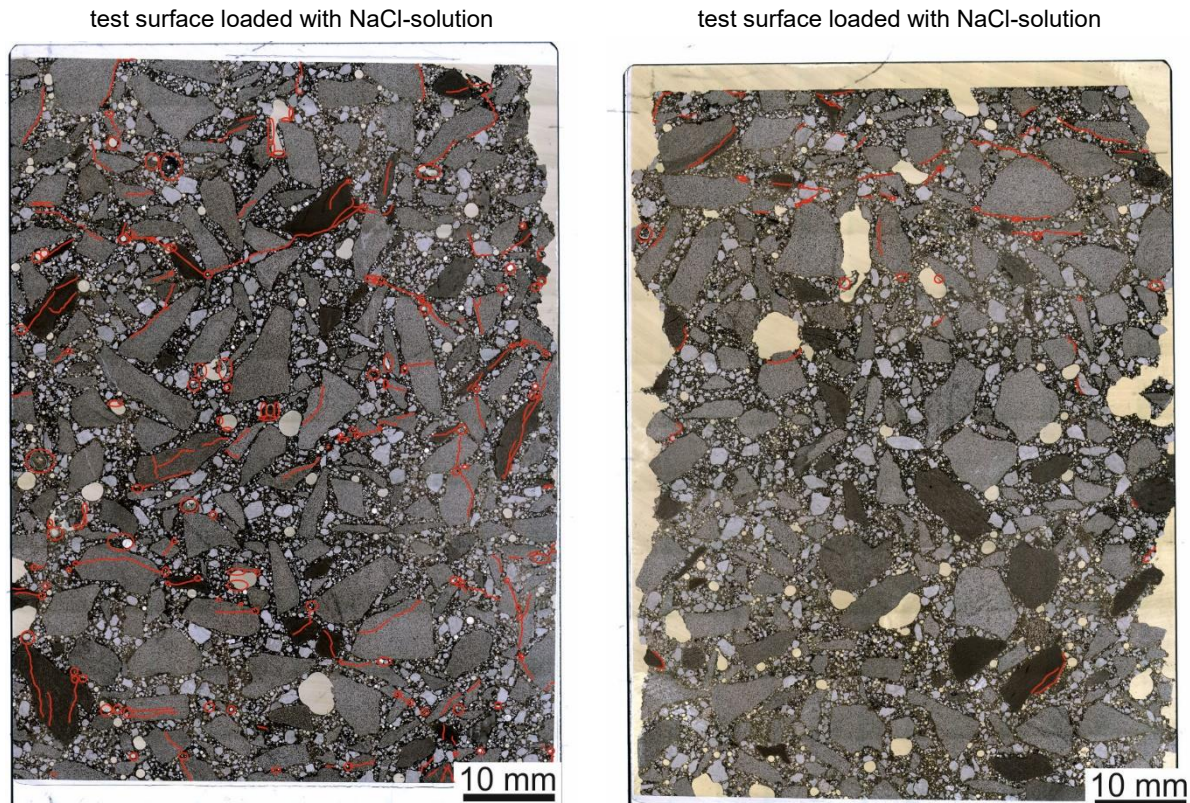


Figure 4.4: Thin section micrographs of sample cross-sections of concrete prisms after cyclic climate storage test with sodium chloride solution. Without (left) and with (right) internal hydrophobic treatment. Cracks and AAR-characteristics are highlighted in red.

Thin section microscopic investigations of the exposed aggregate concrete without hydrophobic treatment indicate severe damage due to AAR and secondary ettringite formation over the entire cross section (Figure 4.4, left). The coarse alkali-sensitive aggregates are often disrupted, and nearby pores are filled with AAR gel.

In the concrete prisms with hydrophobic treatment, there is little evidence of AAR characteristics and secondary ettringite formation (Figure 4.4, right). A very few characteristics were found in the uppermost parts of the concrete prism cross-section, where influence of the de-icing salt solution placed on the testing surface is high. Although not many AAR characteristics were found, the upper part of the cross-section shows many cracks, mostly within the cement paste. Most of the cracks appear in the transition zone (ITZ) between aggregate grains and cement paste matrix.

The investigations carried out by means of thin section microscopy suggest that the internal hydrophobic treatment of exposed aggregate concrete has great potential for AAR mitigation. As mentioned above, AAR characteristics in concrete with hydrophobic treatment are mostly confined to the uppermost layer, which may be due to a smaller sodium penetration depth in hydrophobic concrete compared to the reference concrete. Nevertheless, the uppermost 30-40 mm of the thin section comprise many cracks which cannot be assigned to a distinct deterioration mechanism. Further detailed investigations into this aspect are planned. Since most of the cracks are considered to form within the ITZ, it may be concluded that the ITZ is weakened due to hydrophobic treatment.

The findings of the thin section microscopy correspond to de-icing salt penetration determined by LIBS.



Thus, the comparative presentation in Figure 4.5 of sodium distribution images and the depth profiles thus determined show that in the reference concrete, a great deal of sodium penetrated throughout the whole cross section and only a small gradient developed from the test surface, where the solution was applied, to the underside of the test block. In contrast, the sodium only penetrated to a maximum depth of 35 to 40 mm in the concrete with hydrophobic treatment. The striking features in this case are the very high sodium content on the outer concrete boundary zone treated with NaCl solution, and the development of a very steep gradient to a depth of approx. 10 mm.

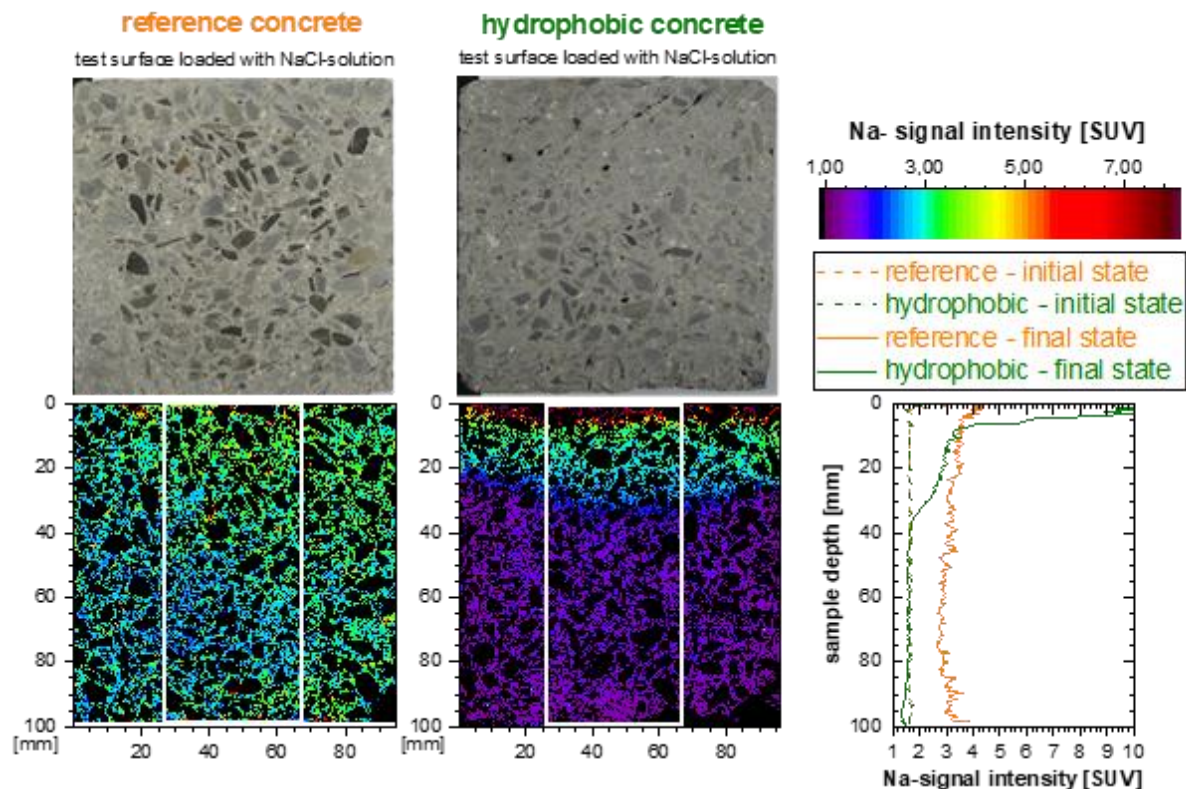


Figure 4.5: Sodium distribution in cross-sections of concrete prisms after 12 cycles of the cyclic climate storage test with NaCl-solution analysed by LIBS.

## 5. CONCLUSION AND OUTLOOK

The initial findings of the research project to give a holistic evaluation of internal hydrophobic treatment as a novel AAR prevention strategy for heavily used concrete pavement presented here permit the following conclusions:

- Due to antagonism between the additives used here, an increased quantity of air entraining agent in the fresh concrete is also required when hydrophobic agents are used in concrete pavement. The increased quantity of air entrainment agent ensures that the normative required air entrainment level in fresh concrete can be achieved. Recent investigations with a further developed silane-based hydrophobing agent and an adapted air-entraining agent show, that their addition in the exposed aggregate concrete can be significantly reduced.
- The influence of internal hydrophobic treatment of concrete pavement on damaging AAR is more strictly evaluated under cyclic climate storage test than under the 60°C concrete prism test with external alkali application. Despite this, we also demonstrated under cyclic climate storage test that if a suitable agent is selected, internal hydrophobic treatment drastically reduces the AAR damage process. This permits the conclusion that the novel AAR prevention strategy does indeed have the potential to make borderline aggregates usable, which was our aim.

- The disadvantages of the application of hydrophobic agents in the exposed aggregate concrete mixture used, that was the least favourable in relation to AAR testing, are the deterioration in mechanical properties and in resistance to freeze-thaw with de-icing salt. However, recent studies show that the use of a further developed silane-based hydrophobing agent with an adapted air entraining agent can significantly reduce the deterioration of both, mechanical properties and resistance to freeze-thaw with de-icing salt.
- In order to apply this novel AAR prevention strategy in practice, further holistic optimising of the performance of construction materials is urgently necessary. As well as the performance of the hydrophobic agent, this should include cement and aggregate selection, mixing and casting technology, mechanical performance, resistance to freeze-thaw with de-icing salt and AAR performance.

## 6. ACKNOWLEDGEMENT

First, the authors wish to thank the Federal Ministry of Transport and Digital Infrastructure for funding this project. We would also like to say thank you to Dipl.-Phys. G. Wilsch und Dipl.-Ing. K. Borchardt (BAM) for the performance and evaluation of the LIBS measurements.

## 7. REFERENCES

- [1] Weise, F.; Kind, T.; Stelzner, L.; Wieland M.: Dunkelfärbung der Betonfahrbahndecke im AKR-Kontext. *Beton- und Stahlbetonbau*, 113 (2018), Issue 9, Verlag Ernst & Sohn, Berlin, pp. 647-655.
- [2] Bundesministerium für Verkehr Bau und Stadtentwicklung (04/2013): Allgemeines Rundschreiben Straßenbau (ARS) No. 04/2013: Vermeidung von Schäden an Fahrbahndecken aus Beton in Folge von Alkali-Kieselsäure-Reaktion (AKR). Bonn, 2013.
- [3] Weise, F.; Schrang K.: Bewertung und Optimierung der Hydrophobierung zur Verminderung des AKR-Schädigungsfortschrittes in Fahrbahndeckenbetonen, Berichte der Bundesanstalt für Straßenwesen, Unterreihe "Straßenbau", Bergisch Gladbach, 2016.
- [4] Bérubé, M.-A.; Chouinard, D.; Pigeon, M.; Frenette, J.; Boisvert, L.; and Rivest, M.: Effectiveness of sealers in counteracting alkali-silica reaction in plain and air-entrained laboratory concretes exposed to wetting and drying, freezing and thawing, and salt water. *Canadian Journal of Civil Engineering*, 29(2), 289-300, 2002.
- [5] Bérubé, M.-A.; Chouinard, D.; Pigeon, M.; Frenette, J.; Rivest, M. and Vézina, D.: Effectiveness of sealers in counteracting alkali-silica reaction in highway median barriers exposed to wetting and drying, freezing and thawing, and deicing salt. *Canadian Journal of Civil Engineering*, 29 (2), 329-337, 2002.
- [6] Wehrle, E. R.: The Effect of Coatings and Sealers Used to Mitigate Alkali-Silica-Reaction and/or Delayed Ettringite Formation in Hardened Concrete. Thesis Master of Science in Engineering, University of Texas at Austin, 2010.
- [7] Medeiros, MHF; Helene, P.: Surface treatment of reinforced concrete in marine environment: Influence on chloride diffusion coefficient and capillary water absorption. *Construction and Building Materials* 23(3), 1476-1484, 2009. <https://doi.org/10.1016/j.conbuildmat.2008.06.013>
- [8] Schäffel P, Neue Ansätze zur Vermeidung einer schädigenden Alkali-Kieselsäure-Reaktion in Beton für Fahrbahndecken. *Beton- und Stahlbetonbau*, 111 (2017), Issue 12, Verlag Ernst & Sohn, Berlin, pp. 116-124.
- [9] Gerdes, A.; Oehmichen, D.; Preindl, B. and Nüesch, R: Chemical reactivity of silanes in cement-based materials. 4th International conference on water repellent of buildings materials, Aedifico Publishers, Stockholm (SE), 2005, pp. 47-58.
- [10] Oehmichen, D. S.: Mechanismen der Hydrophobierung zementgebundener Werkstoffe mit siliciumorganischen Verbindungen. Dissertation, Universität Fridericiana zu Karlsruhe (TH), 2008.
- [11] De Vries, I.J. and Polder, R.B.: Hydrophobic treatment of concrete. *Construction and Building Materials* 11(4): 259-265, 1997. [https://doi.org/10.1016/S0950-0618\(97\)00046-9](https://doi.org/10.1016/S0950-0618(97)00046-9)

- [12] Tian, Y.; Wang, P.; Zhao, T.; Ma, Z.; Jin, Z. and Zhao, H.: Influence of Water-Repellent Treatment with Silicon Resin on Properties of Concrete. *Advances in Materials Science and Engineering* 2019 12. 10.1155/2019/5743636
- [13] Xian, Y.-Z.; Wittmann, F.; Zhao, T.-j. and Giessler, S.: Chloride penetration into integral water repellent concrete. *Restoration of Buildings and Monuments* 13(1), 17-24, 2007.
- [14] Zhang P, Wittmann F, Zhao T, (2009) Capillary Suction of and Chloride Penetration into Integral Water Repellent Concrete/Kapillare Saugfähigkeit und Eindringen von Chloriden in integral hydrophobierten Beton. *Restoration of buildings and monuments* 15(3): 187-194.
- [15] Ma, Z.; Wittmann, FH; Xiao, J. and Zhao, T.: Influence of freeze-thaw cycles on properties of Integral Water Repellent Concrete. *Journal of Wuhan University of Technology-Mater. Sci. Ed.* 31(4): 851-856, 2016. 10.1007/s11595-016-1458-9.
- [16] Ma, Z.; Zhu, F. and Zhao, T.: Effects of surface modification of silane coupling agent on the properties of concrete with freeze-thaw damage. *KSCE Journal of Civil Engineering* 22(2): 657-669, 2018. 10.1007/s12205-017-1718-z.
- [17] Milenkovic, N.; Staquet, S. and Lecomte, J-P.: Non-ionic silane emulsion as integral water repellent–impact on cement hydration process. *Proceedings of 7th International Conference on Water Repellent Treatment and Protective Surface Technology for Building Materials*, 2014.
- [18] Spaeth, V.; Delplancke-Ogletree, M.; Lecomte, J.; De Clercq, H. and Charola, A.: Hydration process and microstructure development of integral water-repellent cement based materials, *Hydrophobe V*, 5th International Conference on Water Repellent Treatment of Building Materials. *Aedificatio*, Brussels, 2008, p. 254.
- [19] DIN EN 12350-4: Prüfung von Frischbeton – Teil 4: Verdichtungsmaß; Beuth Verlag, 2019.
- [20] DIN EN 12350-7: Prüfung von Frischbeton - Teil 7: Luftgehalt - Duckverfahren; Beuth Verlag, 2019.
- [21] DIN EN 12350-6: Prüfung von Frischbeton - Teil 6: Frischbetonrohddichte; Beuth Verlag, 2019.
- [22] DAfStb-Heft 422: Prüfung von Beton–Empfehlungen und Hinweise als Ergänzung zu DIN 1048. Beuth Verlag GmbH Berlin-Köln, 1991.
- [23] DIN EN 12390-3: Prüfung von Festbeton - Teil 3: Druckfestigkeit von Probekörpern; Beuth Verlag, 2019.
- [24] DIN EN 12390-5: Prüfung von Festbeton - Teil 5: Biegezugfestigkeit von Probekörpern; Beuth Verlag, 2019.
- [25] Arbeitsanleitung zur Bestimmung der charakteristischen Spaltzugfestigkeit an Zylinderscheiben als Eingangsgröße für die Bemessung von Betondecken für Straßenverkehrsflächen - AL Sp-Beton, Forschungsgesellschaft für Straßen- und Verkehrswesen (FGSV), Cologne, 2016.
- [26] DIN EN 12390-13: Prüfung von Festbeton – Teil 13: Bestimmung des Elastizitätsmoduls unter Druckbelastung (Sekantenmodul); Beuth Verlag, 2013.
- [27] Setzer MJ, Fagerlund G, Janssen DJ, (1996) CDF test — Test method for the freeze-thaw resistance of concrete-tests with sodium chloride solution (CDF). *Materials and Structures* 29(9): 523-528. 10.1007/bf02485951.
- [28] TP B-StB, Technische Prüfvorschriften für Verkehrsflächenbefestigungen - Betonbauweisen TP B-StB Teil 1.1.09: AKR-Potenzial und Dauerhaftigkeit von Beton (60 °C-Betonversuch mit Alkalizufuhr). In: *Forschungsgesellschaft für Straßen- und Verkehrswesen - Arbeitsgruppe Betonbauweisen (Ed.) FGSV Verlag, Cologne, 2018, pp. 1-13.*
- [29] Borchers I; Rønning TF; Wigum BJ; Lindgård J (2019): RILEM Recommended Test Method: AAR-12. Determination of binder combinations for non-reactive mix design or the resistance to alkali-silica reaction of concrete mixes using concrete prisms – 60 °C test method with alkali supply (Final draft RILEM/TC 258-AAA-WP1-N038)
- [30] Rønning TF, Lindgård J, Borchers I (2021) ASR performance testing concepts – RILEM AAR-10, AAR-11 and AAR-12. *Proceedings of the 16th ICAAR, Lisbon, Portugal*

- [31] TP B-StB, Technische Prüfvorschriften für Verkehrsflächenbefestigungen - Betonbauweisen TP B-StB Teil 1.1.10: AKR-Potential und Dauerhaftigkeit von Beton (Klimawechselagerung). In: Forschungsgesellschaft für Straßen- und Verkehrswesen - Arbeitsgruppe Betonbauweisen (Ed.) FGSV Verlag, Köln, 2018, pp. 1-19.
- [32] Wilsch G, Weritz F, Schaurich D, Wiggenhauser H, (2005) Determination of chloride content in concrete structures with laser-induced breakdown spectroscopy. *Construction and Building Materials* 19(10): 724-730. <https://doi.org/10.1016/j.conbuildmat.2005.06.001>
- [33] Gottlieb, C.; Günther, T.; Wilsch, G.: Impact of grain sizes on the quantitative concrete analysis using laser-induced breakdown spectroscopy. *Spectrochimica Acta Part B: Atomic Spectroscopy*, vol. 142, pp. 74-84, 2018.
- [34] Weise, F., Millar, S. und G. Wilsch: Analyse des Tausalzeintrags in Fahrbahndeckenbetone mit neuartiger Prüftechnik. In: *Beton und Stahlbetonbau*, 113 (2018), Heft 9, Verlag Ernst & Sohn, Berlin, pp. 656-666.
- [35] DIN EN 480-11: Zusatzmittel für Beton, Mörtel und Einpressmörtel - Prüfverfahren - Teil11: Bestimmung von Luftporenkennwerten in Festbeton; Beuth Verlag, 2005.
- [36] ZTV Beton-StB 07: Zusätzliche Technische Vertragsbedingungen und Richtlinien für den Bau von Tragschichten mit hydraulischen Bindemitteln und Fahrbahndecken aus Beton. FGSV Verlag, Cologne, 2007.