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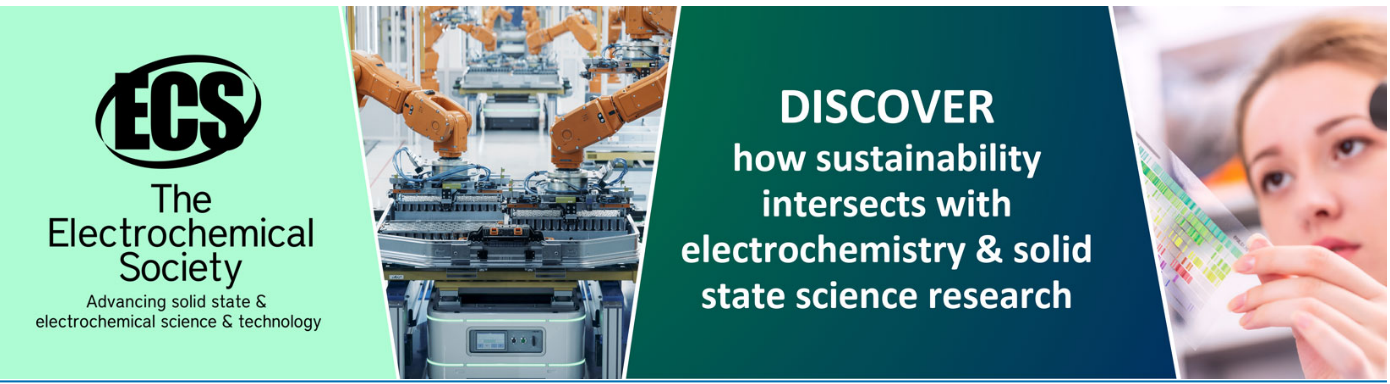

Old cement-based render as the cause of extremely low carbonation of 100-year bridge concrete

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Abstract. In-situ research and laboratory examination provided on concrete core samples from old bridge structures confirmed that a thin layer of ordinary cement-based render coat protects the underlying concrete from carbonation. The average measured value by phenolphthalein test was less than 2 mm after more than 100 years of service life in exposure class XC3 of EN 206. Low carbonation depth is explained by the presence of a thin (2-4 mm) layer of the protective render coat (PRC) situated on the bridge concrete. The place, where the PRC was of good quality was almost impermeable and the carbonation of the concrete underneath was even 0 mm. If the PRC locally spalled, the carbonation depth of the same concrete, at the same structure and environment reached at this place even more than 80 mm. It was observed that low carbonation of concrete significantly depends on the non-permeability of the PRC. A narrow free space filled with the carbonates causes increased non-permeability of the PRC creating thus the built-in limestone-based (anti-carbonation) barrier with the ability to dramatically reduce CO_2 penetration into the beneath concrete over time. Values from in-situ and laboratory research are presented in the article with the explanation of these phenomena.

1. Introduction

In-situ research of a 125 years old Monier type concrete bridge at Krásno nad Kysucou in 2014 observed that a (2-4) mm thick PRC protected the underlying concrete from carbonation [1]. The repeated measurements performed in 2015 by three independent workplaces (STU Bratislava, TU Žilina and TSÚS Bratislava) proved the previous result. The same results were found on the 100-year bridges Sládkovičovo and Rimavská Sobota. The overall diagnostics of the old bridges were divided into four main phases. The first phase was concerned by visual observation of the bridge and site-determinations for consequent testing, the second included the whole non-destructive testing and taking the concrete cores for laboratory mechanical, microstructure and pore structure tests. The third phase consisted of extensive laboratory tests described below. The fourth, now experimentally ongoing phase, deals with the development of modern surface treatment from today's materials.

2. Methods of testing

In-situ tests applied in the current project concerned the following procedures: 1) testing concrete by hardness method using Schmidt hammer, model N according to STN 73 1373, 2) ultrasonic examination of concrete by STN 73 1371 using PUNDIT apparatus searching for the homogeneity of concrete material and hence the mechanical properties, 3) measurements of surface tensile strength of concrete according to STN EN 12 636, 4) measurements of surface permeability of uncovered and covered concrete by the PRC measured by Torrent method [2] (figure 1(a) and 1(b)) and 5) carbonation depth by phenolphthalein test. The taken cylindrical cores with diameter 100 mm and length at least 300 mm were tested for volume density (VD), dynamic modulus of elasticity, Young's (static) modulus of elasticity and compressive strength according to STN 73 1371, STN ISO 6784 and STN EN 123903, respectively. The cylindrical concrete specimens were half broken in the laboratory by longitudinal splitting. Phenolphthalein test was repeated on the first part and the second part was used to study the microstructure and pore structure. Consequently, two sub-samples were chosen for in-deep detail verifications – surface layer: directly exposed to prolonged exposure to CO_2 from the air and – internal layer: covered with an overlay of concrete kept out of direct contact with open air.

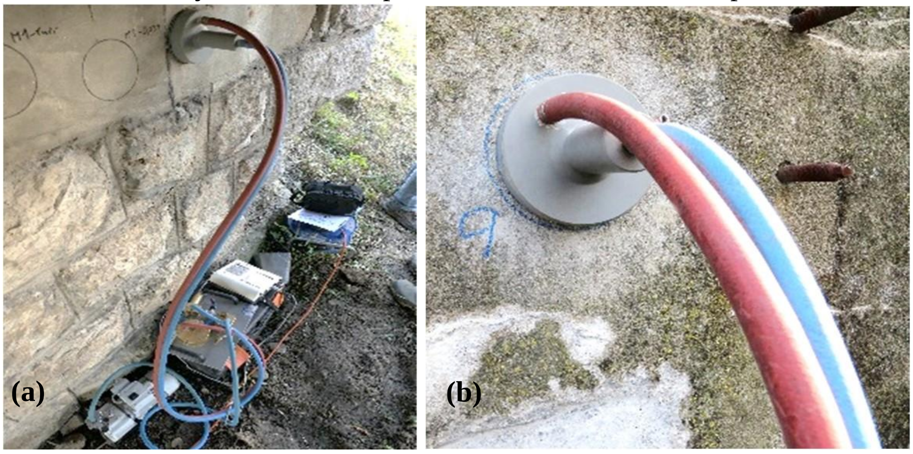


Figure 1. Torrent device for the on-site surface permeability measurement.

Subsequently, the sub-samples were crushed, heated at 60 °C to constant weight and ground for fineness passing 0.063 mm for next analytical procedures. Chemical analysis of the ground concrete matrix (without large aggregate grains) was performed in concordance with STN 72 010. The X-ray diffraction analyses were made on the automatic theta/theta X-ray diffractometer STOE & Cie GmbH (Germany) using the program Bede ZDS W95/98/NT for assessing the records and run in a 2Θ range of 5-65°. CuK_{α} radiation and Ni-filter were used. Thermal analyses were conducted at the NETZSCH apparatus STA 449 F3 Jupiter (Germany). Samples weighing 100 mg were heated in flowing air within the heating range (20-1100) °C and at a heating rate 10 °C/minute. The microstructure of bulk concrete samples (without large aggregate grains) was studied by scanning electron microscopy on the JEOL 7500F apparatus (Japan). The samples were fixed using a two-component epoxy paste in aluminium discs with a diameter of 25 mm, which are used to transfer the sample to the interior of the microscope. These prepared samples were plated with a mixture of gold-palladium under argon. For plating the spreader device Balzers was used. The image was captured electronically using the program "PC SEM" (version 3.0.1.8). Optical microscopy was carried out on a digital device VHX-5000 with CMOS image sensor 1/1 8 virtual pixels 1600 (H)×1200 (V) from Keyence International (Belgium). The present state of concrete is assessed on the base of the above set of the obtained results.

3. Results and Discussion

In-situ investigation revealed the relationship between the permeability measured on the PRC and the carbonation depth of the underlying concrete. Most of the measured placed appeared to be almost impermeable (measured coefficients of permeability were below $0{,}01\times10^{-16}$ m²) and at these places, the underlying concrete showed negligible carbonation depth [3] (max. 2 mm) even after being exposed to XC3 exposure class of STN EN 206+A1 for more than 100 years. At some cases, negligible carbonation was measured also if the permeability results were a bit higher. It was found that even a small crack (crack width below 0.05 mm) caused higher permeability results and also a higher carbonation depth at this location. The results of the in-situ measurements are presented in tables 1 - 3 and figures 2 and 3 for different more than 100 years old bridges.

This article is mainly focused on the bridge Sládkovičovo and Rimavská Sobota (only partially to Krásno nad Kysucou) with the observed negligible depth of carbonation. The carbonation was assessed by the own methodology based mainly on TG-DTA analysis supplemented by the XRD technique. These techniques in concrete containing limestone and dolomite stone failed to distinguish the origin of carbonates: the one when calcite is formed by the carbonation from the one when it is derived from the used aggregate. The reliable use of TG-DTA and XRD techniques is guaranteed in concrete made with siliceous aggregate. The mineralogical composition of the aggregates confirmed SiO_2-based character by the XRD analysis [4].

Table 1. Results of in-situ measurement of carbonation depth at the bridge in Sládkovičovo.

Sample		Coefficient of permeability	Average carbonation depth	Notes
Denotation	Surface	kT(x10^{-16} m²)	(mm)	
G1	PRC	0.073	<1	High-quality cement-based render
G2	PRC	0.002	<1	High-quality cement-based render
M3	PRC	0.039	<1	High-quality cement-based render
M4	PRC	0.246	<1	High-quality cement-based render
M9	PRC	0.189	<1	High-quality cement-based render
M10	PRC	0.062	<1	High-quality cement-based render
M6	PRC	0.123	10	Lower quality cement-based render
M2	PRC	0.178	15	Lower quality cement-based render
M7	PRC	4.943	20	Lower quality cement-based render
M8	PRC	8.464	20	Lower quality cement-based render
M1	PRC	>10	25	Small crack of width less than 0,05 mm in the render
M5	PRC	>10	30	Lower quality render, cavern below the cement-based render
B1	Uncovered concrete	>10	60	Spalled render
B2	Uncovered concrete	>10	80	Spalled render

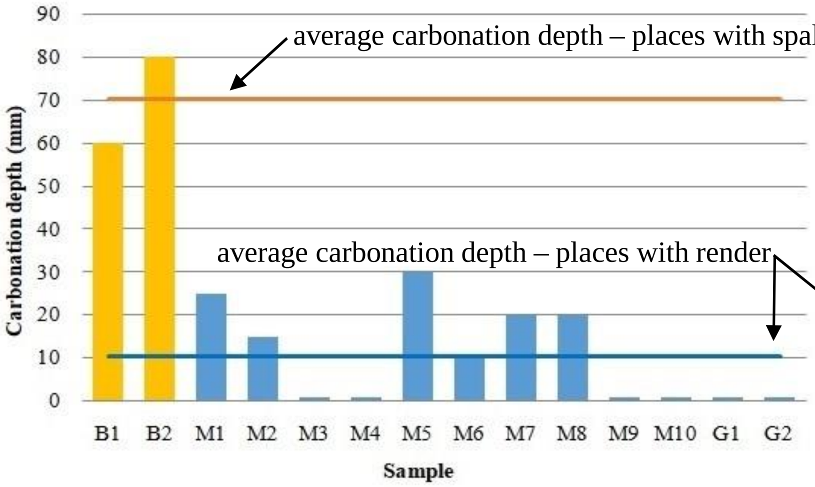
Table 2. Results of in-situ measurement of carbonation depth at the Bridge in Krásno nad Kysucou.

Sample		Coefficient of permeability	Average carbonation depth	Notes
Denotation	Surface	kT(x10^{-16} m²)	(mm)	
E1	PRC	Not measured	<4	High-quality cement-based render
E2	PRC	Not measured	<4	High-quality cement-based render

Table 3. Results of in-situ measurement of carbonation depth at the Bridge in Rimavská Sobota.

Sample		Coefficient of permeability	Average carbonation depth	Notes
Denotation	Surface	kT(x10^{-16} m²)	(mm)	
C1	PRC	0.001	<2	High-quality cement-based render
C2	PRC	0.001	<2	High-quality cement-based render
C3	PRC	7.163	15	Small crack of width less than 0.05 mm in the render
D1	Uncovered concrete	>10	50	Spalled render

Carbonation of the underlying concrete is closely related to the impermeability of the PRC layer as stated in tables 1 to 3. Figures 4(a) and 4(b) illustrate differences between the microstructure of the unprotected concrete surface and surface-protected by the PRC.



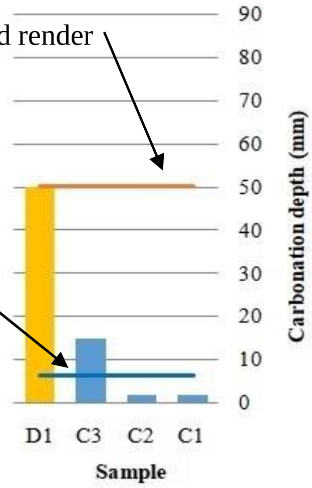


Figure 2. Results of in-situ measurement of carbonation depth at the Bridge in Sládkovičovo.

Figure 3. Results of in-situ measurement of carbonation depth at the bridge in Rimavská Sobota.

Concrete with direct contact to air demonstrates the evident amount of the coarse crystallized carbonation products, while that PRC-protected is densified by fine-grained carbonate alternates. The reduced content of coarse-grained $CaCO_3$ in the original, 100 - year - old PRC is attributed to a narrow space capable for its formation. When yet formed, the spatial deficiency of the PRC does not allow further CO_2 penetration into the concrete beneath. The carbonation depth of the concrete specimen with the uncovered and covered surface is illustrated in Figure 5(a) and 5(b).

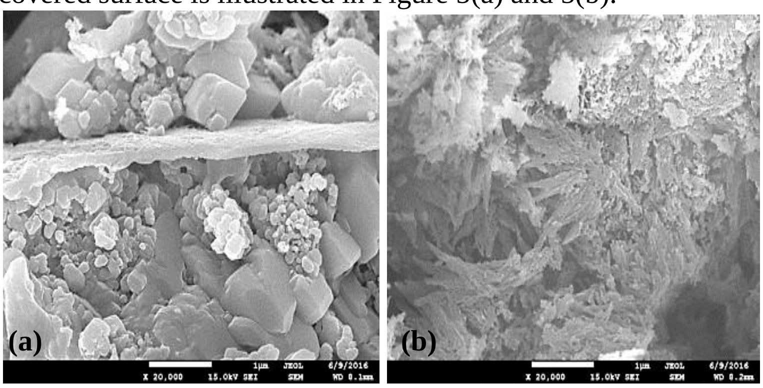


Figure 4. The microstructure of uncovered (0-20) mm surface concrete B1 (a) and surface-protected concrete by the PRC situated over M3 (b).

4. Degree and stage of carbonation

The degree of carbonation (CD) as the CaO_{Carb}/CaO_{Total} ratio×100 (% wt.), was calculated from TGDTA results and chemical analysis. CaO_{Carb} means the CaO content bound in $CaCO_3$ originated from carbonation reaction and CaO_{Total} concerns CaO bound in $CaCO_3$, $Ca(OH)_2$, gel-like hydration products (C-S-H, C-A-H) and $CaSO_4 \times 2H_2O$. The extent of carbonation attack is also specified by the degree of modification changes (DMC) given by the $CaCO_{3,\ \text{coarse-grained}}/CaCO_{3,\ \text{fine-grained}}$ ratio. The fine-grained $CaCO_3$ is detected by TG-DTA between (600-750) °C and coarse-grained $CaCO_3$ between (750-

1100)°C. The extent of CO_2 attack is characterized by four stages of carbonation (I<55 %; II: 55-65 %; III. 66-80 %; IV.>80 %) [4]. Table 4 summarizes the carbonation characteristics of uncovered concrete, PRC-protected concrete and PRC themselves.

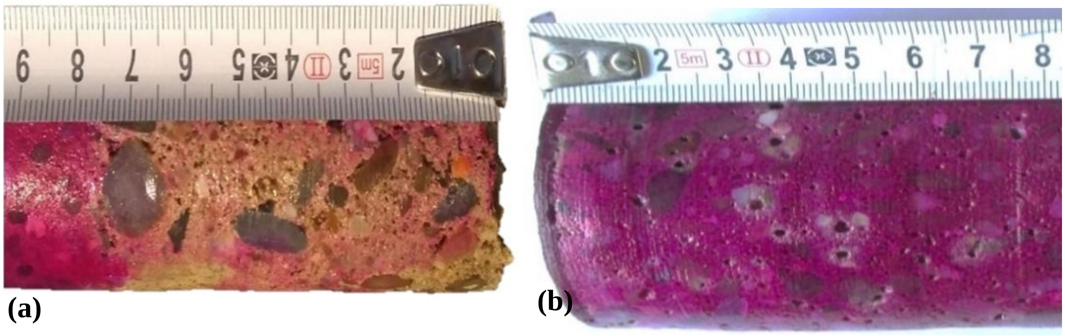


Figure 5. Carbonation depth of uncovered concrete B1 (a) and concrete below the PRC M3(b) characterized by the low permeability of 0.073×10^{-16} m^2.

Table 4. The assessment of carbonation attack by the results of chemical and thermal analysis.

Sample as marked in Tables 1 to 3 and Figure 2	CaO_{total} (% wt.)	CaO_{Carb} (% wt.) occurring in			Assessment of carbonation		
		fine - grained $CaCO_3$	coarse- grained $CaCO_3$	total $CaCO_3$	CD (%)	DMC (-)	Carbonation stage (-)
B1 - surface	9.09	2.40	7.87	10.27	113.0	3.3	IV
B1 - internal	8.51	1.40	3.08	4.49	52.8	2.2	I
M3 - surface	9.86	1.77	3.87	5.64	57.2	2.2	II
M3 - internal	7.06	1.41	2.83	4.24	60.1	2.0	II
PRC over M3	29.11	5.05	10.19	15.24	52.4	2.0	I
D1 - surface	15.66	4.91	9.55	14.46	92.3	1.9	IV
D1 - internal	19.41	1.75	9.48	11.23	57.9	5.4	II
C2 - surface	20.68	2.10	10.79	12.89	62.3	5.1	II
C2 - internal	19.42	1.63	8.41	10.04	51.7	5.2	I
C1 - surface	19.90	1.80	8.78	10.58	53.2	4.9	I
C1 - internal	16.07	1.67	7.36	9.03	56.2	4.4	II
PRC over C2	20.25	4.32	12.14	16.46	81.3	2.8	IV
PRC over C1	20.15	4.42	13.40	17.82	88.4	3.0	IV

Concrete samples (surface is 0-20 mm and internal is approximately 280-300 mm from the surface) from Sládkovičovo bridge show lower CaO_{Total} content compared to those of Rimavská Sobota. This fact indicates differences in cement content in both types of concrete. Concrete samples from Rimavská Sobota contain more carbonation products. The PRC over M3 records more CaO_{Total} than PRCs over C1 and C2. This indicates a higher proportion of cement binder in PRC over M3 compared to PRCs over C1 and C2. Both bridges consistently confirm that in the surface application of PRC, the carbonation stage (SC) of covered concrete moves at levels II. and I, while uncovered concrete is characterized by stage IV. Significantly higher degree of modification changes in concrete from Rimavská Sobota compared to Sládkovičovo bridge indicates the higher conversion of fine-grained $CaCO_3$ to coarsegrained crystals. This may be due to a lower proportion of cement-based binder and therefore to the easier conversion of the carbonates present to the coarse-grained modification. The same assumption applies to the PRCs. The PRC from Sládkovičovo is characterized by the SC I, while from Rimavská

Sobota by the SC IV. Despite this fact, PRCs from Rimavská Sobota bridge eliminate the carbonation attack in 100 years of operation by the same way as that from Sládkovičovo with the SC I. The achieved results confirm the anti-carbonation effect of applied PRCs regardless of the achieved degree of carbonation, degree of modification changes and carbonation stage. It is apparent from this finding that an important property of PRC in eliminating the carbonation attack is the sealing ability by accumulating carbonates in the narrow PRC layer and thereby increasing the impermeability against further penetration of CO_2 into the interior of the underlying concrete.

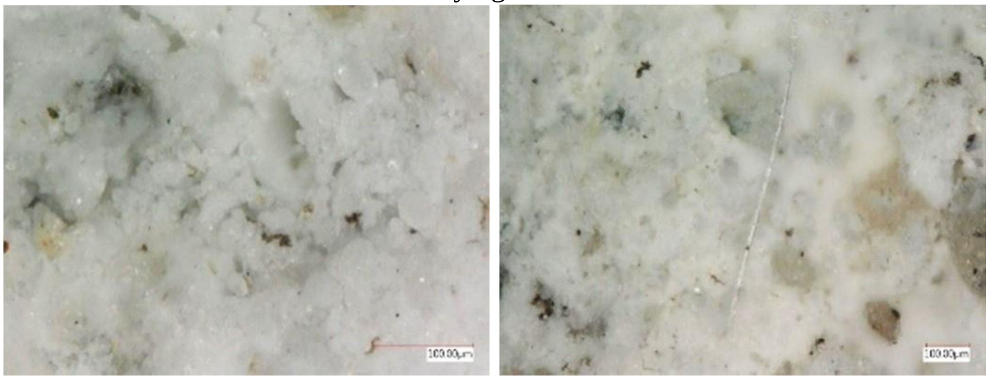


Figure 6. Dense barrier created from the carbonation products in the space-tight PRC M3.

The thin PRC layer is characterized by a dense carbonate substance even up to the amorphous state boundary, which is referred to as "carbonate milk" (a designation that has not been used in the literature yet). The images from the optical microscope at various magnifications show invisibly but later demonstrably accumulated carbonation milk within the PRC (figure 6). Shining needles confirm also the presence of crystal-developed coarser $CaCO_3$ compressed within the PRC thickness. The carbonate milk has such a low permeability with optimally functional PRCs that the spatially sealed barrier of carbonation products is created, preventing thus carbonation of old concrete effectively.

5. Conclusions

Based on the results of the series of the performed tests, the following conclusions are drawn:

- The in-situ measurements of carbonation depth show that a high quality (2-4) mm thin cementbased protective render coat can effectively protect the underlying concrete against carbonation within the 100-year service life of a bridge.
- Carbonation depth of the underlying concrete depends upon the non-permeability of the PRC. The close mutual correlation between the depth and extent of carbonation phenolphthalein, TGDTA) and the coefficient of surface permeability (Torrent method) was found.
- The very low permeability of the PRC is caused by the accumulated carbonates in a narrow spatial area of the PRC; the formed carbonation milk condenses the space up to the impermeable barrier for CO_2.

6. References

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