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Corrosion protection by mineral coatings of drinking water reservoirs made of concrete

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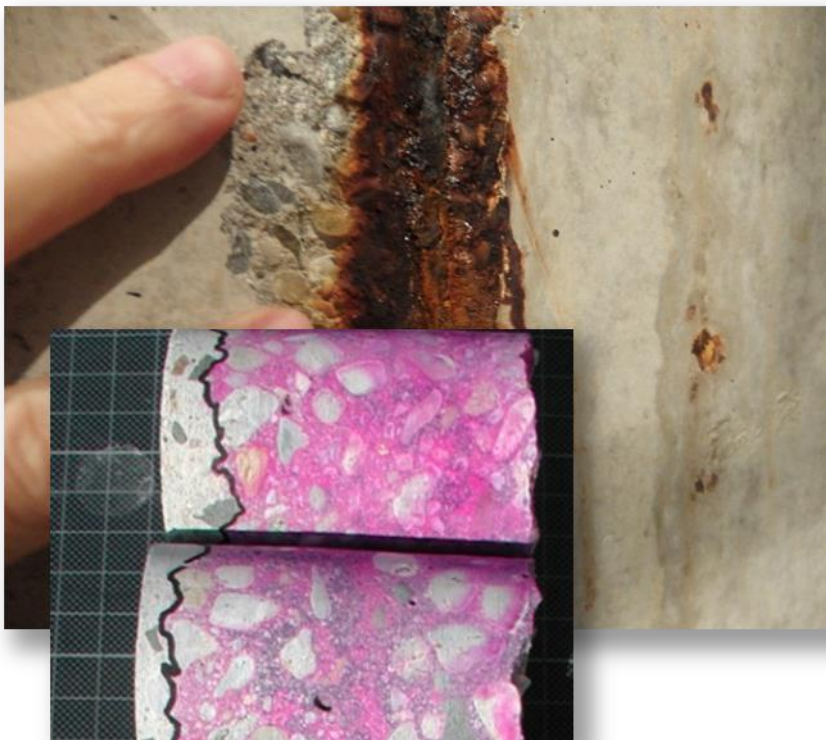
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Introduction

As part of the revision of DVGW Code of Practice W 300 Parts 1 to 5, essential technical requirements for materials and surfaces for the construction and repair of concrete drinking water tanks have been defined. For the use of mineral protection systems, the guarantee of durability must be ensured, taking into account the special stresses within drinking water tanks. Furthermore, a realkalization of leached concrete surfaces is assumed for selected mineral systems.

Within the framework of a DVGW research project, the processes occurring during the leaching and realkalization of concrete surfaces and mineral protection systems were investigated in laboratory tests. In six months of storage tests in demineralized water, significant surface changes were observed both on lower-quality concrete surfaces and on XTWB-compliant concretes and DVGW-W 300-5-compliant mineral

protection systems. Leaching could be detected up to a depth of three millimeters. Due to the pronounced hydrolytic corrosion, calcium silicate cement paste was completely decomposed on the surface. A commercial calcium-aluminate-based protective system played a special role, leaching more strongly in some cases but showing no visually superficial signs of corrosion. The use of soft tap water did not lead to any comparatively pronounced damage or leaching. Leaching could be accelerated by means of electric fields, but untypical surface changes resulted.

No deeply leached concrete surfaces could be obtained by means of the leaching tests. Nevertheless, in order to test the realkalization of concrete surfaces under ambient conditions relevant to drinking water, tests were carried out on carbonated concrete, which were to be realkalized by applying mineral protection systems. The tests showed a two-stage realkalization process, which took place distinctly directly after application as so-called contact realkalization, followed by a diffusion-controlled migration of alkalis in accordance with the root-time law. Important application, storage, concrete and mortar parameters were investigated as factors influencing the realkalization process. Based on the laboratory tests, an empirical model was developed to describe and estimate the realkalization.

The results essentially confirm the application limits for cementitious coatings as a lining principle set out in DVGW Code of Practice W 300, and the specifications of the code are on the safe side. In particular, the limit value of the total porosity is taken as the characteristic value of the hydrolysis resistance of cementitious coatings. The leaching tests showed that not only a low porosity is decisive for a high resistance to water loading, but also the type of cement, the surface treatment and the compaction are to be considered as influencing factors. In the case of linings, an alkaline coating with realkalization depot should be used, whereby it must be checked whether sufficient realkalization of the concrete can be ensured. Limiting values for the application are not defined in the code of practice, and on the basis of the available research results, the factors influencing realkalization are to be specified more precisely for the user, figure 1.

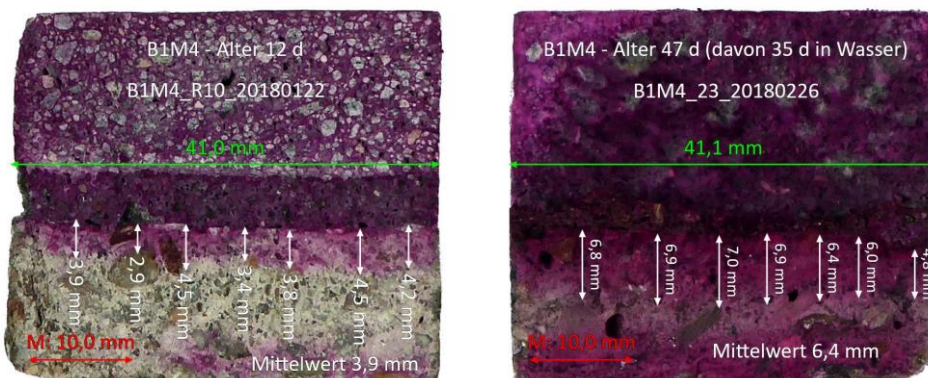


Figure 1: Realkalization depth of B1M4, left: at the age of 12 d before the start of water storage, right: at the age of 47 d after 35 d water storage.



Figure 2: a) Realkalization after 35 days storage under 100 % RH , b) subsequent dry storage under 60 % RH after 28 days , c) subsequent dry storage at 60 % RH after 112 days

In general, it can be stated that a sufficient moisture content is necessary for an alkalinity increase of the carbonated concrete edge zone to be achieved. A relative humidity of 80 % as well as of 60 % does not lead to a significant increase of the realkalization progress beyond the contact realkalization. At 80 % relative humidity, the realkalization depth remains constant as a function of time, and at 60 % there is a decrease in the realkalization depth with increasing test time, figure 2.

Contact realkalization and diffusion-controlled realkalization

On the basis of the laboratory tests, it was found that a distinction must be made between contact realkalization and diffusion-controlled realkalization. Contact realkalization refers to the initial realkalization of the concrete edge zone, which is particularly influenced by the initial moisture from prewetting and mortar moisture (application and curing). The actual ambient conditions, such as humidity, play a subordinate role at this stage. The duration depends on the hardening speed of the mortar and the time and type of curing. Decisive for the depth of contact realkalization is the alkalinity of the fresh mortar, the hardening speed and the capillary water and alkali absorption of the old concrete. After hydration of the mineral material, an equilibrium moisture content of the mortar is established as a function of the relative humidity. The decisive influence during diffusion-controlled realkalization is the moisture supply. If the humidity is too low, realkalization progress beyond contact realkalization is not possible and a decline of the initial realkalization front cannot be excluded. In the following, the properties of contact and diffusion controlled realkalization are explained.

Immediately after contact with water, hydration starts in mineral materials, so that alkali sulfates, alkali hydroxides, free calcium oxide and calcium sulfate go into solution. In the initial stage of hydration, the alkalinity of the pore solution is formed by the hydroxide ions of calcium and the alkalis sodium and potassium. In the first hours of hydration, the calcium ion concentration exceeds the saturation concentration of calcium hydroxide in water. In relation to the pH of contact realkalization during the solidification phase of the mortar, the exceeding of the saturation concentration assumes a special significance. Comparative investigations with the indicators phenolphthalein and thymolphthalein initially showed an increase in the pH of the realkalized range > 10 (transition point thymolphthalein). This phase of realkalization exclusively comprises the first hours to a maximum of 24 hours of hydration. Subsequently, a decrease of the realkalization front with a pH > 10 can be

observed, which at an age of 28 days only affects the contact joint between mortar and old concrete.

In the further course of hydration, the alkalinity of the solution is caused practically only by sodium and potassium hydroxides, since almost all calcium has disappeared from the solution and the solubility of calcium hydroxide decreases with increasing pH. As long as portlandite is present in the hardened cement paste, the calcium saturation concentration is ~20 mmol/l. In terms of diffusion-controlled realkalization, it can be assumed that there is a stabilized calcium concentration in the pore solution and that there is a thermodynamic equilibrium between dissolved calcium hydroxide, crystalline portlandite and calcium silicate hydrate comparable to the leaching of the hardened cement paste. The pH of the pore solution can no longer reach a value > 10 during diffusion-controlled realkalization. On the basis of the indicator tests it was shown that the pH value must be close to the phenolphthalein transition point pH ~ 8.

Influence of humidity on the realkalization progress

The relationship between high humidity and large realkalization depths can be explained on the basis of the sorption isotherm. In hygroscopic, porous building materials, the sorption isotherm is S-shaped and only increases sharply at humidities above 95 % RH [29]. Thus, at high humidities, capillary conduction can increasingly run as the primary transport process and, accordingly, alkalis are transported from the mortar together with the moisture into the concrete. In addition, at high humidities, a sorbate film is formed on the pore surfaces of the microstructure. Since this increases proportionally to the relative humidity, more alkalis are also transported with increasing humidity. In addition, the mobility of the water molecules increases continuously as the sorbate film grows. Consequently, this transport process is the predominant one in the water-saturated pores of the specimens stored in tap water and at 100 % RH, figure 3.

Alkali transport as a result of permeation can be largely excluded in tap water, since this transport process takes place exclusively in areas near the surface and, due to the density and layer thickness of the mortar, the influence at the bond joint to the concrete substrate is negligible.

At low relative humidities, only vapor diffusion takes place in the area of capillary condensation. Significant alkali transport, on the other hand, is only to be expected in the liquid phase. At low relative humidities, the sorbate film does not reach the necessary layer thickness for sufficient mobility of the calcium and hydroxide ions. In addition, the moisture gradient decreases with decreasing relative humidity, which is why the rate of water vapor transport generally decreases.

By prestoring the carbonated concrete substrates at 1% CO₂ concentration in a climatic cabinet and at (50 ± 5) % relative humidity, capillary suction occurs as an additional effect due to the prewetting and mortar application. Basically, the capillary suction of the hardened cement paste decreases strongly with increasing moisture content and reaches negligible values close to 100 % RH. Capillary suction can only occur in empty pores, but fine pores fill up at a relative humidity of 50 % or more due to capillary condensation.

A correlation between pore space and the amount of water that can be absorbed exists with respect to the moisture storage function. At a low w/c ratio, where the pore space is predominantly gel pores, most of the pores are filled by pure absorption. With a large proportion of capillary pores, it is necessary to fill the pore space by capillary condensation and capillary water absorption. It can be assumed that alkali transport is fundamentally possible only in connected capillary pores, so that pure absorption is negligible in terms of real alkalization.

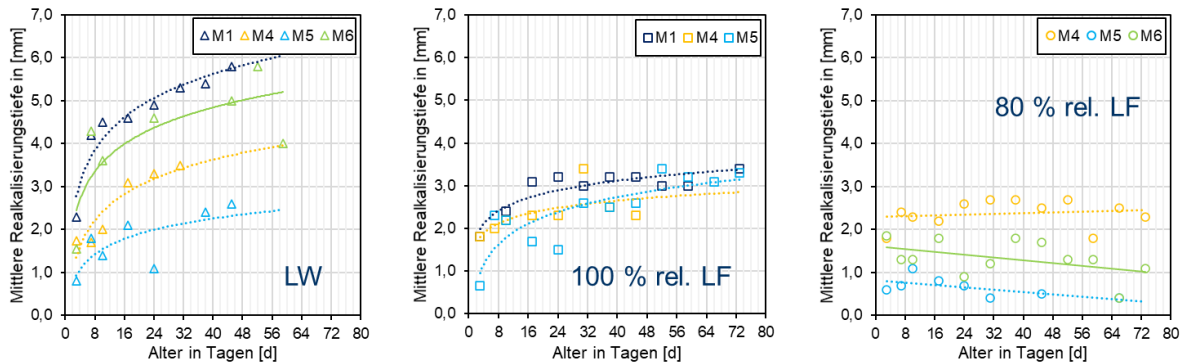


Figure 3: Influence of humidity on the realkalization depth - Water storage, 100% of humidity, 80 % of humidity of different mortars

Stability of the realkalization

The indicator tests with thymolphthalein showed that an alkaline environment with a $\text{pH} < 10$ can be formed during realkalization. Thus, the newly formed alkali buffer does not reach the pH of an intact alkaline cement paste ($\text{pH} > 12$). The buffering effect of the realkalization is thus much lower than the initial situation before carbonation of the hardened cement paste. In addition, no new CH is formed in crystalline form, so that no further buffer can be built up.

Another important aspect is that the alkali transport takes place exclusively in the pore system of the old concrete and the initially high pH value is established exclusively in the aqueous solution. As soon as the relative humidity of the environment drops to such an extent that further alkali transport into the old concrete is greatly slowed down or prevented, the sulfate ions contained in the pore solution of carbonated concrete could lead to a reduction of the pH value below the phenolphthaleine transition point even in the previously realkalized range by means of an ion exchange reaction. Since the alkali buffer of the realkalization is much lower than before the carbonation, it cannot be excluded that an immediate carbonation of the exposed fracture surface occurs.

The results of test series 2 and 3 show that the stability of the realkalization must also be considered as a function of the degree of hydration or drying of the repair mortar. After a few weeks, an equilibrium moisture content is established in both the mortar and the concrete as a function of the ambient moisture content. Until the equilibrium moisture is reached, alkali transport may occur under certain circumstances. Since the mobility of the water molecules decreases accordingly over time, the alkali transport decreases. A comparable effect can also be observed when moisture is removed from specimens previously stored in water. As the mortar and concrete dry out, the alkali supply is also cut off and further progression can take place.

In conclusion, the realkalization can be considered as a temporary condition, which is only stable in case of a sufficient moisture supply and exclusively influences the alkalinity of the pore space. The alkalinity limit is defined as the turnover point of the phenolphthalein test and in the leached as well as in the carbonated area a time-dependent shift of the alkalinity limit due to the realkalization can be observed. However, the alkalinity of the pore solution and the cement paste is below the transition point of thymolphthalein ($\text{pH} < 10$). Accordingly, the pH in the realkalized zone is lower than in an intact cement paste structure.

The realkalization of the subgrade concrete by the application of mineral materials is not the only alkalinity change that could be detected on the basis of the tests. During water storage, an alkalinity increase also takes place in the range of residual alkalinity of the subgrade concrete. Water storage leads to an increase in retroactive alkalinity, which, however, does not show a clear time-dependent increase. Hydration of non-hydrated clinker may play a role here, or also a transport of dissolved alkalis of the alkaline concrete towards the carbonated concrete edge zone. In practice, this effect occurs only to a limited extent, since there is usually no constant moisture in the component during carbonation but alternating wet/dry phases. In the case of a previously leached concrete, the hydration of non-hydrated clinker can be neglected due to the permanent exposure to water.

Modelling to describe the realkalization behaviour of cementitious materials

Due to the concentration gradient between highly alkaline mortar and leached or carbonated concrete, a transport of dissolved Ca^{2+} and OH^- ions takes place in the direction of the lower concentration. The transport of alkalis causes an increase in alkalinity. On the basis of the available measured values, the alkali release takes place exclusively in the pore space.

When considering the underlying realkalization processes, a distinction must be made between contact realkalization and diffusion-controlled realkalization. Contact realkalization is the initial realkalization of the concrete edge zone, which is particularly influenced by the initial moisture from prewetting, the mortar moisture (application and curing). The actual ambient conditions, such as humidity, play a minor role at this stage. The duration depends on the hardening rate of the mortar and the time and type of curing. The depth of contact re-alkalization is determined by the alkalinity of the fresh mortar and the curing speed. After hydration of the mineral material, an equilibrium moisture content of the mortar is established as a function of the relative humidity. The decisive influence during diffusion-controlled realkalization is the moisture supply. Only the formation of a sorbate film on the pore surface enables alkali transport and, accordingly, only significant depth-dependent realkalization can take place from 95 % relative humidity. A lower relative humidity does not lead to a significant increase of the realkalization progress during the hydration phase of the mortar without a moisture supply due to curing. After completion of hydration, a decrease in the initial contact realkalization can be expected to some extent at low humidities.

The course of the realkalization at a relative humidity > 95 % corresponds to a root-time function. At lower relative humidities, no effective progression of the realkalization into depth can be assumed. A derivation of the mathematical functions

beyond contact realkalization (diffusion-controlled realkalization) is possible. This shows the realkalization progress in concrete as a function of the repair mortar. It is obvious that there is a differentiated initial value due to the contact realkalization, but the time-dependent course is to be understood as a parallel shift of the function. It is shown that when the cement type of the subgrade concrete is changed, there is no parallel shift of the function, but a corresponding reduction of the slope has to be provided. The w/c ratio of the subgrade concrete has an effect on the contact-realkalization, but not significantly on the further course.

The following basic mathematical equation can be derived from the present experimental results. The contact re-alkalization, characterized as RK, is to be taken as a characteristic value describing the alkali release of the mortar as a function of the substrate concrete during mortar curing and the first days of curing. The higher the porosity of the substrate concrete, the greater the possible depth of contact realkalization. Within the scope of the research project, the influencing factors of contact realkalization could be identified, but the delimitation of the individual parameters is not possible on the basis of the available results.

The diffusion-controlled realkalization RD follows a root-time function, which can be derived from the available measured values as a constant factor of 0.425. The moisture storage and cement type of the subgrade concrete are included as reduction factors in the equation accordingly.

	$x_R(t) = R_K + R_D \times F_L \times F_Z \times \sqrt{t}$
$x_R(t)$	Realkalization depth in [mm] related to time (t)
R_K	Contact realkalization in [mm]
R_D	Factor of diffusion controlled realkalization [-]
F_L	Reduction factor of the type of storage [-]
F_Z	Reduction factor of the cement type of the subgrade concrete [-]
	Time in [d]

Cement type	Reduction factor F_Z	Storage type	Reduction factor F_L
CEM I	1,0	Water	1,0
CEM II/A-LL	0,7	> 95 % rel. LF	0,6
CEM III/A	0,4	60-80 % rel. LF	0,0

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Essential findings

Within the scope of the project, investigations were carried out for the scientific description and more precise evaluation of the alkalinity depot and the realkalization capability of mortars and concretes. For this purpose, the corrosion and re-alkalization mechanisms were investigated, taking into account the high demands placed on mineral coating systems, as defined in the DVGW Code of Practice W 300 in the field of drinking water storage and supply. In addition, test methods applicable in the future were developed for determining the corrosion resistance and the realkalization capability of mineral repair systems, which are to be verified in further investigations.

The results obtained in the research project will enable the regulations laid down in DVGW Code of Practice W 300 to be specified more precisely in the next revision and expanded on the basis of scientific findings. This will give contractors and planners greater security for the long-term repair of drinking water tanks, as well as highlighting potential savings and thus enabling more cost-effective repair measures using cement-bound linings.

Leaching of cement-bound surfaces

In the laboratory tests, deeper leached concrete surfaces could not be achieved either in drinking water or in demineralized water. Whether concrete surfaces with reduced surface alkalinity with depths of up to 20 mm can result from leaching reactions could not be confirmed within the scope of the project. Furthermore, the leached layers of concrete achieved in the project already showed reduced mechanical integrity. It must be questioned whether such leached layers remain on the surface during surface preparation prior to the application of protective mortar layers by e.g. HDW or compressed air blasting with solid abrasive. Further investigations must be carried out to clarify this.

As described, condensation may occur on the ceiling due to the high humidity in the water chamber. Due to the change of the aggregate state, the water is distilled and the degree of attack of the water increases. Testing with demineralized water in the laboratory tests is much sharper, but only water storage was provided in the tests. Since in practice there is often a leaching problem on the ceiling surfaces and it is not possible to deduce the results on condensate, further investigations can be carried out for clarification.

Realkalization of cementitious materials

According to the work order, the realkalization deposit can be specified more precisely as a concept in DVGW Code of Practice W 300-3. Depending on the ambient conditions, the substrate and the repair mortar, it is possible to apply simplified calculations of the realkalization depth. For this purpose, additional safety factors should be applied to the results of laboratory tests for application to structural concrete. The lining principles can be adapted with new scientific findings.

In order to make it easier for building owners to estimate the long-term maintenance and service life of drinking water reservoirs in the future, it is possible to provide guidance on service life prediction analogous to the yellow print of the "Maintenance Guideline". For the carbonation of concretes and mortars, correspondingly simplified calculations can be applied for the dimensioning of mineral mortar systems and the service life. For the leaching or hydrolysis resistance of cementitious surfaces, no simplified assumptions are provided in the yellow print. Further investigations could be used to develop a simplified concept for estimating the service life of mineral substrates as a function of water composition and environmental conditions. The development of a test method for hydrolysis resistance could also indicate which approved mortar systems can be used for which application.

Literature

Final report of DVGW research project "Corrosion protection by mineral coatings taking into account the requirements of the new DVGW Code of Practice W 300:2014", DVGW- Funding reference W-5-01-14, W 201835, Univ.-Prof. Dr.-Ing. Wolfgang Breit Technische Universität Kaiserslautern, Melanie Merkel, M. Eng. Technische Universität Kaiserslautern, Univ.-Prof. Dr.-Ing. Michael Raupach RWTH Aachen University, Dr.-Ing. Robert Schulte Holthausen RWTH Aachen University; Published by DVGW Deutscher Verein des Gas- und Wasserfaches e. V. Technical and Scientific Association