

Mechanisms of chemical re-alkalization using hybrid alkali-activated mortars

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PREFACE

The presented PhD thesis was prepared during my employment as a research assistant at the Institute for Building Materials Research (ibac) at RWTH Aachen University under the supervision of Univ.-Prof. Dr.-Ing. Michael Raupach. The investigations were mainly carried out within a research project funded by the German Research Foundation (DFG) titled “Mechanisms of the chemical re-alkalization of carbonated concrete and the application of alternative binders”, starting in 2024, and the associated preparatory work.

The laboratory tests and results are presented in a cumulative format consisting of five peer-reviewed publications. This is preceded by an introductory part in which the motivation and relevance of the presented research is discussed. It also contains a detailed presentation of the materials and methods used. Finally, it concludes with a summary of the knowledge gained in the doctoral thesis regarding the chemical re-alkalization and the application of hybrid alkali-activated binders as well as the resulting objectives for future research.

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SUMMARY

The durability of existing steel-reinforced concrete structures is significantly limited by carbonation-induced corrosion of the reinforcement. Against the background of aging existing reinforced concrete structures and increasing requirements for resource-efficient and low-CO₂ construction materials, the development and scientific assessment of durable repair methods is of high relevance. Chemical re-alkalization (CRA) represents a widely applied repair technique aiming to restore the alkaline conditions required for steel passivation by transporting alkaline pore solution from a surface-applied repair mortar into carbonated concrete. However, the underlying mechanisms of CRA, particularly when using alternative binder systems, are not yet sufficiently understood.

The present thesis investigates the mechanisms of CRA with a focus on hybrid alkali-activated binders (HAABs). These binders combine a reduced Portland cement content with alkaline activation and thus offer the potential to reconcile durability-oriented repair strategies with sustainability requirements. The work addresses the influence of carbonation-induced material changes, binder chemistry, alkali transport processes, and pore solution composition on the effectiveness of CRA.

A comprehensive review of CRA of carbonated concrete forms the basis of this dissertation. The review summarizes previously investigated repair materials and addresses carbonation-induced changes in pore solution chemistry and concrete pore structure. The pozzolanic reactivity of carbonation products in contact with portlandite is identified as a potentially inhibiting factor for CRA that has not yet been systematically investigated. To characterize carbonation-related changes, non-destructive unilateral hydrogen nuclear magnetic resonance (¹H NMR) was applied to cement-based mortars and validated against established methods. The results confirm the suitability of ¹H NMR for assessing carbonation progress and pore structure evolution.

Experimental investigations show that HAAB-based repair mortars enable re-alkalization depths of up to 33 mm. Quantitative LIBS-based analysis of potassium transport enabled the development of an adapted diffusion model distinguishing an initial suction phase, governed by the suction factor a and controlled by the initial pore solution pH, and a diffusion phase, governed by the deceleration factor b and controlled by the potassium concentration gradient between mortar and concrete. The developed model provides an analytical framework for the quantitative assessment of the suitability of different repair mortars for CRA.

LIST OF PAPERS

Peer-reviewed publications that are published as open access in journals listed in Web of Science

- I. Glawe, C.; Raupach, M. Review of basics and new opportunities for the chemical re-alkalization of carbonated concrete including the application of alkali-activated materials. *Magazine of Concrete Research*, **2024**. <https://doi.org/10.1680/jmacr.24.00026>
- II. Glawe, C.; Georget, F.; Raupach, M.; Matschei, T. Multi technique characterization of the carbonation affected zone including non-destructive single sided ^1H NMR. *Cement and Concrete Research*, **2024**. <https://doi.org/10.1016/j.cemconres.2024.107438>
- III. Glawe, C.; Raupach, M. Application of hybrid alkali-activated binders for chemical re-alkalization. *Materials and Structures*, **2025**.
<https://doi.org/10.1617/s11527-025-02732-8>
- IV. Glawe, C.; Raupach, M. Quantitative analysis of the alkali transport during chemical re-alkalization using laser-induced-breakdown spectroscopy. *Corrosion and Material Degradation*, **2025**. <https://doi.org/10.3390/cmd6030043>
- V. Glawe, C.; Raupach, M. Modeling of the chemical re-alkalization of concrete by application of alkaline mortars. *Materials*, **2026**. <https://doi.org/10.3390/ma19020278>

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1. Glawe, C.; Raupach, M. Zerstörungsfreie Messung der Carbonatisierungstiefe mittels einseitiger Wasserstoffkernspinresonanz – Potenziale und Anwendungsgrenzen. 8. Kolloquium Erhaltung von Bauwerken: Beurteilung, Instandsetzung und Denkmalpflege von Bauwerken Tagungshandbuch 2023. *expert Verlag GmbH*, **2023**.
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3. Glawe, C.; Raupach, M. Zerstörungsfreie Messung der Carbonatisierungstiefe mittels einseitiger Wasserstoffkernspinresonanz. *ce/papers*, **2023**.
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5. Glawe, C.; Tusch, A.; Raupach, M.; Breit, W. Zur Auslaugung von Trinkwasserbehältern. *Deutscher Ausschuss für Stahlbeton*, **2023**.
6. Tusch, A.; Glawe, C. Entwicklung eines Prüfverfahrens zur Bewertung von Hydrolysebeständigkeit und Dauerhaftigkeit mineralischer Beschichtungen in Kontakt mit Trinkwasser. *DVGW*, **2024**.

CONTENT

Preface.....	I
Acknowledgement.....	II
Summary.....	III
List of papers	IV
Content.....	VI
List of Figures	1
List of Tables	6
List of Abbreviations, chemical formulas and mathematical symbols.....	8
1. Introduction.....	11
1.1 Objective.....	12
1.2 Structure of the thesis	12
2. Theoretical background	15
2.1 The life cycle of reinforced concrete	15
2.2 Limiting environmental influences on the durability with focus on concrete carbonation	16
2.2.1 Carbonation-based corrosion of the reinforcement.....	18
2.3 Extension of the service life by repair	20
2.3.1 Assessing the as-is status of a component.....	21
2.3.2 Repair in case of carbonation-based corrosion.....	26
2.4 References	28
3. Basics and new opportunities for the chemical re-alkalization of carbonated concrete including the application of alkali-activated materials.....	31
3.1 Abstract	31
3.2 Introduction.....	31
3.3 Initial situation – carbonated concrete	32

3.4	Principles of re-alkalization techniques.....	34
3.4.1	Electrochemical realkalization	34
3.4.2	Chemical re-alkalization.....	37
3.5	Influencing factors CRA.....	45
3.5.1	Condition of the carbonated concrete	45
3.5.2	Conditions after the application of material.....	46
3.5.3	Carbonation Resistance of the re-alkalised concrete	47
3.6	Re-alkalization in standards and regulations	48
3.7	Validation of CRA.....	50
3.7.1	Conclusion.....	50
3.7.2	Outlook.....	51
3.8	References	51
4.	Multi-technique characterization of the carbonation affected zone including non-destructive single sided ^1H NMR.....	59
4.1	Abstract	59
4.2	Introduction.....	59
4.3	Materials and methods.....	61
4.3.1	Sample preparation.....	63
4.3.2	Methods.....	65
4.4	Results.....	68
4.4.1	Subdivision of the carbonated area based on ^1H NMR	68
4.4.2	Characterization of the areas	71
4.5	Measurements on concrete samples	75
4.6	Discussion.....	78
4.6.1	Comparison of the carbonation progress by ^1H NMR and phenolph-thalein.....	78
4.6.2	Structural and mineralogical changes through carbonation by different techniques..	79
4.6.3	Requirements and limits of measuring carbonation by single-sided ^1H NMR	80

4.7	Conclusion.....	80
4.8	Outlook	81
4.9	References.....	82
5.	Application of hybrid alkali-activated binders for chemical re-alkalization	87
5.1	Abstract	87
5.2	Introduction.....	87
5.3	Materials and methods.....	91
5.3.1	Development of mortar mixtures with high substitution rates.....	95
5.3.2	Application of the mortar systems on the carbonated concrete	96
5.3.3	Storage of the composite systems during re-alkalization	97
5.3.4	Determination of the re-alkalization depth.....	97
5.4	Results.....	102
5.4.1	Progression of the CRA over time	102
5.4.2	Diiferentiation of the phases during re-alkalization	104
5.5	Discussion.....	108
5.5.1	Influence of the alkali-activation on the re-alkalization process	108
5.5.2	Application of alternative indicators to investigate the progress of chemical re-alkalization.....	109
5.5.3	Applicability of the re-alkalization coefficient.....	111
5.6	Conclusion.....	111
5.7	Outlook	112
5.8	References.....	113
6.	Quantitative Analysis of the alkali transport during chemical re-alkalization using laser-induced breakdown spectroscopy.....	117
6.1	Abstract	117
6.2	Introduction.....	117
6.3	Materials and Methods.....	122

6.3.1	Preparation of the concrete	122
6.3.2	Application of the repair mortar.....	126
6.3.3	Analysis of the CRA.....	127
6.3.4	Adaption of the diffusion model to predict d_{CRA}	134
6.4	Results.....	135
6.4.1	Potassium penetration over time	135
6.4.2	Correlation of indicator tests and LIBS.....	139
6.4.3	Parametrization of the investigation results	143
6.4.4	Prediction of d_{CRA}	146
6.5	Discussion.....	147
6.5.1	Comparison of the results with previous studies	147
6.5.2	LIBS for the analysis of CRA.....	148
6.5.3	Application potential and limitation of the prediction model	150
6.6	Conclusions	152
6.7	Outlook	152
6.8	Appendix A.....	153
6.9	References	154
7.	Modeling the chemical re-alkalization of concrete by application of alkaline mortars	158
7.1	Abstract	158
7.2	Introduction.....	158
7.3	Materials and methods.....	163
7.3.1	Extraction of the pore solution.....	166
7.3.2	Measurements on the extracted pore solutions	167
7.3.3	Measurements on the mortar disks.....	168
7.3.4	Re-evaluation of previously published LIBS profiles of the mortar and concrete potassium concentration	170
7.4	Results.....	172

7.4.1	Chemical characterization of the repair mortars.....	173
7.4.2	Structural characterization of the repair mortars.....	175
7.4.3	Concentration gradient decay rate	178
7.4.4	Influences on early state CRA.....	180
7.4.5	Influences on later state CRA	185
7.5	Discussion.....	187
7.6	Conclusions.....	190
7.7	Outlook	191
7.8	References.....	191
8.	Conclusions and recommendations.....	195
8.1	Summary of the main findings in response to the research questions.....	195
8.2	Scientific contribution - positioning the results within existing research.....	199
8.3	Implications for construction practice	201
8.4	Limitations of this study and recommendation for future research.....	203
8.5	References.....	204

LIST OF FIGURES

Figure 1-1:	Schematic overview of the structure of the thesis with regard to the topics covered.	14
Figure 2-1:	Life-Cycle of a concrete structure based on [4].....	15
Figure 2-2:	The corrosion model according to Tuutti [5].....	16
Figure 2-3:	Photographic documentation of damage to steel-reinforced concrete components caused by carbonation [15].....	19
Figure 2-4:	Corrosion of steel in carbonated concrete.....	20
Figure 2-5:	Schematic representation of the service-life of a building structure including the possibility of repair taken from [20] and modified based on [21].....	21
Figure 2-6:	Planning and execution procedure in case of concrete replacement as the selected repair method according to [20].	22
Figure 2-7:	Example of a steel reinforcement rebar with visible cross-sectional loss due to carbonation-based corrosion [15].....	24
Figure 3-1:	Pourbaix diagram showing the different states of steel depending on the steel's potential and the pH of the environment and the influence of carbonation (highlighted) [11].	34
Figure 3-2:	Scheme of the ERA and the contributing processes: electroosmosis, diffusion, absorption and electrolysis [28].....	36
Figure 3-3:	Schematic representation of the processes during CRA starting from the carbonated concrete (left) with a carbonated and uncarbonated zone, to the re-alkalized concrete (right) with the applied repair mortar resulting in changed pH values within the re-alkalized zones including the reversed re-alkalization.	37
Figure 3-4:	Development of the number of publications on CRA with differentiation of the research subject regarding the materials used for CRA.	38
Figure 3-5:	Schematic representation of the reversed re-alkalization as introduced by [37].	41
Figure 3-6:	Time- and humidity-dependent differentiation of the different phases of the CRA according to [42].....	42
Figure 3-7:	Comparison of the re-alkalization coefficient of mortars and alkaline solutions.	44
Figure 3-8:	Results of the measurement of the corrosion current density of steel reinforcement embedded in non-carbonated, carbonated and re-alkalized concrete [65].....	48
Figure 3-9:	Extract of the technical rule for maintenance showing the maximum carbonation depth to be re-alkalized using method 7.4 [17].....	49

Figure 4-1:	Results of XRD of the raw white Portland cement.....	62
Figure 4-2:	Scheme of the preparation of the TGA and XRD samples by over-drilling a disk of WPC (I) with a smaller diameter (II) followed by separating (III) and depth graded partial grinding in 500 μm steps (IV) of the first 5 mm of the sample surface.	64
Figure 4-3:	(a) Single-sided ^1H NMR MOUSE Type PM25 (Magritek) with a maximum measurement depth of 25 mm (b) improved Signal-to-Noise by averaging 10 experiments with 1024 scans each (right).....	66
Figure 4-4:	a) Carbonation depth over the sample cross-section as an overlay compared to the measuring points to calculate the carbonation depth and the results of the Single-Sided ^1H NMR on naturally carbonated WPC sample in the dried (b) and water saturated state (c).....	69
Figure 4-5:	Overview images taken by light microscopy (a) and SEM-BSE (b) showing the cross section of the naturally carbonated WPC with highlighted subdivision of Zone A and Zone B area and the area of surface irregularities based on the NMR results as well as the carbonation depth by phenolphthalein.	72
Figure 4-6:	(a) Results of the TGA and (b) the derived proportion of the different components.	73
Figure 4-7:	CO_2 and SO_3 profiles measured by CSA with indicated carbonation depth by phenolphthalein test and C-S-H profile by ^1H NMR measurement in the dried state.	73
Figure 4-8:	Correlation of the phase proportions resulting from the different analysis showing the sensitivity of the different methods regarding structural and mineralogical phases through carbonation.	75
Figure 4-9:	Results of the Phenolphthalein test (c) + (d) and ^1H NMR measurements on non-carbonated concretes (a) + (b) and the same concretes carbonated under accelerated conditions (3 % CO_2) for 90 days (e) + (f).	76
Figure 4-10:	Comparison of the effects of carbonation on the different structures in cement-based materials derived from different analysis methods.....	79
Figure 5-1:	Excerpt from the technical rule for maintenance illustrating the repair method called chemical re-alkalization (procedure 7.4) [2].	88
Figure 5-2:	Schematic representation of the principle of CRA with d_c = carbonation depth, d_{CRA} = re-alkalization depth, reversed re-alkalization = rear-side re-alkalization, CH = $\text{Ca}(\text{OH})_2$, CC = CaCO_3 , OH = hydroxides, C-S-H = Calcium- Silicate-Hydrates, S-H = Silicate-Hydrates [3].....	89

Figure 5-3:	Schematic overview of the experimental procedure.	91
Figure 5-4:	Influence of a) the substitution rate and b) the potassium hydroxide to calcined clay ratio (KOH/C) on the compressive strength	95
Figure 5-5:	Sequence of steps during the application of the repair mortars in the production of the composite systems: a filling the first layer of repair mortar b distributing and compacting the material c application of the second layer of the repair mortar d compacting the second layer e and f peel off to smoothen the surface.....	97
Figure 5-6:	Correlation of the values for d_{CRA} obtained by the different indicators Phenolphthalein and Mordant Orange 1.....	100
Figure 5-7:	Calibration solutions for checking the color change points of the indicators.	100
Figure 5-8:	Definition of the different areas as a result of CRA (rear-side re-alkalization was not visible on these samples).....	101
Figure 5-9:	Evolution of d_{CRA} of the different composite systems over time under cyclic watering.....	105
Figure 5-10:	Evolution of d_{CRA} of the composite systems during the suction phase.....	106
Figure 5-11:	Maximum re-alkalization depths reached by the different repair mortars after 90 days.....	107
Figure 6-1:	Summary of the progression of the CRA over time using different substrate concretes based on the literature [3, 6, 7, 9, 10].....	120
Figure 6-2:	Results of the preliminary test to determine the influence of the pre-wetting method on the suction phase using repair mortars enriched with fluorescent Uranine.....	125
Figure 6-3:	Representation of the definition of the different areas displayed by the indicator solutions Phenol-phthalein and Mordant Orange 1.	129
Figure 6-4:	(a) Composition of the calibration mixtures and (b) range of potassium concentrations (mixtures were sorted in order of the potassium concentration for visualization).	130
Figure 6-5:	(a) Installed calibration tablet in the LIBS chamber and (b) magnification of the measuring field.	131
Figure 6-6:	Exemplary representation of the measuring field of the LIBS measurement with excluded aggregates and the resulting depth profile of the averaged potassium concentration.....	132
Figure 6-7:	Example of the evaluation process to determine the potassium diffusion coefficient based on the LIBS depth profiles.....	134

Figure 6-8:	Quantitative depth profiles showing the mean potassium concentration of the different composite systems after different storage duration and the corresponding values for d_{CRA} and the maximum potassium concentration in the substrate concrete. (a) OPC. (b) 50C. (c) 50C 0.5 KOH. (d) 50C 0.5 KOH KWG. (e) 50C 0.5 KWG. (f) 50C 2.3 KOH and (g) 50C 2.3 KOH KWG.....	138
Figure 6-9:	Evolution of the re-alkalization depth d_{CRA} over time with linear regression to calculate the re-alkalization coefficient k_{CRA}	139
Figure 6-10:	Correlation of d_{CRA} and the penetration depth of potassium where $K > 0.57$ wt% (corresponds to the maximum potassium concentration of the substrate concrete).	141
Figure 6-11:	Potassium concentration at the color change in the indicator.	142
Figure 6-12:	Visualization of the bi-directional alkaline loss of the repair layer as a result of leaching and CRA.....	142
Figure 6-13:	Correlation of the specific diffusion coefficient and the re-alkalization coefficient with linear regression excluding outliers (50C 2.3 KOH KWG, 50C 0.5 KOH KWG).	144
Figure 6-14:	Evolution and fitting of the attenuation factors of the different materials over time.	145
Figure 6-15:	Comparison of the calculated and measured values for d_{CRA}	146
Figure 6-16:	Correlation of the measured re-alkalization depths and the re-alkalization depth calculated using k_{CRA} compared to the calculation using the attenuation factor β	147
Figure A6-1:	Comparison of the measured values and the values which were calculated based on the root-time law using the diffusion coefficient after 1 day to replace the re-alkalization coefficient (determined after 90 days).	153
Figure 7-1:	Schematic representation of the adapted diffusion law by Glawe et al. and the impacts of the material-specific factors a and b on the time-dependent evolution of d_{CRA} [10].	161
Figure 7-2:	Overview of the experimental procedure applied on the mortar samples and the pore solution obtained by pore solution expression (PSE).....	164
Figure 7-3:	Schematic representation of the pore solution extraction device.....	166
Figure 7-4:	Measuring cell for the resistivity measurements of the pore solutions.....	167
Figure 7-5:	Schematic representation of the calculation of the potassium concentration at the interface area of concrete and mortar with different states of the concentration	

	gradient, e.g., (a) concrete has a higher potassium concentration than mortar, (b) mortar has a higher potassium concentration than the concrete.	171
Figure 7-6:	pH values of the different mixtures in the fresh state and after 1, 7 and 28 days (n = 3).....	174
Figure 7-7:	Electrical conductivity of the different mixtures after 1, 7 and 28 days (n = 1).	174
Figure 7-8:	Electrical resistivities (n = 3) of the mortars (a) and the corresponding pore solutions (b) (n = 1).	176
Figure 7-9:	Formation factors of the different mortars at sample ages of 1, 7 and 28 days.	176
Figure 7-10:	Total porosity and proportion of capillary pores of the mortar mixtures (n = 1).	177
Figure 7-11:	Results of the potassium concentration gradient decay rate ($CGDR_K$) calculated based on the LIBS measurements of Glawe et al. [10] for the different time periods: (a) 1 to 28 days, (b) 1 to 7 and 7 to 28 days (n = 1).	179
Figure 7-12:	Correlation of the pH (a) and the electrical conductivity (b) of the pore solution of the mortar after 1 day with the suction factor a.	182
Figure 7-13:	Correlation of the capillary pores (a) and the formation factor (b) of the mortars with the suction factor a.	184
Figure 7-14:	Correlation between the deceleration factor b and the changes in the formation factor of the mortars at sample ages of 1 and 28 days.....	186
Figure 7-15:	Correlation of the deceleration factor b and the potassium concentration gradient decay rate between 1 and 28 (a) and 7 and 28 (b) days of CRA.....	186
Figure 8-1:	Schematic summary of the semi-empirical model of the CRA and the material-related influences on the suction factor a and the deceleration factor b.....	197
Figure 8-2:	Summary comparison of the investigated materials (HAAB) with previous research on CRA based on paper I using the re-alkalization coefficient k_{CRA}	198

LIST OF TABLES

Table 2-1:	Overview of the corrosion-promoting exposure classes [10].	17
Table 2-2:	Classification of concrete based on the mechanical properties according to [20].	25
Table 2-3:	Overview of the repair methods depending on the condition of the component in case of carbonation according to DIN EN 1504-9 and the technical rule for maintenance (German guideline) [23, 32].	26
Table 4-1:	Oxide and phase composition of the WPC used in this study.	62
Table 4-2:	Composition and compressive strength after 28 days of the investigated samples	63
Table 5-1:	Oxide composition of the used binders.	92
Table 5-2:	Overview of the investigated mixtures for the repair mortars and the substrate concrete	94
Table 5-3:	Composition of the indicator solutions.	98
Table 5-4:	Results of the indicator tests at the different times after spraying the indicator on the sample surface.	99
Table 5-5:	Overview of the results of the indicator tests of all composite system at the different times after application of the repair mortar (blue line marks the mean re-alkalization depth with the standard deviation in light blue).	103
Table 6-1	Comparison of LIBS with traditional analysis methods for chemical re-alkalization	121
Table 6-2:	Oxide composition of the used binders.	122
Table 6-3:	Mixtures of the investigated substrate concrete and the repair mortars	124
Table 6-4:	. Characteristics of the indicator solutions.	127
Table 6-5:	Potassium content of the used components.	130
Table 6-6:	Results of the calculation of the re-alkalization coefficient k_{CRA} including the measure of certainty.	140
Table 6-7:	Fitted diffusion coefficients and surface concentrations of the different composite systems based on the LIBS data obtained after one day.	143
Table 6-8:	Results of fitting the power equation (Equation (5)) to the attenuation factors of the different materials.	145
Table A6-1:	Composition of the LIBS calibration mixtures.	154
Table 7-1:	Oxide composition of the used materials.	163

Table 7-2:	Mixtures of the investigated pastes based on [10].	164
Table 7-3:	Mixtures of the investigated mortars based on [10].	165
Table 7-4:	Values for the factors a and b taken from [10].	173
Table 7-5:	Results of the calculation of the potassium gradient between mortar and concrete after 1, 7 and 28 days according to Equation (5) ($n = 1$)	179
Table 8-1:	Summary of the practice-relevant features of the currently known re-alkalization materials.	202

LIST OF ABBREVIATIONS, CHEMICAL FORMULAS AND MATHEMATICAL SYMBOLS

Abbreviations			
(H)AAB	(Hybrid) alkali-activated binder	RH	Relative humidity
^1H NMR	Proton nuclear magnetic resonance	RM	Repair mortar
A	Amplitude; Area	R_t, R_z	Roughness
A1, A2,...	Concrete class 1 to 5	SCM	Supplementary cementitious material
BIM	Building information modeling	SCTZ	Structural and chemical transition zone
BSE	Back scattered electron	SEM	Scanning electron microscope
c	Concentration	S/N	Signal/Noise
C	Calcined clay	T	Temperature
CAZ	Carbonation affected zone	T_2	Transversal relaxation time
CEM	Cement	TGA	Thermogravimetric analysis
CPMG	Carr-Purcell-Meiboom-Gill	$t_{av.}$	Available remaining service life
CRA	Chemical re-alkalization	t_i	Time of inspection
C_s	Surface concentration	t_N	Time of new construction
CSA	Carbon-Sulfur-analysis	$t_{pla.}$	Remaining service life as planned
CTZ	Chemical transition zone	$t_{R,target}$	End of planned remaining service life
DIN EN	National and European standard	TR IH	German guideline for concrete repair
DTG	Derivative thermogravimetry	V_H	Electrode potential against standard hydrogen electrode
ERA	Electro-chemical re-alkalization	Vol.	Volume
FTIR	Fourier transform infrared	w/b	Water-to-binder ratio
$f_{c,28d}$	Compressive strength after 28 days	WPC	White Portland cement
GWP	Global warming potential	$\bar{X}$	Mean value
L	Liter	X-ray	Electromagnetic wave
LIBS	Laser-induced breakdown spectroscopy	XC	Exposure class with corrosion risk by carbonation
LOI	Loss in ignition	XD	Exposure class with corrosion risk by chlorides
MIP	Mercury intrusion porosimetry	XRD	X-ray diffractometry
MOUSE	Mobile universal surface explorer	XRF	X-ray fluorescence
OPC	Ordinary Portland cement	Δt_{pla}	Planned time of service life
PE	Polyethylene	Φ_{NMR}	Porosity by ^1H NMR
Ref.	Reference		

Chemical formulas			
AFm	Aluminat-Ferrit-Monosulfate phase	NaOH	Sodium hydroxide
AFt	Aluminate–Ferrite–Trisulfate phase	Cl	Chloride
Al ₂ O ₃	Aluminum oxide	CO ₂	Carbon dioxide
C-S-H	Calcium silicate hydrate	CO ₃	Carbonate
C ₁₃ H ₈ N ₃ NaO ₅	Mordant orange	CuK α	Copper K α X-ray radiation
C ₂₀ H ₁₄ O ₄	Phenolphthalein	e ⁻	Electron
Ca	Calcium	Fe ₂ O ₃	Iron(III) oxide
C $\bar{C}$	Calcium carbonate	Fe ₃ O ₄	Iron(II,III)oxide
CH, Ca(OH) ₂	Calcium hydroxide (portlandite)	H	Hydrogen
H ₂ O	Water	H ₂ CO ₃	Carbonic acid
K	Potassium	O ₂	Molecular Oxygen
K ₂ O	Potassium oxide	OH ⁻	Hydroxide ion
KOH	Potassium hydroxide	SH	Silicate hydrate
KWG	Potassium water glass	SiO ₂	Silicon dioxide
MgO	Magnesium oxide	SO ₃	Sulfate
Na	Sodium	TiO ₂	Titanium dioxide
Na ₂ O	Sodium oxide		

Mathematical symbols	
a	Suction factor
b	Deceleration factor
$\beta(t)$	Attenuation factor
$CGDR_K$	Potassium concentration gradient decay rate
$c_{K,C}$	Potassium concentration in concrete
$c_{K,M}$	Potassium concentration in mortar
$D(RM); D_{K,1d}(RM)$	Potassium diffusion coefficient of concrete measured after 1 day depending on the repair mortar
$d_C; d_K$	Carbonation depth
d_{CRA}	Re-alkalization depth
erf	Error function
FF	Formation factor
k_{CRA}	Re-alkalization coefficient
ρ	Electrical resistivity
σ	Electrical conductivity
X_R	Re-alkalization potential

1. INTRODUCTION

The evolution of steel reinforced concrete goes back to the year 1867, when Joseph Monier, a gardener and building contractor, registered the first patent for reinforced concrete flower pots. Since then steel reinforced concrete has become *the* building material when it comes to constructions with high performance and durability. At the same time, the pursuit of continuous improvement in the properties of reinforced concrete is the basis for numerous research projects, in which entire institutes specialize in the further development of the building material.

When it comes to steel reinforced concrete, a distinction must be made between mechanical performance and durability. The mechanical performance describes the properties of steel reinforced concrete in the early age and during the service life of the building structure while the durability defines the resistance of the structure against environmental influences [1]. This distinction also means that a good mechanical performance does not necessarily result in a sufficient durability.

The reinforcement of concrete using steel rebars provides a perfect example where improved performance does not necessarily equate to improved durability. More precisely, the embedded steel reinforcement indeed results in an increase of tensile and flexural strength, cracking behavior and fatigue strength, to name just a few properties. However, by introducing steel into the structure, the durability can be decreased when no proper protection of the reinforcement is ensured. Normally, the protection of the steel reinforcement against corrosion is given by the concrete in a chemical and structural way. Based on its property to create an alkaline environment for the steel through the hydration of the clinker and the resulting pore solution with a pH higher than 12.5, the concrete cover additionally acts as a protection layer against corrosion by corrosion-promoting substances such as the CO₂ from the atmosphere [2]. However, during the service-life of a steel reinforced concrete structure, these corrosion-promoting substances can reach the embedded reinforcement which then can result in corrosion and, in the worst case, lead to failure of the component.

To prevent the scenario of component-failure, the corrosion of the steel-reinforcement can be prevented by a number of repair methods which focus on maintaining the protection layer as well as its high pH value. One of these methods is the chemical re-alkalization (CRA) which represents a straight-forward approach to prevent carbonation-based corrosion by the application of an alkaline repair mortar on top of the carbonated concrete to enable the transport of the pore solution of the mortar into the underlying substrate concrete to restore the alkalinity [3]. By this, the service-life of the structure can be extended as well as the excessive consumption of building

materials to re-build structures can be reduced. This sustainability aspect can be further enhanced if clinker-reduced materials are used for the repair. But to ensure the applicability of these new binders, the requirements for repair materials must be met. In the best case, the use of new binders enables further development of repair methods and the definition of application limits.

1.1 OBJECTIVE

The main focus of this work is to explore the application limits of the CRA, while using conventional clinker-based materials as well as clinker-reduced or clinker-free materials such as (hybrid) alkali-activated binders ((H)AAB). While there are already initial approaches to describe the processes and the main influencing factors during CRA, these have so far only been determined in combination with on ordinary Portland cement (OPC) based repair mortars. By introducing new components in case of the production of clinker-reduced binders or (H)AAB, the potential of these materials as repair mortars needs to be verified also taking into account the relevant exposure classes leading to carbonation-based corrosion.

Further, the process of the CRA starting with the preparation of the substrate concrete and the application of the materials up to the post-treatment and determination of the success of the methods needs to be reviewed. The present work aims to answer the following questions:

- What conditions are necessary for the CRA to successfully re-alkalize carbonation depths greater than the so far maximum investigated depth of 14 mm?
- How do different re-alkalization materials and their properties influence the effectiveness and limitations of the CRA?
- Which properties of the substrate concrete relevant to CRA are affected by the carbonation and how can these changes be assessed?
- Can the transport mechanisms and phases governing the CRA and their temporal evolution be quantified?
- How can the CRA be parameterized to further develop existing models for a comparative assessment of re-alkalization materials?

1.2 STRUCTURE OF THE THESIS

The sections (3 to 7) of this thesis in form of papers, are dedicated to the various parts of the system as it exists during CRA. In advance (section 2), an introduction to the concepts of durability and life cycles of reinforced concrete structures and the damage mechanisms that primarily

influence them, with a focus on concrete carbonation, will be provided. Building on this, an insight into various repair methods and the corresponding regulations is given.

As a transition from the theoretical background to the application-related studies, the first paper (Paper I) gives a review on the state-of-the-art of the CRA as well as future perspectives concerning the introduction of clinker-reduced binders into the field of concrete repair. Since the review summarizes the state of research on CRA, it is arranged as a supplementary part of the introduction in paper form.

Initially, and as a necessity for the investigations regarding the CRA, carbonated concrete is used, the structure and chemistry of which has been altered during carbonation. Accordingly, the second paper (Paper II) presents various investigation methods for determining the carbonation progress of concrete and their correlation in order to explore the possibility of a non-destructive measurement of the carbonation process. The carbonated concrete is then re-alkalized using mortars based on the previously mentioned types of binders (clinker-based, clinker-reduced and HAAB) which results are described in the third paper (Paper III).

Building on paper three, which primarily serves as a proof-of-concept for the application of novel binders as re-alkalization materials, paper four (Paper IV) is dedicated to a more detailed investigation of the transport processes during the CRA with the help of laser-spectroscopic measurements.

Since paper four provides a new approach to mathematically describe the CRA by adapting the existing diffusion model using the suction and the deceleration factor, the material-based influences on these factors are analyzed in paper five (Paper V). With this, the basis for the formulation of requirements for repair mortars is established.

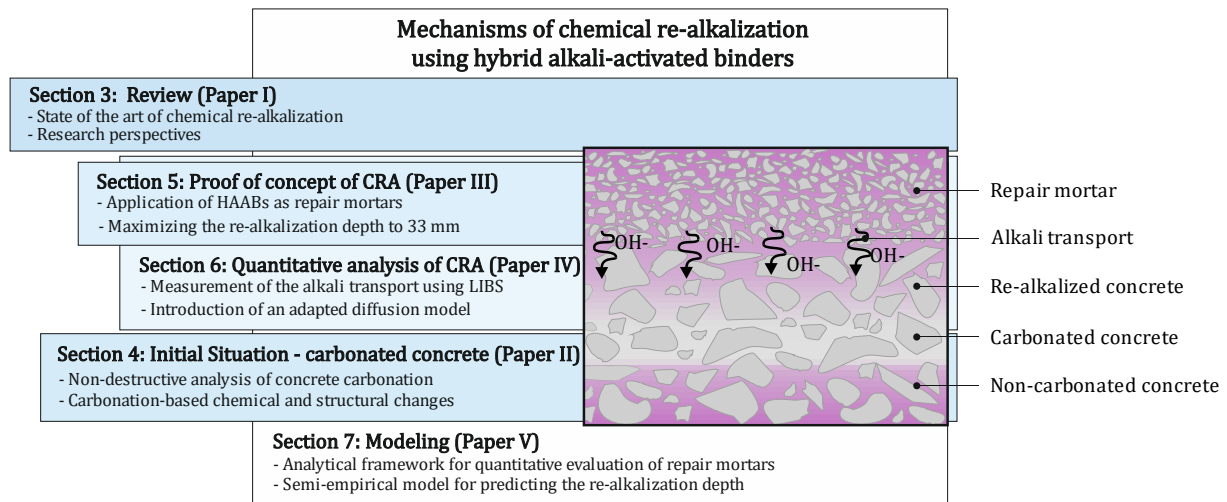


Figure 1-1: Schematic overview of the structure of the thesis with regard to the topics covered.

The main findings of the different papers are discussed and summarized in each paper separately. At the end of the thesis (section 8), the conclusions of the various papers are brought together in order to answer the research questions mentioned above. Above all, the deviations of the obtained results from previous literature are worked out and discussed here. At the same time, the process for generating the various research data will be critically examined in order to determine potential for improvement as well as to provide an outlook for further research.

2. THEORETICAL BACKGROUND

2.1 THE LIFE CYCLE OF REINFORCED CONCRETE

The life cycle of reinforced concrete or a building structure in general includes the different phases starting from the raw material extraction through the production of the building structure to the service life, followed by dismantling or demolition with subsequent recycling, if possible (compare Figure 2-1). All of these different phases hold potential to contribute to a longest possible life cycle of a component. In the case of the service life, the duration of the life cycle can be increased above all if the selection of materials as well as the manufacture and maintenance of the component are adapted as well as possible to the exposure class and the safety requirements.

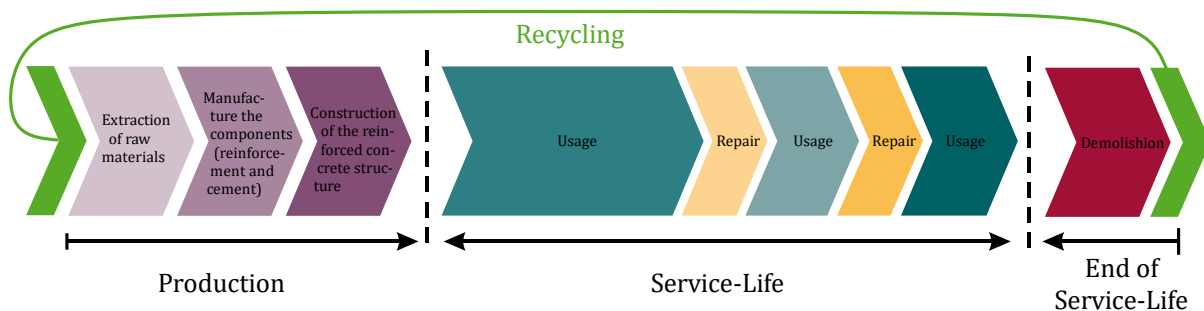


Figure 2-1: Life-Cycle of a concrete structure based on [4].

The common expectation of the service life of a steel reinforced concrete structure is around 50 years. However, due to the constantly fast-growing population, realistic service-life prediction can no longer be based solely on the current impacts on a structure. As a result, buildings are currently frequently exposed to unplanned loads, which causes the previously assumed service life to deviate. For future new buildings, it is therefore important to optimize the performance based on new calculation models to ensure sufficient durability. With regard to existing structures, rehabilitation or repair offer the best opportunity to adapt them to new requirements.

This can be done not only with regard to performance and durability, but also concerning the sustainability of the building by focusing on the materials used for the repair.

2.2 LIMITING ENVIRONMENTAL INFLUENCES ON THE DURABILITY WITH FOCUS ON CONCRETE CARBONATION

The service life of reinforced concrete is strongly influenced by natural damage mechanisms that are caused by the interaction of the concrete with the environment. The most common limiting factor for the durability of reinforced concrete structures is the penetration of corrosion-promoting substances such as chlorides and CO_2 into the concrete. While chloride exposure is mainly caused by de-icing salt or occurs in coastal regions, the damage by the ingress of CO_2 into the concrete is inevitable as soon as the concrete gets in contact with the atmosphere.

The Tuutti corrosion model (compare Figure 2-2) offers a model analysis of the influence of both corrosion-promoting substances [5]. The model defines two phases within the lifetime or service-life of a steel reinforced structure leading to the point at which the repair of the component becomes necessary. This time span is limited by the acceptable penetration depth of the corrosion-promoting substance and can be divided into the two phases *initiation* and *propagation*.

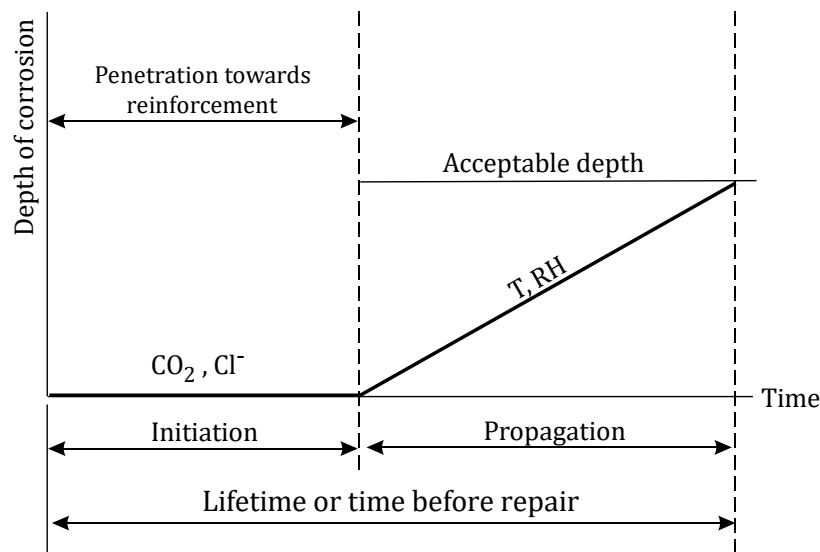


Figure 2-2: The corrosion model according to Tuutti [5].

The initiation phase comprises the penetration of the substance through the concrete surface layer towards the steel reinforcement. The duration of the initiation phase can vary, e. g. depending on the present concrete as well as the available amount of the penetrating substance [6, 7]. The transition of the initiation phase to the propagation phase is determined by the point in time at which corrosion first occurs. The propagation of the corrosion is mainly controlled by the temperature and the relative humidity and therefore by the environmental conditions the building structure is exposed to [8, 9].

By introducing so-called *exposure classes*, the various environmental conditions a building is exposed to can be classified in terms of the risk of corrosion (compare Table 2-1).

Table 2-1: Overview of the corrosion-promoting exposure classes [10].

Class	Definition of the environment	Examples as assignments of the exposure classes
XC1	Dry to constantly wet	Interior building components with normal humidity; concrete continuously immersed in water
XC2	Wet, rarely dry	Parts of water tanks; foundation components
XC3	Moderate humidity	Building components to which the outside air has frequent or constant access
XC4	Alternating wet to dry	Exterior components with direct irrigation
XD1	Moderate humidity	Chloride-contaminated air; industrial environments
XD2	Wet, rarely dry	Concrete exposed to chloride-containing water
XD3	Alternating wet to dry	Bridge decks, parking structures, road structures exposed to de-icing salts
XS1	Exposed to airborne sea salts	Coastal structures without direct seawater contact
XS2	Permanently submerged in seawater	Submerged marine structures
XS3	Tidal, splash and spray	Marine structures in tidal or wave splash zones

If the component has been subjected to corrosion by the penetration of CO_2 , this is referred to as carbonation-based corrosion. Focusing on carbonation-based corrosion, the repair therefore has to be planned in consideration of the conditions which led to the carbonation in the first place. Next to the concrete itself, the carbonation-promoting conditions by the environment are defined as the exposure classes XC1 to XC4 in the European standard DIN EN 206-1, which applies in Germany in the form of DIN 1045-2 [10, 11]. Both standards regulate which concrete quality must be used at a minimum depending on the exposure class, while the minimum thickness for the concrete cover is specified by DIN EN 1992-1 [12].

The higher the exposure class, the higher is the carbonation rate. The influence of humidity is therefore decisive for the carbonation rate and the resulting corrosion risk during the service life. In short, carbonation hardly or not at all occurs in ambient conditions that are too dry or too humid. Regarding the exposure classes, this would lead to low risk for carbonation in case of XC1 and XC2. Although carbonation progresses significantly under XC3 conditions due to moderate

humidity, the availability of moisture is often insufficient to sustain relevant corrosion of the reinforcement. Consequently, the highest corrosion risk occurs under XC4 exposure, where alternating wet and dry conditions promote both carbonation and corrosion processes. Repair measures therefore primarily need to address structures exposed to XC4, while XC3 is mainly critical with regard to carbonation depth rather than immediate corrosion damage.

2.2.1 CARBONATION-BASED CORROSION OF THE REINFORCEMENT

The carbonation of concrete begins the moment the manufactured component comes into contact with the atmosphere after hardening. The penetration of CO_2 into the concrete causes a reaction of the calcium-based, soluble components of the cement matrix such as $\text{Ca}(\text{OH})_2$ which can be present in soluble form as well as the solid form, called Portlandite. Since these components also ensure the alkaline environment in the concrete, which is a prerequisite for the passivating protective layer on the steel reinforcement, the reaction of these components with the penetrating CO_2 to form insoluble calcium carbonate (CaCO_3) lowers the pH value in the pore solution of the concrete (see e.g. [13, 14]).

While the mechanisms of the carbonation are described in detail in Paper II (section 4), the present chapter should provide a corrosion-focused presentation of the corrosion mechanisms with emphasis on carbonation. Using the fundamentals of carbonation-induced corrosion, the necessity of methods to maintain or restore the alkaline environment in concrete is highlighted to prevent damages which can occur in form of concrete spalling leading to the exposure of the reinforcement as shown in Figure 2-3. If no preventative measures are taken, the reinforcement may lose cross-section, which in the worst case can lead to the failure of the component.

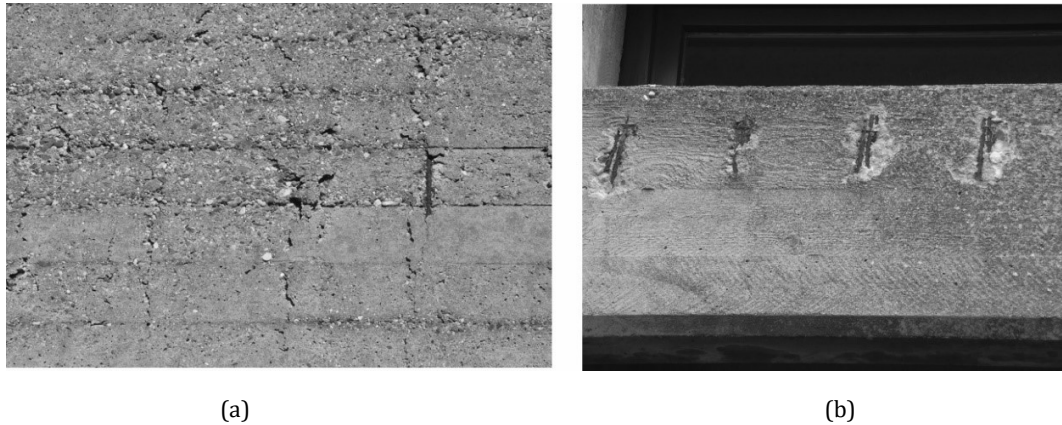


Figure 2-3: Photographic documentation of damage to steel-reinforced concrete components caused by carbonation [15].

Based on its alkaline composition, the pore solution of the concrete enables the formation of a corrosion-inhibiting protective layer at the steel-concrete-interface (compare Figure 2-4). The so-called passive layer is characterized by a thin oxide layer and cannot be resolved using conventional microscopic methods. However, the presence of this iron-oxide layer (Fe_2O_3) can be verified by electrical methods which was demonstrated in numerous researches in the past (see e. g. [16-18]).

In case of carbonation, the environment for the steel reinforcement within the concrete changes as the alkaline conditions become altered until the pH of the pore solution drops below about 9. As a consequence, the passive layer becomes unstable and corrosion can occur in presence of water and oxygen.

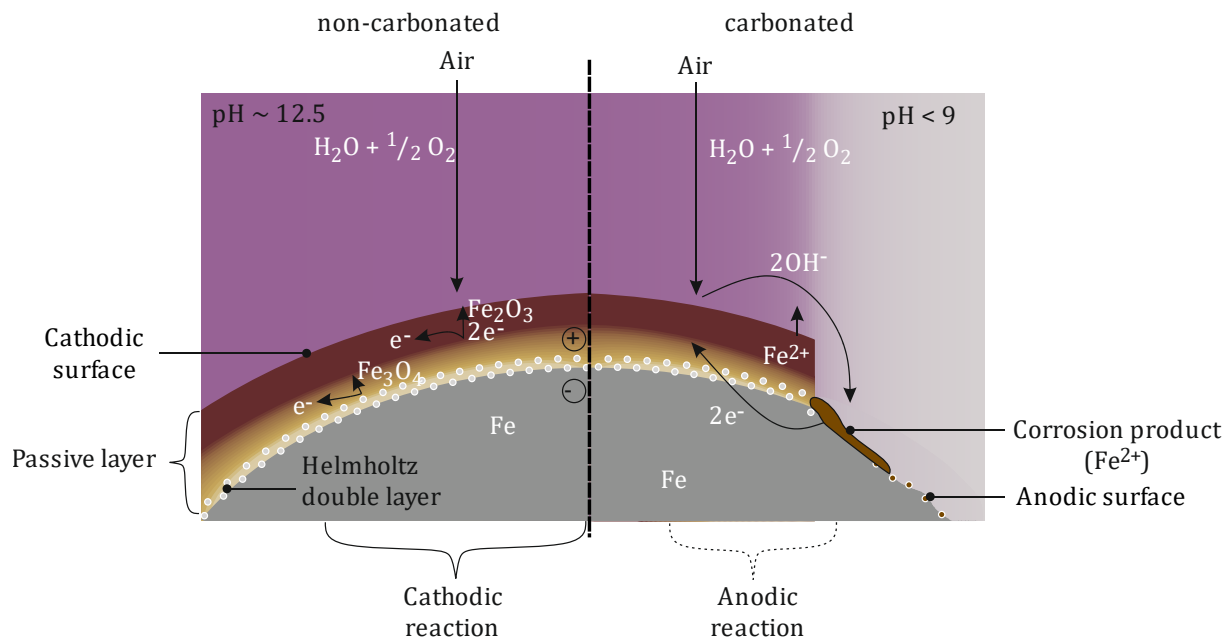


Figure 2-4: Corrosion of steel in carbonated concrete.

The progression of the corrosion is characterized by the corrosion rate which quantifies the material loss on the steel surface during the corrosion process. This cross-sectional loss varies dependent on the present type of corrosion. Compared to chloride-induced corrosion, the carbonation-based corrosion is defined by a lower corrosion rate as the result of a lower ratio of the cathodic to anodic area [19]. Therefore, the corrosion through carbonation appears in a uniform corrosion compared to the chloride-based corrosion which normally is characterized by local pitting corrosion with higher local corrosion rates.

2.3 EXTENSION OF THE SERVICE LIFE BY REPAIR

In case obvious damage to the component, the acceptable depth of corrosion, which is considered as the erosion limit or required performance, or at least the propagation phase is reached, it can be attempted to repair the building structure. By repairing, the durability of the building structure can be restored to a certain extent and the service life can be extended. The outcome of the repair should be that the achieved, new remaining service life corresponds to the remaining design service life of the building structure (compare Figure 2-5).

However, this requires that the repair work be carried out in accordance with the requirements placed on the component. These requirements are influenced by the environmental influences affecting the component, as well as by the existing concrete itself.

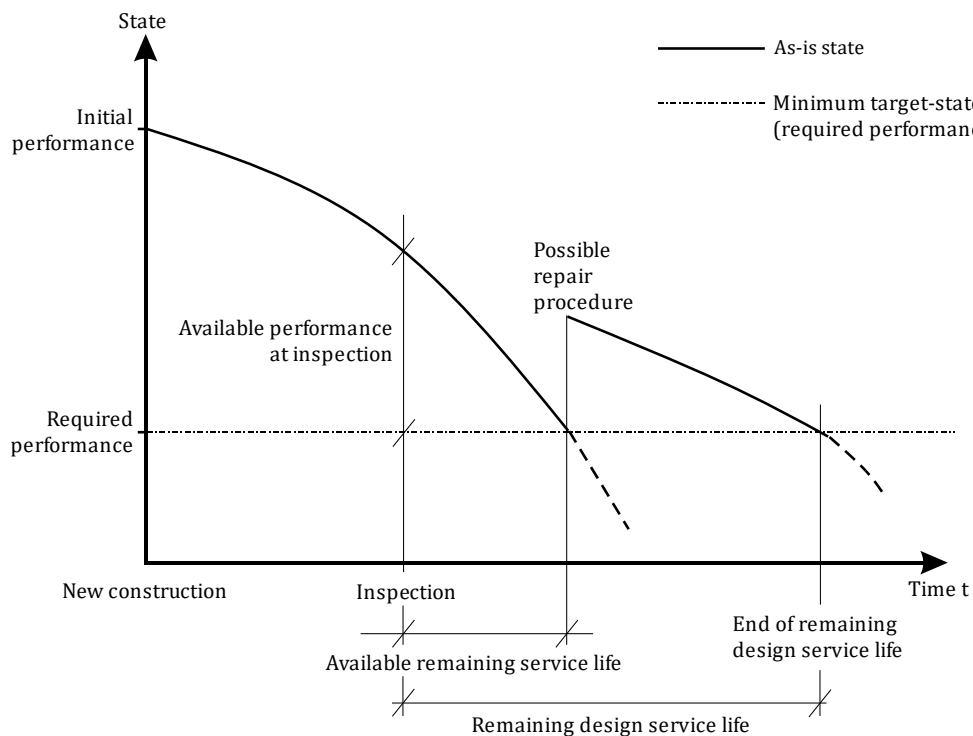


Figure 2-5: Schematic representation of the service-life of a building structure including the possibility of repair taken from [20] and modified based on [21].

2.3.1 ASSESSING THE AS-IS STATUS OF A COMPONENT

For planning the protection or repair and in addition to study the available, historical information (e. g. previous repairs and maintenance actions), it is also a basic requirement to assess the current conditions of the component. The resulting information forms the basis for the further course of the repair work including the selection of the repair methods as well as the repair materials as shown in Figure 2-6. In the best case, the causes of damage can be determined based on the written documentation of the building. However, this requires the completeness of the existing documentation, which is often not the case. Especially in case of an execution error during construction, this can be difficult to trace. Alternatively, the condition of the component can be recorded within a building diagnostic. The diagnosis can be used to decide whether the repair should aim at replacing damaged concrete or preventing damage to the concrete to protect the embedded steel reinforcement against corrosion.

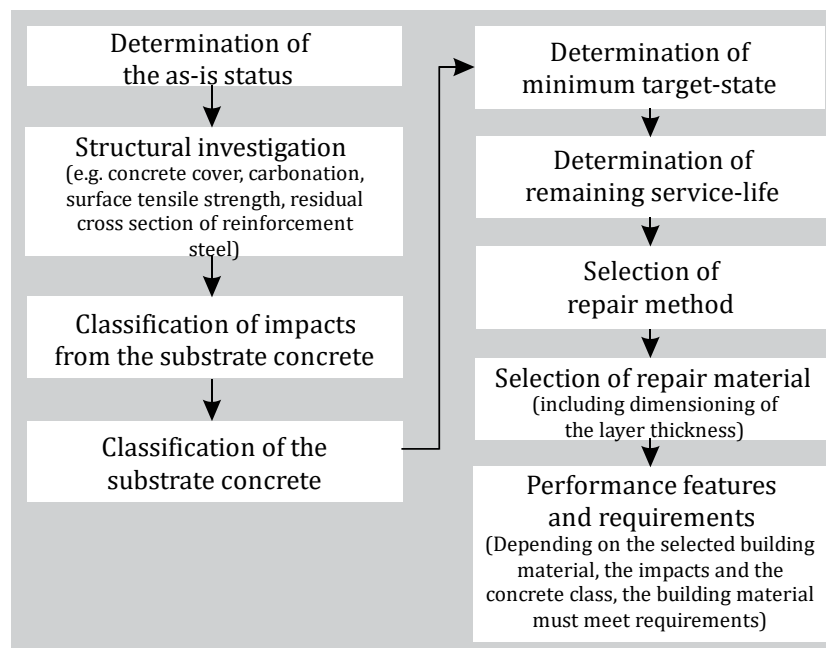


Figure 2-6: Planning and execution procedure in case of concrete replacement as the selected repair method according to [20].

In any case, the determination of the conditions which lead to the damage is crucial to ensure an adequate protection or repair of the concrete component. Therefore, the determination of the as-is status is part of the regulations dealing with the repair of concrete structures both nationally and internationally [20, 22, 23]. A comparison of the different regulations can be found in [24].

While the data determined from the building diagnosis can already be digitalized and recorded as part of BIM models and can serve as the basis for fully automated prediction models, the various tests on the building are usually carried out manually [20, 24].

Before the structural investigation of the concrete component is initiated, a visual inspection is carried out to determine superficial deviations, if available, which makes it possible to initially identify endangered areas of the component. During this inspection, special attention is paid to:

- Cracks
- Spalling
- Exposed reinforcement
- Leaking water
- Surface discoloration
- Deflection or buckling of the surface

In case none of the mentioned traits is present, but other characteristics of the component (e. g. former design service-life is nearly reached, re-use/conversion of the component or changes of exposition) give reason to think of a reduced durability, other area-wide investigations can be conducted. An overview of the possible investigation methods which can be used in a non-destructive way is given in [25]. The focus lies on the condition of the reinforcement and the passivating properties of the concrete. Next to monitoring systems which allow a permanent measurement of specific parameters (e. g. moisture) in the concrete, potential mapping, in particular, is a common method for large-scale investigation of concrete components during building diagnostics. This method allows mapping of the corrosion-activity of the embedded reinforcement enabling the localization of critical areas regarding the corrosion of the reinforcement [26]. While potential mapping is more suitable for the analysis of chloride-induced pitting corrosion, for the detection of carbonation-based corrosion, resistivity measurements should be preferred [27]. Using resistivity measurements, only the maximum possible corrosion rate can be detected because the resistivity of the concrete is influenced by multiple properties such as the temperature, the moisture distribution and the quality of the concrete [28].

A combination of both methods yield the possibility to determine the areas with high risk or ongoing corrosion which are then examined in more detail to define the requirements for the repair [26, 29].

For the determination of the concrete cover there are various methods available that can be used predominantly non-destructively. An overview of the various methods can be found in [30]. This report also includes a detailed description of the procedures and how they are to be applied. Theoretically, the concrete cover, which gives the thickness of the concrete layer protecting the top reinforcement layer, was adapted according to the exposure class and based on the concrete used. Especially in the case of local repairs, it is important to determine the concrete cover as accurately as possible. Further, if the concrete is contaminated with chloride, the concrete cover in combination with the chloride diffusion resistance of the concrete can be used to predict when repair by concrete replacement will be necessary [12]. The same applies to the prediction of when carbonation-induced corrosion is most likely to occur.

In case the progression of the carbonation is characterized by the carbonation depth which gives the thickness of the layer within the concrete cover with a decreased pH of the concrete's pore solution below 9. For the determination of the carbonation depth, usually representative drill cores are extracted from the structure and examined according to [31]. Using the carbonation depth in combination with modeling as described in [12], the duration can be quantified during

which the reinforcement will be protected against carbonation-based corrosion. In case the carbonation resistance of the present concrete was determined beforehand or based on multiple detections of the as-is status during the component's service life, the timing of carbonation-induced corrosion can be predicted using the root-time law and the determined concrete cover. The progression of carbonation with regard to the thickness of the concrete cover influences the decision whether the carbonated concrete has to be removed and replaced to maintain a sufficient protection of the reinforcement or if other repair methods can be applied. The different repair methods which can be used to ensure the passivity of the reinforcement will be discussed in section 2.3.2.

In addition to the carbonation depth, the condition of the steel reinforcement is relevant for the selection of the repair method and normally is characterized by the residual cross section of the reinforcement steel. Since carbonation-based corrosion leads to a nearly uniform development of the corrosion process, the residual cross section can be determined on manually exposed reinforcement.



Figure 2-7: Example of a steel reinforcement rebar with visible cross-sectional loss due to carbonation-based corrosion [15].

In addition to diagnosing the structural damage and its causes, the concrete itself must be characterized so that the appropriate repair products can be selected. To ensure compatibility between the underlying concrete and the repair material later on, various properties of the concrete must be considered when selecting a suitable repair material. The compressive strength

as well as the surface tensile strength of the concrete play a particularly important role here, preventing the development of damaging stresses after the application of the concrete replacement in the form of a repair mortar. The existing, damaged concrete can be classified into different concrete classes based on its compressive strength and surface tensile strength (compare Table 2-2). Both parameters can be determined using core samples taken from representative areas of the structure.

Table 2-2: Classification of concrete based on the mechanical properties according to [20].

Concrete class	Compressive strength	Surface tensile strength	
		Mean value	Smallest value
		MPa	
A1	≤ 10	< 0.8	< 0.5
A2	> 10	≥ 0.8	≥ 0.5
A3	> 20	≥ 1.2	≥ 0.8
A4	> 30	≥ 1.5	≥ 1.0
A5	> 75	≥ 2.5	≥ 2.0

If the concrete shows insufficient resistance values, it may be unsuitable for the application of a repair mortar and must be removed. In any case, before applying any mortar, loose particles must be removed from the concrete to ensure sufficient adhesion between the concrete and the applied material.

2.3.2 REPAIR IN CASE OF CARBONATION-BASED CORROSION

When assessing a component, a distinction is made between corrosion risk and active corrosion. Accordingly, there are both preventive repair methods and methods that are used in cases of existing corrosion. Table 2-3 summarizes the possible repair methods depending on the condition of the component.

Table 2-3: Overview of the repair methods depending on the condition of the component in case of carbonation according to DIN EN 1504-9 and the technical rule for maintenance (German guideline) [23, 32].

Structural condition	Repair category	Procedure	Method
Depassivation expected within service life	Preventive	- Increasing the concrete cover through coating	7.1
		- Crack filling (non-structural)	7.6
		- Anti-carbonation surface protection coatings	7.7
Early state corrosion	Repair with preservation of substance	- Chemical re-alkalization by diffusion	7.4
		- water-repellent surface treatments	8.1
		- Surface coatings	8.3
Early state corrosion, drying not possible	Re-alkalizing methods	- Electrochemical re-alkalization	7.4
		- Chemical re-alkalization by diffusion	
Advanced corrosion	Substance-replacing repair measures	- Extensive concrete replacement (hand-applied or sprayed mortar) with cross-section enlargement	7.2
Corrosion, load-bearing capacity significantly reduced	Structural strengthening methods	- Reinforcement replacement or supplementation	Principle 4
		- Plate or laminate strengthening (e.g. CFRP, steel plates)	
		- Structural crack injection	

Is there already active carbonation-based corrosion on the steel reinforcement, there is always the option to shield the building component against the environment using coatings which prevent the penetration of moisture or CO₂ and therefore inhibit the carbonation of the concrete. For this, surface protection systems can usually be used which, however, are only used for large-scale repairs (see e. g. [33, 34]).

Another option is to restore the conditions in the concrete that enable the steel reinforcement to be protected against corrosion. In the case of carbonation-based corrosion, the original alkalinity of the concrete is lost due to the carbonation process. The hydroxides in the pore solution of the

concrete react with the CO_2 from the environment, which leads to the precipitation of insoluble carbonates and a reduction of the pH value. If the carbonation now progresses to or even beyond the reinforcement, the reinforcing steel becomes de-passivated and corrosion follows. To counteract this process and restore the passivation of the reinforcement (re-passivation), it is possible to raise the pH value of the concrete again by introducing new alkaline components into the concrete.

This goal is pursued by the repair method of the *chemical re-alkalization*, which is regulated both in Germany and Europe. While this principle already is regularly applied, especially in Germany, the European standard DIN EN 1504 part 9 comments on the procedure as follows: *“Experience with this procedure to date is limited. Nevertheless, different approaches have been applied in certain situations in some parts of Europe.”* This is consistent with the results of the literature review on this repair principle, which are summarized in the first paper (Paper I) of this dissertation. Although the method is based on several scientific studies, most of these were conducted on outdated concrete.

Furthermore, these studies contain contradictions regarding the necessary conditions that must be met to ensure successful repair, especially regarding the necessary moisture conditions. Particular attention should be paid to the fact that the maximum carbonation depth of 40 mm permitted by the German guideline has not yet been successfully re-alkalized in any scientific work.

The requirements for repair materials are also not explicitly formulated. The only certainty is that the mortar must be alkaline. In the case of new types of composite cements, the alkalinity of the mortar can be impaired by the replacement of clinker, which is evident from the pH values of the pore solution being lower than those of OPC-based mortars [35]. Since the investigations in this thesis show that even the use of OPC-based binders leads to reduced re-alkalization compared to alkali-activated binders, the influence of cement substitution on the use of these binders as repair materials is questionable, which is why the development of special re-alkalization materials should be investigated.

However, the approach of chemical re-alkalization offers the potential to further investigate and, if possible, optimize this repair principle with regard to its implementation and the materials used.

2.4 REFERENCES

- [1] Stark, J.; Wicht, B., Dauerhaftigkeit von Beton. **(2013)**
- [2] Pourbaix, M., Thermodynamics and corrosion. *Corrosion Science* **(1990)** 30, 963-988.
[https://doi.org/10.1016/0010-938X\(90\)90205-J](https://doi.org/10.1016/0010-938X(90)90205-J)
- [3] Bier, T. A., Carbonation and realkalization of cement paste and concrete. Ph.D. Thesis, Universität Fridericiana zu Karlsruhe, **(1988)** Karlsruhe, 23.12.1987.
- [4] Forschungsgemeinschaft Transportbeton e.V., **(2024)** Dauerhaftigkeit von Beton nach dem Performance-Prinzip - Annahmeprüfungen auf der Baustelle / Abnahmeprüfungen am Bauwerk. *Ruhr-Universität Bochum (RUB) und Technische Universität München (TUM)*.
- [5] Tuutti, K., Corrosion of steel in concrete. Ph.D. Thesis, **(1982)**
- [6] Angst, U.; Elsener, B.; Larsen, C. K.; Vennesland, Ø., Critical chloride content in reinforced concrete—A review. *Cement and concrete research* **(2009)** 39, 1122-1138.
- [7] Bertolini, L.; Elsener, B.; Pedferri, P.; Redaelli, E.; Polder, R. B., **(2013)** Corrosion of steel in concrete: prevention, diagnosis, repair. *John Wiley & Sons*.
- [8] Andrade, C.; Izquierdo, D., Propagation period modeling and limit state of degradation. *Structural Concrete* **(2020)** 21, 1720-1731. <https://doi.org/10.1002/suco.201900427>
- [9] Andrade, C.; Castillo, A., Evolution of reinforcement corrosion due to climatic variations. *Materials and corrosion* **(2003)** 54, 379-386.
- [10] DIN 1045-2: Tragwerke aus Beton, Stahlbeton und Spannbeton – Teil 2: Beton – Festlegung, Eigenschaften, Herstellung und Konformität – Anwendungsregeln zu DIN EN 206-1. *Beuth*, **(2023)** Berlin.
- [11] DIN EN 206-1 Beton – Festlegung, Eigenschaften, Herstellung und Konformität. *Beuth*, **(2021)** Berlin.
- [12] DIN EN 1992-1-1: 2011-01 Eurocode 2: Bemessung und Konstruktion von Stahlbeton- und Spannbetontragwerken - Teil 1-1: Allgemeine Regeln und Regeln für Hochbauten, Brücken und Ingenieurbauwerke; Deutsche Fassung EN 1992-1-1:2023. *Beuth*, **(2025)** Berlin.
- [13] Papadakis, V. G.; Vayenas, C. G.; Fardis, M. N., A reaction engineering approach to the problem of concrete carbonation. *AIChE Journal* **(1989)** 35, 1639-1650.
<https://doi.org/10.1002/aic.690351008>
- [14] Groves, G.; Rodway, D.; Richardson, I., The carbonation of hardened cement pastes. *Advances in Cement research* **(1990)** 3, 117-125.
<https://doi.org/10.1680/adcr.1990.3.11.117>
- [15] Raupach, M.; Büttner, T., **(2014)** Concrete repair to EN 1504: diagnosis, design, principles and practice. *CRC Press*.

- [16] Achenbach, R., Corrosion protection of steel reinforcement by alternative binder types. Ph.D. Thesis, RWTH Aachen University, **(2024)** 14.06.2024.
- [17] Raupach, M.; Schiessl, P., Monitoring system for the penetration of chlorides, carbonation and the corrosion risk for the reinforcement. *Construction and Building Materials* **(1997)** 11, 207-214. [https://doi.org/10.1016/S0950-0618\(97\)00039-1](https://doi.org/10.1016/S0950-0618(97)00039-1)
- [18] Angst, U. M.; Geiker, M. R.; Alonso, M.; Polder, R.; Isgor, O. B.; Elsener, B.; Wong, H.; Michel, A.; Hornbostel, K.; Gehlen, C.; François, R.; Sanchez, M.; Criado, M.; Sørensen, H.; Hansson, C.; Pillai, R.; Mundra, S.; Gulikers, J.; M. Raupach; Pacheco, J.; Sagüés, A., The effect of the steel-concrete interface on chloride-induced corrosion initiation in concrete: a critical review by RILEM TC 262-SCI. *Materials and Structures* **(2019)** 52, 88. <https://doi.org/10.1617/s11527-019-1387-0>
- [19] Michael, R., Zur chloridinduzierten Makroelementkorrosion von Stahl in Beton. Ph.D. Thesis, RWTH Aachen University, **(1992)**
- [20] Deutsches Institut für Bautechnik (DIBt) Technische Regel - Instandhaltung von Betonbauwerken (TR Instandhaltung) - Teil 1: Anwendungsbereich und Planung der Instandhaltung. *Deutsches Institut für Bautechnik (DIBt)*, **(2020)** Berlin.
- [21] ISO 16311-1:2024. Maintenance and repair of concrete structures - Part 1: General principles. *International Organization for Standardization (ISO)*, **(2024)** Geneva.
- [22] ISO 16311-2:2024. Maintenance and repair of concrete structures - Part 2: Assessment of existing concrete structures. *International Organization for Standardization (ISO)*, **(2024)** Geneva.
- [23] DIN EN 1504-9:2008. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 9: General Principles for the Use of Products and Systems. *Beuth*, **(2008)** Berlin.
- [24] Morgenstern, H., Zeitlich und räumlich aufgelöste Zustandsbewertungen und-prognosen über mit Diagnosedaten angereicherte BIM-Modelle als Entscheidungshilfe bei der Instandsetzungsplanung. RWTH Aachen University, **(2023)** Aachen,
- [25] Deutsche Gesellschaft für Zerstörungsfreie Prüfung e.V. -DGZfP- Fachausschuss für Zerstörungsfreie Prüfung im Bauwesen - Unterausschuss Korrosionsnachweis bei Stahlbeton Merkblatt B12. Merkblatt zum Korrosionsmonitoring bei Stahl- und Spannbetonbauwerken. **(2018)** Berlin.
- [26] Ebell, G.; Burkert, A.; Mietz, J., Detection of reinforcement corrosion in reinforced concrete structures by potential mapping: Theory and practice. *International Journal of Corrosion* **(2018)** 2018, 3027825. <https://doi.org/10.1155/2018/3027825>

- [27] Wong, H. S.; Angst, U. M.; Geiker, M. R.; Isgor, O. B.; Elsener, B.; Michel, A.; Alonso, M. C.; Correia, M. J.; Pacheco, J.; Gulikers, J., Methods for characterising the steel–concrete interface to enhance understanding of reinforcement corrosion: a critical review by RILEM TC 262-SCI. *Materials and structures* (2022) 55, 124.
<https://doi.org/10.1617/s11527-022-01961-5>
- [28] Robles, K. P. V.; Yee, J.-J.; Kee, S.-H., Electrical resistivity measurements for non-destructive evaluation of chloride-induced deterioration of reinforced concrete—A review. *Materials* (2022) 15, 2725.
- [29] Elsener, B.; Andrade, C.; Gulikers, J.; Polder, R.; Raupach, M., Half-cell potential measurements—Potential mapping on reinforced concrete structures. *Materials and Structures* (2003) 36, 461-471.
- [30] Deutsche Gesellschaft für Zerstörungsfreie Prüfung e.V. -DGZfP- Fachausschuss für Zerstörungsfreie Prüfung im Bauwesen - Unterausschuss Bewehrungsnachweis bei Stahlbeton Merkblatt B 02. Merkblatt zur zerstörungsfreien Betondeckungsmessung und Bewehrungsortung an Stahl- und Spannbetonbauteilen. (2021) Berlin.
- [31] DIN EN 12390-10: 2019-08 Testing of hardened concrete-Part 10: Determination of carbonation resistance of concrete at atmospheric concentration of carbon dioxide. *Beuth*, (2019) Berlin.
- [32] Deutsches Institut für Bautechnik (DIBt) Technische Regel - Instandhaltung von Betonbauwerken (TR Instandhaltung) - Teil 2: Merkmale von Produkten oder Systemen für die Instandsetzung und Regelungen für deren Verwendung. *Deutsches Institut für Bautechnik (DIBt)*, (2020) Berlin.
- [33] Bruns, M.; Raupach, M.; Grünzig, H.; Schneck, U., Realkalisation of Facades Results of a Research Project. *Restoration of Buildings and Monuments* (2005) 11, 285-296.
<https://doi.org/10.1515/rbm-2005-5986>
- [34] Antons, U., Untersuchungen zur Dauerhaftigkeit hydrophober Schichten im Beton mittels NMR. Ph.D. Thesis, RWTH Aachen University, (2017)
- [35] Vollpracht, A.; Lothenbach, B.; Snellings, R.; Haufe, J., The pore solution of blended cements: a review. *Materials and Structures* (2016) 49, 3341-3367.
<https://doi.org/10.1617/s11527-015-0724-1>

3. BASICS AND NEW OPPORTUNITIES FOR THE CHEMICAL RE-ALKALIZATION OF CARBONATED CONCRETE INCLUDING THE APPLICATION OF ALKALI-ACTIVATED MATERIALS

3.1 ABSTRACT

Corrosion of steel in steel-reinforced concrete is one of the main factors limiting the durability of existing reinforced concrete components. Based on the corrosive circumstance, there are different methods of prevention and repair which can be applied to the concrete. In case of carbonation-initiated corrosion, the chemical re-alkalization is one of the standard measures to counteract the alteration processes in the concrete which lead to corrosion of the reinforcement. This review paper summarizes the current state of research on carbonated concrete chemical re-alkalization with regard to the various materials that have been investigated over time for their applicability to this repair measure. This review summarizes current research results in the field of carbonated concrete and the proven pozzolanic reactivity of the carbonation products in contact with portlandite which suggests an inhibitory effect on chemical re-alkalization, although the influence of this has not yet been investigated. Further, there are initial approaches that deviate from the application of a classic Portland cement as a repair material, but their applicability in practice must be questioned. The use of alternative binders and the associated different composition of the pore solution and the varying alkalinity of these binders, such as composite cements with a high substitution rate or alkaline-activated binders, have not yet been brought into connection with repair processes such as chemical re-alkalization, although the chemical composition of the binders is of the greatest importance for a successful application of the repair measure.

3.2 INTRODUCTION

Re-alkalization of carbonated concrete is one of the main repair measures to extend the durability of steel reinforced concrete, which is the most commonly used building material. Due to the constantly growing numbers of existing structures suffering from carbonation, possibilities to counteract the alteration processes resulting from the reaction of concrete with carbon dioxide and minimizing the consumption of cement-based materials are of great importance.

To prevent corrosion of the steel reinforcement in concrete, the alkaline conditions in the building component's structure, which create a corrosion protection layer on the steel surface, must be maintained and the ingress of corrosive substances must be avoided. The loss of alkalinity of concrete is caused by leaching processes when components are in contact with water [1] and by

carbonation resulting from the reaction of carbon dioxide with the hydroxides of the pore solution due to the diffusion of atmospheric carbon dioxide into concrete [2, 3]. Both processes lead to a decrease of the hydroxide ions in the pore solution of the concrete, and these hydroxide ions are required to form the passivation layer on the steel reinforcement. Passivation is the formation of a protection layer that develops on steel reinforcement over time, which prevents corrosion after steel is embedded in cement-based concrete. The passivation layer dissolves when the pH of the concrete's pore solution drops below about 9, meaning the steel open to attack from chlorides or other corrosion-promoting substances [4, 5]. It is thus of great importance to maintain or restore the conditions in the concrete that lead to formation of the passivation layer to ensure the durability of the structure.

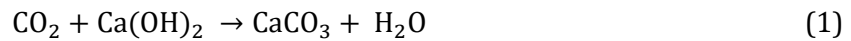
For restoration of the alkaline conditions in concrete, which is necessary after carbonation, different approaches can be used. The repair measures are regulated in standards and vary between removing carbonated concrete and replacing it, and rebuilding alkalinity by the application of an alkaline repair material on the underlying carbonated concrete [6]. Repair measures that can be applied to maintain or rebuild alkalinity without removing carbonated concrete are called chemical re-alkalization (CRA). CRA is based on moisture-based diffusion of the alkaline components from the applied material into the carbonated concrete. By repairing concrete structures, the durability can be extended and the consumption of carbon dioxide intensive materials can be minimized.

This paper serves as a review of the state of the art regarding the re-alkalization of carbonated concrete, with a focus on the CRA. The current procedures in regulations are summarized, along with research studied concentrating on further possibilities to rebuild the alkalinity in carbonated concrete to prevent reinforcement corrosion. In particular, the applications of these researches are discussed and it is noted that further basic research into the re-alkalization process is needed [7]. Based on this review, new perspectives in the field of CRA are approached, especially regarding the use of low-clinker building materials.

3.3 INITIAL SITUATION – CARBONATED CONCRETE

The carbonation of concrete occurs when concrete structures are in contact with the atmosphere, making carbonation one of the main reasons for the limited durability of steel-reinforced concrete. Carbonation starts when carbon dioxide penetrates the porous structure of cement-based materials. First, the carbon dioxide reacts with portlandite (Ca(OH)_2), which is solved in the pore solution, and a high pH of about 13 is maintained. The decrease of calcium in the pore solution results in an increasing concentration gradient between the pore solution and the alkaline cement

paste. When all the portlandite is consumed by carbonation, the increased gradient of calcium between the pore solution and the matrix causes carbonic acid (H_2CO_3), formed by carbon dioxide dissolving in water at the pore wall, to react with the calcium of the calcium silicate hydrates (C-S-H), which is one of the main hydration products of cement and water [8]. The products of the carbonation reaction are water and calcium carbonate (CaCO_3), which can occur in polymorphs calcite, aragonite and vaterite [9].



Due to the decrease in hydroxides, the pH of the pore solution can drop below 9, meaning less alkaline conditions within the carbonated area of concrete [2]. Therefore, the protective layer of the steel reinforcement becomes unstable, leading to de-passivation of the reinforcement. The pH value – as the driving force for incipient corrosion – is preceded by the potential of the embedded steel, which can even cause pH-independent immunity against corrosion (e.g. under cathodic protection). The Pourbaix diagram shown in Figure 3-1 shows the theoretical dependency of corrosion on pH and potential, and shows the path of corrosion as a result of carbonation[10, 11]. The corrosion of steel is accompanied by a volume increase. This causes tension within the concrete, leading to cracking or spalling of the concrete cover. Depending on the exposure of the building component, cracks can enable the additional penetration of corrosive substances such as chlorides. The corrosion of steel reinforcement at the steel–concrete interface can be measured in various ways [12]. Along with optical analysis (e.g. microscopy), corrosion can be determined based on changes in the material's behavior when it is used as an electrode, in the case of, for example, measuring the corrosion potential or conducting polarization resistance measurements [13]. The changes in material properties are based on the corrosion processes that result in oxidation of the material starting from the surface of the reinforcement (i.e. the interface between the reinforcement and the surrounding concrete).

In addition to changes in the pore solution and the phase composition of the concrete, structural alteration of the material also occurs during carbonation. These changes are characterized by a change in porosity, which can be a decrease in the overall porosity in the case of concrete made with CEM I (Portland cement) [14, 15] or an increase in porosity for concrete made with CEM III (blast furnace cement). Both will result in a change of the transport properties (e.g. diffusivity) of the concrete [16].

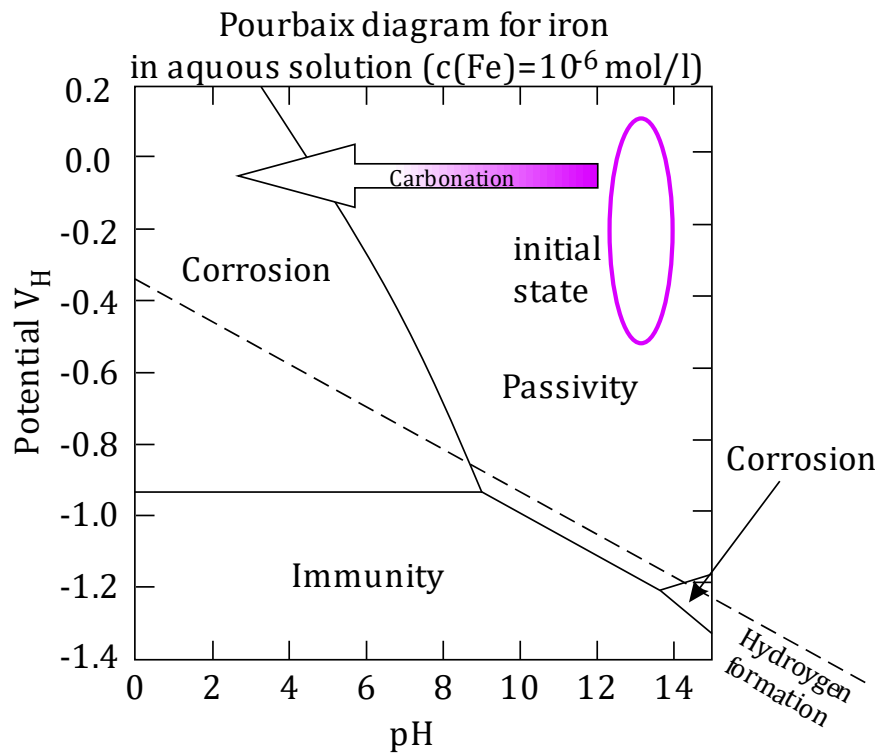


Figure 3-1: Pourbaix diagram showing the different states of steel depending on the steel's potential and the pH of the environment and the influence of carbonation (highlighted) [11].

In the case where reinforcement corrosion has occurred, some measures offer the opportunity to rebuild the durability of reinforced concrete. These measures are usually complex and are internationally regulated in different standards [6, 17-27]. To remove corrosion products from the steel reinforcement, the concrete coating has to be first detached from the reinforcement, and the removal of corrosion products must be carried out without damaging the underlying intact steel. Then, a corrosion protection material can be applied to the reinforcement, followed by replacement of the carbonated concrete. This process can be avoided by preventing corrosion reinforcement, which can be achieved by rebuilding the alkalinity of the pore solution of carbonated concrete through re-alkalization.

3.4 PRINCIPLES OF RE-ALKALIZATION TECHNIQUES

3.4.1 ELECTROCHEMICAL REALKALIZATION

ERA is the re-alkalization of carbonated concrete by inducing an electrical current from an anode placed on top of the carbonated concrete. Normally, sodium carbonate is used as coupling electrolyte for the anodic material. The current passes through the concrete and is directed to the

steel reinforcement which acts as a cathode [28]. The anode and cathode are connected by a transformer rectifier unit. The sodium carbonate is assumed to move through the electric field in the direction of the steel reinforcement, therefore penetrating the carbonated concrete. Enrichment of the electrolyte near the reinforcement should result in re-passivation of the reinforcement based on electrolysis. The principle of ERA is shown in Figure 3-2.

According to the literature [28, 29], the process of ERA is a combination of multiple mechanisms contributing to the RA process. These are

- Absorption
- Diffusion
- Migration
- Electrolysis
- Electroosmosis

The first two mechanisms are based on capillary suction and concentration gradients, respectively, which results in the transport of the alkaline components of the applied electrolyte in the direction of the reinforcement, which is embedded in concrete with reduced alkalinity by carbonation.

Migration is the movement of ions within the electric field – negative ions (OH^-) move towards the anode and positive ions (e.g. Na^+ , K^+) move towards the reinforcement.

Electrolysis takes place at the cathode (reinforcement), generating OH^- ions.



During oxidation, OH^- ions are consumed at the anode.



Electro-osmosis describes the movement of the electrolyte into the concrete and in the direction of the cathodic reinforcement based on the electric field. In addition to re-passivation of the reinforcement, the electrolyte serves as an alkaline puffer. The sodium carbonate reacts with

carbon dioxide from the atmosphere to form sodium hydrogen carbonate in the presence of water. This reaction slows down the carbonation process within the concrete. Research work indicates that ERA does not always lead to a satisfactory result in practice. The durability of ERA was investigated by Tritthart and Baumgartner, who reported that, 2 years after the re-alkalization measure, the alkalinity of the re-alkalized concrete already dropped below a critical point, so that passivation of the steel reinforcement was not ensured [30]. Further information about the influencing factors of ERA can be found elsewhere [29, 31-35].

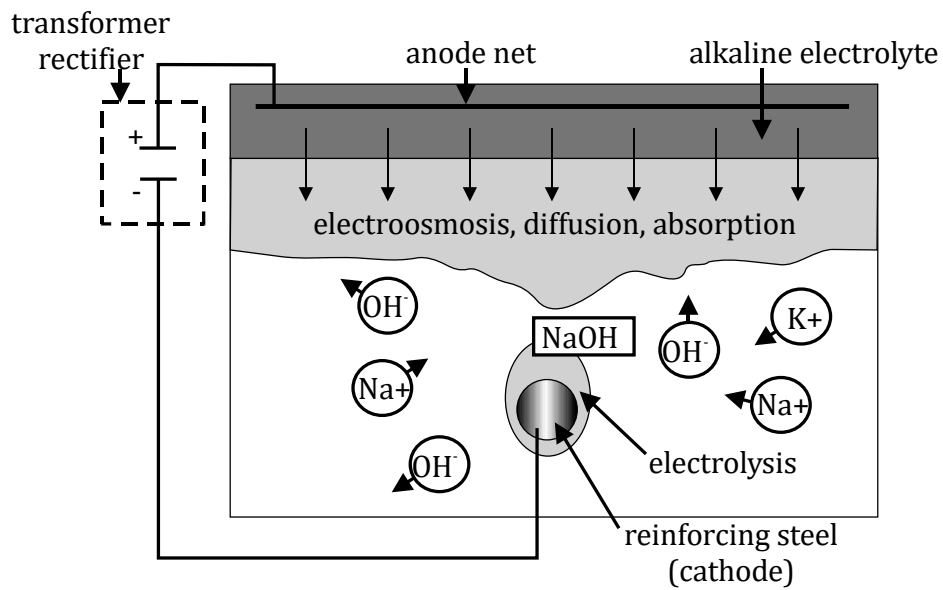


Figure 3-2: Scheme of the ERA and the contributing processes: electroosmosis, diffusion, absorption and electrolysis [28].

3.4.2 CHEMICAL RE-ALKALIZATION

CRA, sometimes also referred to as passive re-alkalization [36], is a repair measure for the re-alkalization of carbonated concrete by diffusion to maintain or restore the passivity of the steel reinforcement [20].

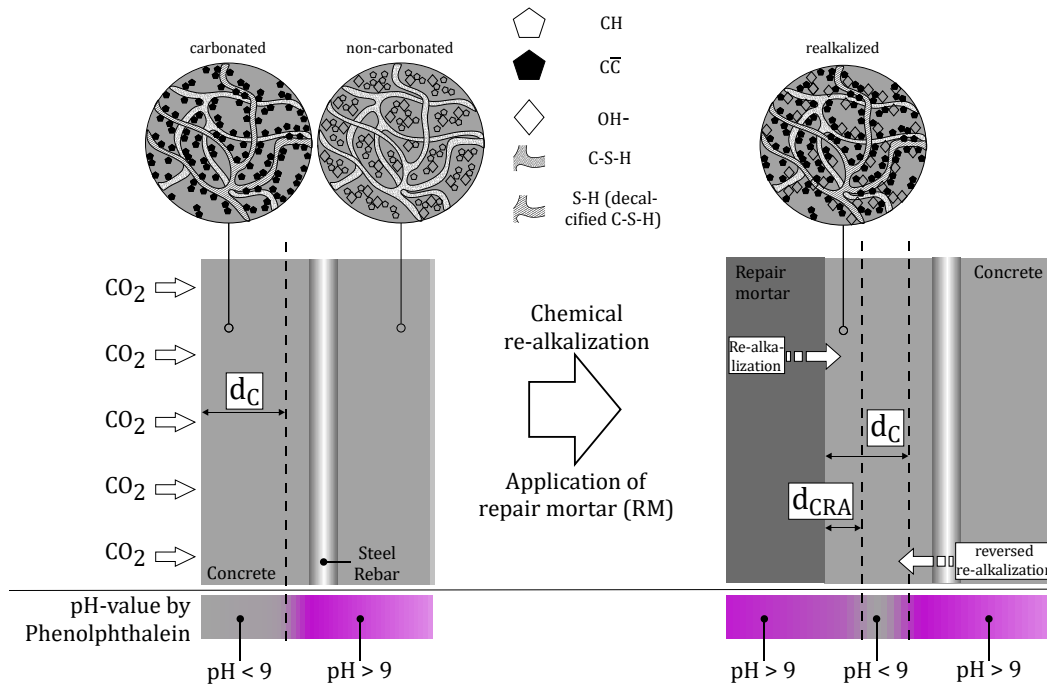


Figure 3-3: Schematic representation of the processes during CRA starting from the carbonated concrete (left) with a carbonated and uncarbonated zone, to the re-alkalized concrete (right) with the applied repair mortar resulting in changed pH values within the re-alkalized zones including the reversed re-alkalization.

Usually, in this repair measure (Figure 3-3), an alkaline cement-based mortar is applied to the carbonated concrete which is pre-wetted, roughened and coated with an adhesive bridge that matches the repair material to ensure a sufficient adhesive bond. This adhesive bond is one of the requirements to enable diffusion between the repair mortar and the underlying carbonated concrete. The diffusion includes the transport of alkali hydroxide ions into the underlying carbonated concrete of a lower pH compared with the mortar. These ions originate from the pore solution of the alkaline (commonly cement-based) repair layer in the form of portlandite or, as investigated by Réus et al., from an alkaline solution (discussed later) [37]. Réus et al. observed re-alkalization starting from the direction of the not-yet-carbonated area of concrete, referred to as reversed re-alkalization. Regardless of the directional starting point, moisture is needed within

the interfacial zone of the repair mortar or the applied solution and the underlying concrete, as well as in the entire carbonated area of the concrete, in order to guarantee a way of transportation for the ions. The moisture can originate from the mixing water of the applied mortar, follow-up treatment after the application or a high relative humidity (RH), which can be provided by rainfall. Next to the adhesive bond, high alkalinity of the repair material and sufficient moisture in the system, there are other requirements to ensure the efficiency of CRA, such as pathways for the transport of hydroxides in the form of the material's porosity. In turn, the porosity is strongly altered during concrete carbonation, which can result in the precipitation of carbonates and the dissolution of C-S-H by decalcification; this results in an increase or decrease in the overall porosity depending on the type of cement used in the carbonating concrete [14]. How all of these materials characteristics and the environmental conditions involved in CRA can enhance or limit the efficiency of CRA will be discussed in more detail later.

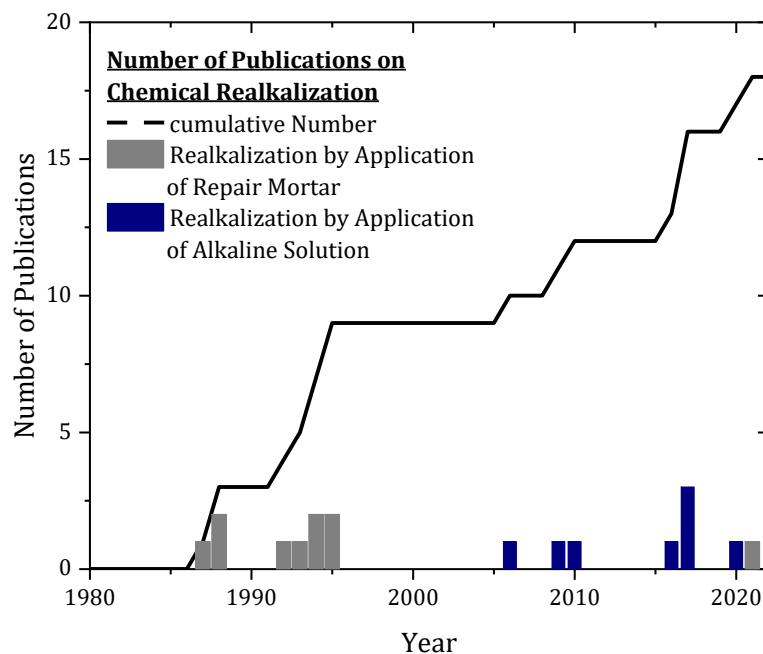


Figure 3-4: Development of the number of publications on CRA with differentiation of the research subject regarding the materials used for CRA.

There is a basic understanding of the theoretical process of CRA, as described above, but there is little application-related research work on CRA using repair mortars. Although Figure 3-4 suggests that research into CRA has been conducted, only one of these research reports were submitted to a scientific journal. Carvalho et al. and Réus et al. confirmed that there were no papers published about CRA until 2020 and they propose a first approach to investigate the potential of different application methods of CRA [37, 38].

Regarding the research work taken into account in the summary in Figure 3-4, the more recent work mainly concerns the application of alkaline solutions, which have not yet found their way into practice. These alkaline solutions do not meet the requirement for the repair material to have its own resistance to carbonation, which means that they do not offer any protection against renewed carbonation of the re-alkalized area. Work conducted before 2000 mainly involved research into carbonated concretes with a porosity (primarily characterized by higher porosity) differing from that of today's concretes. The transferability of the efficiency of CRA to new, more dense concretes is only possible to a limited extent. In addition, the use of alternative binders was not part of the research in any of the included works. Above all, the literature lacks scientific documentation of repair measures for CRA at construction sites, meaning that assumptions from research have not been validated. Therefore, the aim should be to make future research as application-oriented as possible.

CRA BY ALKALINE AQUEOUS SOLUTIONS

Réus et al. conducted CRA using the application of alkaline solutions [37]. In the first step, CEM III concrete samples were carbonated under accelerated conditions at 40 °C, a relative RH of 60 % and a carbon dioxide concentration of 5 % for 18 weeks, yielding a carbonation depth of 16 mm. CRA was carried out by total immersion of the concrete samples in four different types of alkaline solution that differed in their dissolved components (potassium hydroxide, sodium hydroxide, calcium hydroxide and lime (no further specification is provided). Additionally, a commercial solution was used. The samples were immersed for a duration of 31 days maximum and the depth of re-alkalization was determined using a phenolphthalein test. The results showed full re-alkalization by immersion, except in the case of the calcium hydroxide and lime solutions, which showed no re-alkalization even after 9 months of immersion.

In the next step, concrete samples that had been carbonated for 53 weeks under the same accelerated carbonation conditions (resulting in a carbonation depth of 31 mm) were re-alkalized using only potassium hydroxide, sodium hydroxide and the commercial solution. Four different application methods, based on capillary suction, were applied: (a) total immersion, (b) spraying,

(c) brushing and (d) wrapping the specimens in soaked towels. The maximum re-alkalization depth achieved was 19 mm, leaving a carbonated depth of 12 mm. Furthermore, reversed re-alkalization was observed – re-alkalization from the direction of the non-carbonated and alkaline concrete. Regarding the compressive strength of the re-alkalized concrete, no change was observed, which led the authors to conclude that CRA produced no structural changes. Although [37] achieved re-alkalization by applying alkaline solutions on carbonated concrete, these solutions are classified as harmful to humans and are therefore unlikely to become a standardized method. Furthermore, the application methods of total immersion and wrapping in soaked towels, which produced the greatest re-alkalization depths, are difficult to perform when larger areas need to be repaired. Regarding the requirements of the repair materials used for re-alkalization according to standards, the applied material must be able to prevent the underlying concrete from further carbonation as a protective layer. This requires the repair material itself to have carbonation resistance in order to prevent full carbonation of the concrete cover within the remaining service life of the structure [39]. The application of alkaline solutions does not result in a protective layer against further carbonation because the solution is absorbed by the concrete, thus leaving the concrete in direct contact with the atmosphere and thus still allowing the penetration of carbon dioxide. This leads to the immediate new carbonation (re-carbonation) of the re-alkalized concrete. Whether the alkalinity of re-alkalized concrete is stable against carbonation by the application of alkaline solutions has not yet been examined. It could be possible that the application of alkaline solutions achieves an alkaline buffer within the re-alkalized area that is sufficiently high to counteract re-carbonation of the concrete, but further testing needs to be done.

CRA BY HIGHLY ALKALINE HYDROGELS

The application of highly alkaline hydrogels represents a novel approach in the field of CRA of carbonated concrete [40, 41]. Jung synthesized highly alkaline hydrogels based on diallyldimethylammonium hydroxide, which were able to exchange hydroxide ions when applied as a layer on carbonated concrete [40]. The gel can be spread onto a concrete surface due to its consistency (like ultrasound gel). Based on the high proportion of hydrogen in the gel, no external source of moisture is needed to enable the diffusion of hydroxide ions into the underlying concrete. In empirical work, Jung applied hydrogel to prisms of cementitious material that had been naturally carbonated for 1 year, after which full carbonation was achieved according to phenolphthalein testing. After application of the hydrogel, the prisms were sealed using polyethylene foil to maintain the moisture within the hydrogel, enabling maximized transport of

hydroxide ions from the gel into the carbonated prisms. After 60 hours, a re-alkalization depth of 4 mm was measured starting from the prism surface which progressed up to 12 mm after 10 days. Additionally, after 160 hours the originally fully carbonated sample showed a purple core which indicates an increase in alkalinity in this area as well. While describe this phenomenon as a reversed re-alkalization (see Figure 3-5) starting from the alkaline core of the sample in direction of the carbonated rim, Jung attribute the colored core to sample contamination due to a cracking process [37, 40]. Based on the fact that the samples of Jung et al.'s research were characterized by pH below 9 completely, the phenomenon of reversed re-alkalization would be impossible.

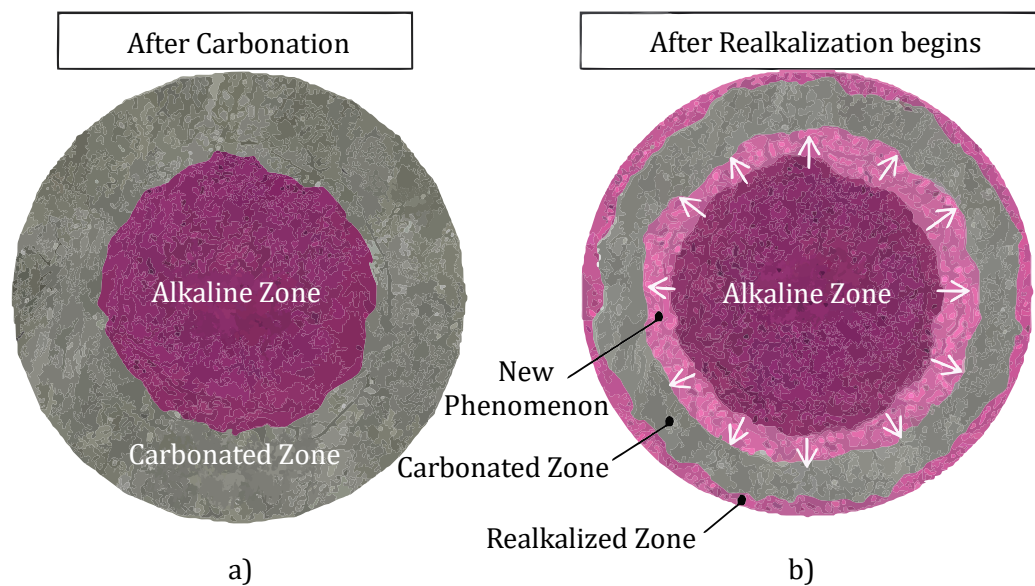


Figure 3-5: Schematic representation of the reversed re-alkalization as introduced by [37].

Even though re-alkalization was enabled using highly alkaline hydrogels, the results can only be used for further research in a restricted manner. In addition to rebuilding the alkalinity of the carbonated concrete, preventing the re-alkalized concrete from re-carbonation is one of the requirements of CRA [17]. In case of the alkaline hydrogel, the applied layer presumably does not act as a protection layer against further carbonation due to the decrease of the gel's alkalinity after re-alkalizing the underlying concrete. Also, to prevent the hydrogel from moisture loss to ensure optimal transportation of hydroxides represents a challenge when working on outdoor building structures. Further, the carbonation resistance of the gel itself is of great interest for the evaluation of the applicability of the material which, based on the high alkaline buffer, could also make it interesting as an additive to enhance the re-alkalization potential in repair materials.

CRA BY ALKALINE REPAIR MORTARS

Instead of using alkaline solutions, the application of repair mortars based on Portland cement is currently state of the art when it comes to the CRA of carbonated concrete on building facades. With this procedure, an increase in the durability of the steel-reinforced concrete structure is achieved, leading to an extended remaining service life. As mentioned earlier, for this repair measure, an alkaline cement-based mortar is applied to carbonated concrete that is pre-wetted, roughened and coated with an adhesive bridge that matches the repair material to ensure sufficient adhesive bond. The actual re-alkalization starts directly after application of the repair material. The procedure is based on the alkalinity of the pore solution of the mortar, which compensates for the decreased pH of the carbonated concrete by capillary suction and diffusion. Re-alkalization by capillary suction occurs directly after application (manually or sprayed) of the mortar on the carbonated concrete. The driving force is the moisture gradient, which results in capillary suction of moisture and the movement of dissolved hydroxides from the mortar into the concrete. This phenomenon has been called piggyback transport[42-44]. Merkel defined the process of re-alkalization by capillary suction as contact re-alkalization, which takes place as soon as the repair mortar comes into contact with the carbonated concrete (Figure 3-6) [42]. In this stage, the re-alkalization shows the highest time-related rate. As noted by Mattila et al., reversed re-alkalization can also be observed during CRA by alkaline repair mortars [45].

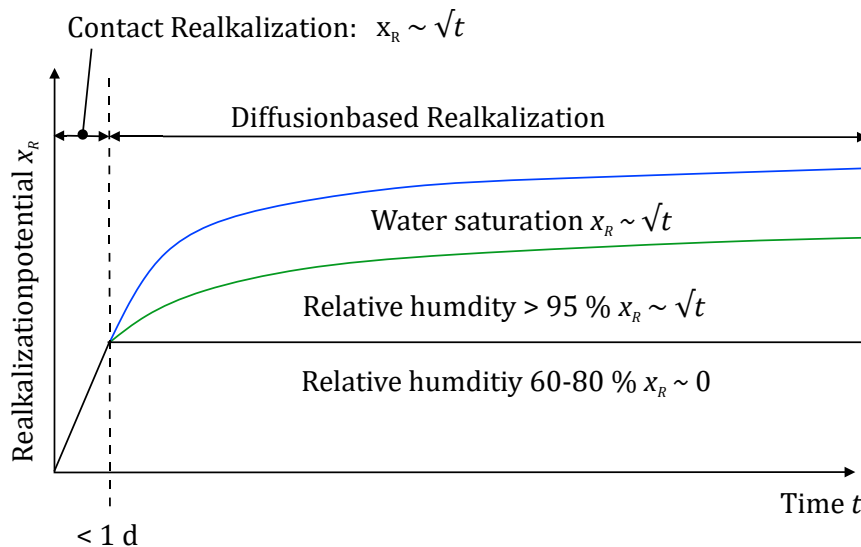


Figure 3-6: Time- and humidity-dependent differentiation of the different phases of the CRA according to [42].

Merkel characterizes the different mortars regarding the re-alkalization potential (X_{RA}) allowing an evaluation of different commonly used mortars for application as repair materials [42]. The re-alkalization potential is defined as the capability of a mortar to restore the alkalinity of a carbonated substrate concrete [43]. Based on this work and to compare the re-alkalization potential of different materials, the re-alkalization coefficient from several studies where evaluated [37, 46-48]. The re-alkalization coefficient (k_{CRA}) was calculated according to Equation 5.

$$k_{CRA} = \frac{d_{CRA}}{\sqrt{t}} \quad (5)$$

with d_{CRA} as the maximum depth of re-alkalization in mm reached after the respective test duration (t).

Figure 3-7 summarizes the different values of k_{CRA} and gives a comparison of the re-alkalization potential of mortars and alkaline solutions. As expected, with application of an alkaline solution, the mean k_{CRA} ($\bar{X}$) (3.1 mm/day^{0.5}) was higher than the mean k_{CRA} of the mortars (1.0 mm/day^{0.5}), regardless of the type of substrate concrete and the material used for re-alkalization. This is because, in the case of an applied solution, a larger amount of moisture is available for piggyback transport. In comparison, the water added to mortar is largely required for hydration of the material and is therefore, after an initial wet phase, no longer available for transport processes such as capillary suction or diffusion. This comparison illustrates the great potential of alkaline solutions for CRA compared with mortars, although mortars have a higher carbonation resistance and act as an additional protection layer against re-carbonation. Whether a combination of these materials in the form of alkali-activated binders (AABs) or composite cements yields the possibility of a high re-alkalization coefficient and a high carbonation resistance at the same time is a subject for future research.

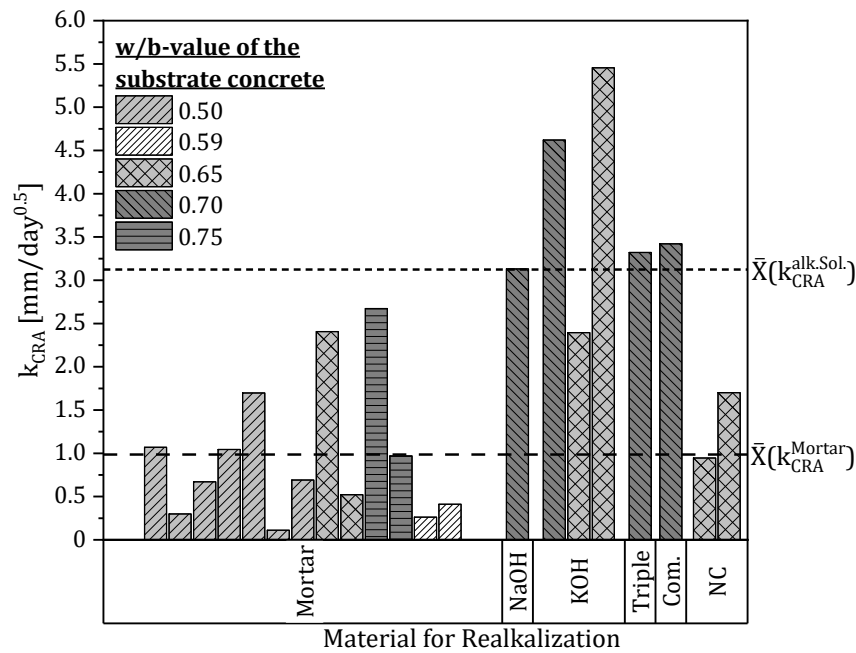


Figure 3-7: Comparison of the re-alkalization coefficient of mortars and alkaline solutions.

A differentiation of the two phases of CRA, as introduced by Merkel as not made because no values of re-alkalization depths (d_{CRA}) during the first day after application of the material for re-alkalization were determined within the publications considered in Figure 3-7 [42]. It can be assumed that mortars and solutions would result in different values of d_{CRA} during the different phases. Whether a difference between the materials within the contact RA would be visible cannot be derived from the results in literature. Due to the higher proportion of available water in the case of the application of alkaline solutions, contact re-alkalization can be assumed to have a higher impact on the total re-alkalization compared with mortars. According to Merkel, in the case of repair mortars, no distinction of the re-alkalization potential regarding the available relative RH during storage in the period of the contact re-alkalization is needed [42]. Applying mortar shortly after mixing implies that the availability of the mixing water is the driving force of the re-alkalization progress during contact re-alkalization. In addition, the phenomenon of reversed re-alkalization starting from non-carbonated concrete was not included in the calculation of the re-alkalization depths considered in Figure 3-7. To quantify the extent of reversed re-alkalization on the total reduction of the carbonated area, this phenomenon must be measured from the start in future experiments.

3.5 INFLUENCING FACTORS CRA

3.5.1 CONDITION OF THE CARBONATED CONCRETE

The efficiency of the re-alkalization process is not only influenced by the re-alkalization material but is also influenced by the carbonated substrate. The influence of the latter was investigated by Merkel and Bier [42, 44]. According to these works, the result of CRA mostly depends on the transport properties of the substrate concrete, which are particularly influenced by its porosity. It is assumed that, the greater the proportion of bigger pores, the better will be the diffusion of alkaline components from the re-alkalization material into the carbonated concrete [49]. In the case of Portland cement-based materials, the overall porosity decreases due to the precipitation of carbonates during carbonation [50]. While most research studies assume that the carbonation of cement-based materials leads to a decrease of all pore types in the carbonated area, there is some evidence that a decrease in overall porosity is accompanied by a redistribution of the pore size distribution, with a shift to larger pores [51, 52]. Coarsening of the pore size distribution would be favorable for the transport processes during re-alkalization by enabling stronger capillary suction when carbonated concrete is in contact with the re-alkalization material. This could also be derived from the lower water retention capacity of carbonated cement pastes [53, 54].

The transport properties of carbonated concrete are also influenced by the phase composition of the carbonated area, which can result in reactive transport of penetrating substances. In the context of re-alkalization, reactions of the penetrating hydroxide ions of the re-alkalization material with the phases present in the concrete after carbonation could lead to a decrease in the penetration depth of the re-alkalizing components, resulting in a decrease of the re-alkalization depth [44]. Regarding the changes during the carbonation of cement-based concrete, degradation of C-S-H phases leads to the formation of decalcified porous silica gel with a lower calcium to silicon ratio than the original C-S-H [55]. The presence of silica gel has been confirmed in multiple studies [44, 48, 56, 57]. Lu et al. and Zajac et al. observed pozzolanic properties of silica gel [58-61]. In contact with portlandite, silica gel reacts to form new C-S-H, allowing the use of carbonated concrete as a recycled supplementary cementitious material (also called concrete fines) in the production of new concrete. For re-alkalization, this would mean reactions of the penetrating hydroxides of the re-alkalization material with the silica gel in the carbonated area, which would inhibit the diffusion process and therefore slow down the re-alkalization. No further explicit research dealing with this inhibiting factor for re-alkalization has been conducted so far. Taking into account the observations of Lu et al. and Zajac et al., the degree of carbonation could be characterized by the proportion of silica gel present in the carbonated concrete which, in turn,

creates requirements for the available alkalis in the repair material in order to still enable deep re-alkalization [58, 60, 61].

3.5.2 CONDITIONS AFTER THE APPLICATION OF MATERIAL

Due to the diffusion of hydroxide ions in the direction of the carbonated concrete by piggyback transport, the presence of sufficient moisture within the system is necessary to ensure re-alkalization [49]. Guse et al. concluded that, under natural conditions, re-alkalization can only take place when at least a cyclic watering is ensured by rainfall [49]. However, in the case of cement-based repair mortars, an adequate follow-up treatment should be conducted to enable a pronounced contact re-alkalization. Investigations concerning the influence of follow-up treatments and environmental conditions were reported by Haardt et al. [47]. They applied cement-based repair mortars in different layer thicknesses on steel-reinforced, naturally carbonated concrete and conducted a follow-up treatment (watering) for 3, 7 and 14 days. The concrete samples showed a carbonation depth of 11 mm. The systems were exposed to different environments (RH of 65 % and 80 %) at a temperature of 20 °C. Additionally, samples were stored in weekly changing conditions from water to dry storage. The re-alkalization depth was determined using phenolphthalein tests after different durations of storage. A longer period of follow-up treatment resulted in faster re-alkalization: follow-up treatment for 14 days resulted in full re-alkalization after 35 days as compared with full re-alkalization after 100 days in the case of treatment for 3 days. Independent of the duration, all the conducted follow-up treatments led to full re-alkalization, even though the systems were stored at 65 % RH afterwards. Similar behavior was shown regarding the different storage climates after the follow-up treatments. The higher the RH the faster was the re-alkalization, with the highest re-alkalization rate for weekly changing conditions from water to dry with a re-alkalization time of 35 days. It should be noted that Haardt et al. investigated concretes with a lower density compared with today's concrete, which could result in lower re-alkalization rates [47]. In contrast, Merkel et al. measured a decrease in re-alkalization depth with increasing storage time at 65 % RH [43]. Even at 80 % RH, there was no increase, but a constant re-alkalization depth was measured, which led Merkel et al. to the assumption that the re-alkalization process cannot run completely under natural conditions when no external water treatment (e.g. rain) can be ensured [43]. Furthermore, they reported that, without additional water treatment, a minimum of 95 % RH is needed to keep the re-alkalization process going and justified that with the presence of a sorbat film at the pore walls which enabled the transport of alkalis through the system, referring to the works of [62, 63]. For the development of suitable materials for the repair of carbonated concrete by CRA, it is crucial to fully understand

the influence of environmental factors on the measure's efficiency. Based on literature dealing with the influence of the conditions after the application of re-alkalization materials on concrete, further research studies should be formulated, such as definition of suitable follow-up treatments adapted to the relative RH on site and the transport properties of the underlying concrete.

3.5.3 CARBONATION RESISTANCE OF THE RE-ALKALISED CONCRETE

When full re-alkalization, as determined by phenolphthalein tests on drill cores, is achieved, re-carbonation of the re-alkalized area has to be prevented. In the case of CRA by cement-based repair mortars, this is normally ensured by the carbonation resistance of the repair mortar itself. In this case, the carbonation resistance is designed to be sufficient so that the carbonation depth will not reach the re-alkalized substrate concrete within the remaining service life of the building structure [17]. Regarding the current need for the development of low carbon dioxide binders (e.g. AABs), the decreased carbonation resistance of such binders needs to be considered when using these materials as repair mortars. At the current time, there is no research dealing with the impact of 'low-carbon' binders on the re-alkalization potential of repair mortars.

In the case of CRA by alkaline solutions or alkaline gels, there is no remaining protection layer against carbonation after the re-alkalization process, which means that re-carbonation can start again immediately. As already mentioned, the buffer capacity of re-alkalized concrete after the application of alkaline solutions against re-carbonation needs to be investigated.

Whether the rebuilding of alkalinity in the carbonated area is sufficient to regenerate carbonation resistance depends on the extent of the increase in pH. In general, the success of re-alkalization is usually evaluated based on the phenolphthalein test, with $\text{pH} > 9$ characterizing the repair measure as successful. A more precise determination of the achieved pH is not usually made, which can result in the assumption that re-alkalization has taken place even if the pH of the re-alkalized area is just slightly above 9. Such low values imply a low alkaline buffer in the pore solution of the system, indicating low resistance against re-carbonation [64].

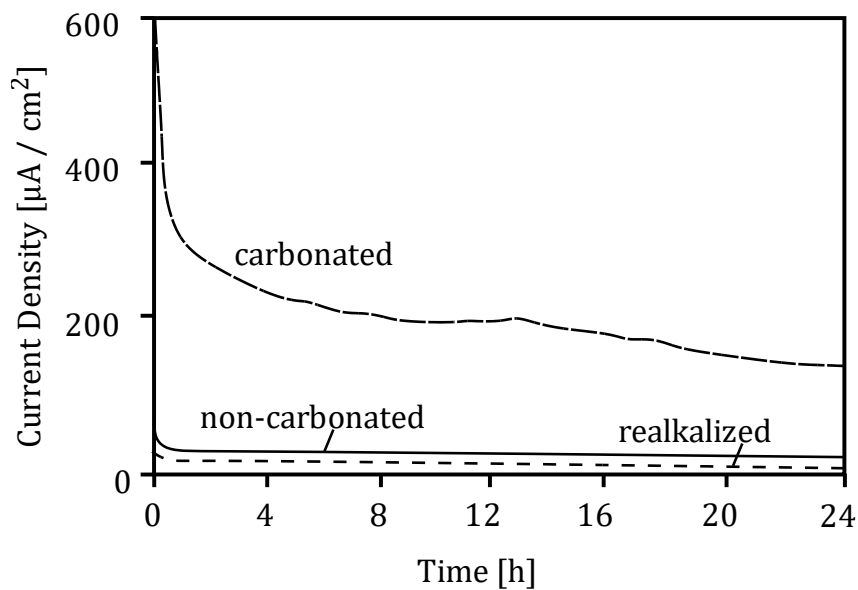


Figure 3-8: Results of the measurement of the corrosion current density of steel reinforcement embedded in non-carbonated, carbonated and re-alkalized concrete [65].

This leads to the question of whether re-alkalization enables full re-passivation of the steel reinforcement in the case of a fully carbonated concrete cover. This was investigated by [65] who detected a corrosion current in steel reinforcement embedded in re-alkalized concrete that was lower than that in uncarbonated concrete. Over a period of 24 h, they monitored the current between the active electrode and the counter electrode of steel embedded in non-carbonated, carbonated and re-alkalized concrete (Figure 3-8). Through this investigation, the meaningfulness of CRA was confirmed and the ultimate goal of re-passivating steel reinforcement in a previously carbonated area can be achieved using CRA.

3.6 RE-ALKALIZATION IN STANDARDS AND REGULATIONS

CRA is, like other repair measures aimed at protecting or restoring passivity, regulated by technical rules for maintenance. In the German guideline for concrete repair it is named the 'realkalization of carbonated concrete by diffusion to remain or rebuild the passivity' (method 7.4) [17]. The method should be applied when the surface of the steel reinforcement in concrete is partially or fully de-passivated or when the layer of non-carbonated concrete above the reinforcement in the direction of the concrete's surface is only a few millimeters thick. The procedure is only applicable if the concrete is not chloride contaminated, and damaged or loose concrete needs to be removed before applying the repair mortar. The maximum carbonation

depth allowed is 40 mm (Figure 3-9). Polymer-modified mortars inhibit the re-alkalization process [42, 49].

In CRA, it is assumed that re-alkalization not only starts from the direction of the repair mortar, but also from the direction of non-carbonated concrete, which still has its original high alkalinity (Figure 3-9). This phenomenon was reported by Réus et al., but the extension of this mechanism has not been investigated for CRA using cement-based materials as repair mortars [37].

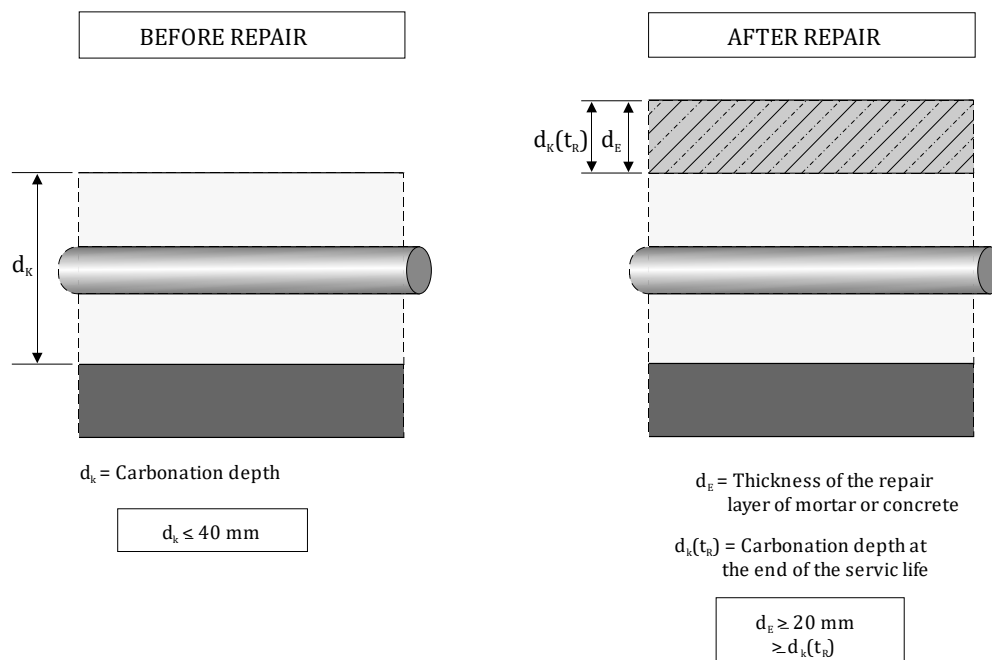


Figure 3-9: Extract of the technical rule for maintenance showing the maximum carbonation depth to be re-alkalized using method 7.4 [17].

The choice of the repair mortar can be simplified using materials stipulated in other regulations [66-70] on the condition that the layer thickness of the repair mortar is calculated to include a remaining service life of the building structure of 50 years, the exposure class and the requirements for the minimum concrete cover as regulated in DIN EN 1992-1-1[71]. In cases with an unknown composition of the repair mortar, calculation of the layer thickness can be based on the exposure class. There is no regulation or standard for the application of alkaline solutions or alkaline hydrogels as RA materials.

3.7 VALIDATION OF CRA

Assessment of the success of the repair measure is basically carried out by the phenolphthalein test [72]. The test enables the determination of areas where the pH of the concrete is below 9, also referred to as the carbonated area. In reverse, through CRA, the pH of the carbonated area is intended to be increased, leading to $\text{pH} > 9$ as indicated by the phenolphthalein test. However, the phenolphthalein test only shows the transition of two different alkalinity milieus ($\text{pH} > 9$ or $\text{pH} < 9$); it does not give information about the total increase in pH due to CRA [73]. To gain deeper insight into the re-alkalization process, different pH indicators that give varying transitions regarding pH can be used [74]. Determining the exact pH of a re-alkalized area would make it possible to investigate the efficiency of CRA and to evaluate the suitability of CRA materials systematically. A higher pH would also indicate a higher resistance to re-carbonation, which would result in a more favorable assessment of the repair measure.

Even though CRA is used to maintain or rebuild the passivity of steel reinforcement, the success of the measure is not validated by examining the embedded steel. Rather, $\text{pH} > 9$ indicates a sufficiently successful protection or restoration of passivity. Detailed studies on whether $\text{pH} > 9$ (without more precise information on the extent of the increase in pH) is sufficient for re-passivation and also provides resistance against re-carbonation are not available.

3.7.1 CONCLUSION

The main conclusions that can be drawn based on the available literature on the CRA of carbonated concrete are the following:

- There are several approaches to achieve CRA of carbonated concrete, which differ in the applied material (cement-based repair mortars, alkaline solutions or alkaline hydrogels). However, only the application of mortars is regulated.
- Regardless of which material is used, the most important requirement for CRA is sufficient moisture to enable the transport of alkaline components from the re-alkalization material into the carbonated concrete. This can be provided by follow-up treatment or environmental conditions.
- Based on the carbonation resistance of the re-alkalization material, an applied mortar layer can also serve as a protection layer against re-carbonation of the re-alkalized concrete. This is not the case for the application of alkaline solutions or hydrogels.
- The condition of the carbonated concrete also influences the efficiency of CRA. Silica gels, which are known to have pozzolanic reactivity, inhibit the transport of alkaline components within carbonated concrete.

3.7.2 OUTLOOK

Regarding the research status of the principle of CRA, the majority of the basic research was carried out on materials that differ greatly from those currently used in construction because most studies were carried out a long time ago. Therefore, the potential of CRA needs to be evaluated by testing current or even future-oriented materials such as low-carbon binders. While CRA using alkaline solutions yields higher re-alkalization coefficients than the use of cement-based mortars, the application of AABs could be promising as a way of combining the high alkalinity of the activator solution with the carbonation resistance of the binder. Furthermore, the processes that occur during CRA should be investigated in more detail to understand the extent of the influences of the different constituents (e.g. silica gel in carbonated concrete or the alkalinity of the re-alkalization material). To evaluate whether CRA enables re-passivation of the steel reinforcement, measurements should be conducted on embedded steel directly. With the help of the basics developed in the literature, which have proven the feasibility of CRA, future studies in the use of new repair materials can increase the efficiency of this repair measure and develop sustainability by preserving existing buildings through the use of materials with a reduced carbon dioxide footprint.

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3.8 REFERENCES

- [1] Schulte Holthausen, R.; Merkel, M.; Breit, W.; Raupach, M., Monitoring the microstructural deterioration of concrete exposed to leaching in purified water. *Civil Engineering Design* (2022) 4, 99-109. <https://doi.org/10.1002/cend.202100051>
- [2] De Weerd, K.; Plusquellec, G.; Revert, A. B.; Geiker, M.; Lothenbach, B., Effect of carbonation on the pore solution of mortar. *Cement and Concrete Research* (2019) 118, 38-56. <https://doi.org/10.1016/j.cemconres.2019.02.004>
- [3] Groves, G.; Rodway, D.; Richardson, I., The carbonation of hardened cement pastes. *Advances in Cement research* (1990) 3, 117-125. <https://doi.org/10.1680/adcr.1990.3.11.117>
- [4] Andrade, C.; Merino, P.; Nóvoa, X.; Pérez, M.; Soler, L., (1995) Passivation of reinforcing steel in concrete. *Materials Science Forum*. 891-898. [doi:10.4028/www.scientific.net/MSF.192-194.891](https://doi.org/10.4028/www.scientific.net/MSF.192-194.891)
- [5] Poursaei, A.; Hansson, C., Reinforcing steel passivation in mortar and pore solution. *Cement and Concrete Research* (2007) 37, pp. 1127-1133.

- <https://doi.org/10.1016/j.cemconres.2007.04.005>
- [6] DIN EN 1504-10:2004. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 10: Site Application of Products and Systems and Quality Control of the Works. German version, EN 1504-10:2003. *Beuth*, (2004) Berlin.
- [7] Angst, U.; Moro, F.; Geiker, M.; Kessler, S.; Beushausen, H.; Andrade, C.; Lahdensivu, J.; Köliö, A.; Imamoto, K.-i.; von Greve-Dierfeld, S., Corrosion of steel in carbonated concrete: mechanisms, practical experience, and research priorities—a critical review by RILEM TC 281-CCC. *RILEM Technical Letters* (2020) 5, 85-100.
<https://doi.org/10.21809/rilemtechlett.2020.127>
- [8] von Greve-Dierfeld, S.; Lothenbach, B.; Vollpracht, A.; Wu, B.; Huet, B.; Andrade, C.; Medina, C.; Thiel, C.; Gruyaert, E.; Vanoutrive, H., Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CCC. *Materials and structures* (2020) 53, 136. <https://doi.org/10.1617/s11527-020-01558-w>
- [9] Šavija, B.; Luković, M., Carbonation of cement paste: Understanding, challenges, and opportunities. *Construction and Building Materials* (2016) 117, pp. 285-301.
<https://doi.org/10.1016/j.conbuildmat.2016.04.138>
- [10] Pourbaix, M., Thermodynamics and corrosion. *Corrosion Science* (1990) 30, 963-988.
[https://doi.org/10.1016/0010-938X\(90\)90205-J](https://doi.org/10.1016/0010-938X(90)90205-J)
- [11] Pourbaix, M., Atlas of electrochemical equilibria in aqueous solutions. *NACE* (1966)
- [12] Wong, H. S.; Angst, U. M.; Geiker, M. R.; Isgor, O. B.; Elsener, B.; Michel, A.; Alonso, M. C.; Correia, M. J.; Pacheco, J.; Gulikers, J., Methods for characterising the steel-concrete interface to enhance understanding of reinforcement corrosion: a critical review by RILEM TC 262-SCI. *Materials and structures* (2022) 55, 124.
<https://doi.org/10.1617/s11527-022-01961-5>
- [13] Martínez, I.; Andrade, C., Examples of reinforcement corrosion monitoring by embedded sensors in concrete structures. *Cement and Concrete Composites* (2009) 31, pp. 545-554.
<https://doi.org/10.1016/j.cemconcomp.2009.05.007>
- [14] Glawe, C.; Georget, F.; Raupach, M.; Matschei, T., Multi technique characterization of the carbonation affected zone uncluding non-destructive sindle sided ^1H NMR *Cement and Concrete Research* (2024) 178, 107438.
<https://doi.org/10.1016/j.cemconres.2024.107438>
- [15] Georget, F.; Prévost, J. H.; Huet, B., Impact of the microstructure model on coupled simulation of drying and accelerated carbonation. *Cement and concrete research* (2018) 104, 1-12. <https://doi.org/10.1016/j.cemconres.2017.11.008>

- [16] Soja, W.; Maraghechi, H.; Georget, F.; Scrivener, K., **(2018)** Changes of microstructure and diffusivity in blended cement pastes exposed to natural carbonation. *MATEC Web of Conferences*. 02009. <https://doi.org/10.1051/mateconf/201819902009>
- [17] Deutsches Institut für Bautechnik (DIBt) Technische Regel - Instandhaltung von Betonbauwerken (TR Instandhaltung) - Teil 1: Anwendungsbereich und Planung der Instandhaltung. *Deutsches Institut für Bautechnik (DIBt)*, **(2020)** Berlin.
- [18] DIN EN 1504-9:2008. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 9: General Principles for the Use of Products and Systems. *Beuth*, **(2008)** Berlin.
- [19] DIN EN 1504-8:2005. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 8: Quality Control and Evaluation of Conformity. German version, EN 1504-8:2004. *Beuth*, **(2005)** Berlin.
- [20] DIN EN 1504-7:2006. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 7: Reinforcement Corrosion Protection. *Beuth*, **(2006)** Berlin.
- [21] DIN EN 1504-6:2006. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 6: Anchoring of Reinforcing Steel Bar. German version, EN 1504-6:2006. *Beuth*, **(2006)** Berlin.
- [22] DIN EN 1504-5:2013. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 5: Concrete Injection. German version, EN 1504-5:2013. *Beuth*, **(2013)** Berlin.
- [23] DIN EN 1504-4:2005. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 4: Structural Bonding. German version, EN 1504-4:2004. *Beuth*, **(2005)** Berlin.
- [24] DIN EN 1504-3:2006. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 3: Structural and Non-structural Repair. German version, EN 1504-3:2005. *Beuth*, **(2006)** Berlin.
- [25] DIN EN 1504-2:2005. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of

- Conformity—Part 2: Surface Protection Systems for Concrete. German version, EN 1504-2:2004. *Beuth*, (2005) Berlin.
- [26] DIN EN 1504-1:2005. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 1: Definitions. German version, EN 1504-1:2005. *Beuth*, (2005) Berlin.
- [27] ISO 16311-3:2014(E) Maintenance and repair of concrete structures - Part 3: Design of repairs and prevention. *International Organization for Standardization (ISO)*, (2014)
- [28] Mietz, J., Electrochemical realkalisation for rehabilitation of reinforced concrete structures. *Materials and Corrosion* (1995) 46, 527-533.
<https://doi.org/10.1002/maco.19950460904>
- [29] Redaelli, E.; Bertolini, L., Electrochemical repair techniques in carbonated concrete. Part I: electrochemical realkalisation. *Journal of Applied Electrochemistry* (2011) 41, pp. 817-827. <https://doi.org/10.1007/s10800-011-0301-4>
- [30] Tritthart, J.; Baumgartner, E., Zerstörungsfreie Korrosionsschutzmaßnahmen. *Schriftenreihe Strassenforschung* (2007)
- [31] Aguirre, A. M.; Gutiérrez, R. M.-d.; Restucci, J. P.; Alvarado, A., Study of a repair technique in carbonated blended mortars: Electrochemical re-alkalization. *Dyna* (2016) 83, 93-99. <https://doi.org/10.15446/dyna.v83n196.49249>
- [32] Bruns, M.; Raupach, M.; Grünzig, H.; Schneck, U., Realkalisation of Facades Results of a Research Project. *Restoration of Buildings and Monuments* (2005) 11, 285-296. <https://doi.org/10.1515/rbm-2005-5986>
- [33] González, F.; Fajardo, G.; Arliguie, G.; Juárez, C.; Escadeillas, G., Electrochemical realkalisation of carbonated concrete: An alternative approach to prevention of reinforcing steel corrosion. *International Journal of Electrochemical Science* (2011) 6, 6332-6349. [https://doi.org/10.1016/S1452-3981\(23\)19684-2](https://doi.org/10.1016/S1452-3981(23)19684-2)
- [34] Tong, Y.; Bouteiller, V.; Marie-Victoire, E.; Joiret, S., Efficiency investigations of electrochemical realkalisation treatment applied to carbonated reinforced concrete—Part 1: Sacrificial anode process. *Cement and Concrete Research* (2012) 42, 84-94. <https://doi.org/10.1016/j.cemconres.2011.08.008>
- [35] Zhu, P.; Zhang, J.; Qu, W., Long-term effects of electrochemical realkalization on carbonated concrete. *Frontiers of Structural and Civil Engineering* (2020) 14, 127-137. <https://doi.org/10.1007/s11709-019-0583-x>
- [36] Mattila, J.; Pentti, M., (1996) The performance of different realkalisation methods. *Concrete in the Service of Mankind: Concrete Repair, Rehabilitation and protection. Proc. of the int. conference held at the University of Dundee, Scotland on 27-28 June 1996*. 483-491.

- [37] Réus, G. C.; Medeiros, M. H. F., Chemical realkalization for carbonated concrete treatment: Alkaline solutions and application methods. *Construction and Building Materials* (2020) 262, 120880. <https://doi.org/10.1016/j.conbuildmat.2020.120880>
- [38] Carvalho, M.; Meira, G.; Ferreira, P.; Medeiros, M., Study of the effectiveness of realkalisation treatment on reinforcement repassivation by using simulated concrete pore solution. *Construction and Building Materials* (2022) 321, 126318. <https://doi.org/10.1016/j.conbuildmat.2022.126318>
- [39] Deutsches Institut für Bautechnik (DIBt) Technische Regel - Instandhaltung von Betonbauwerken (TR Instandhaltung) - Teil 2: Merkmale von Produkten oder Systemen für die Instandsetzung und Regelungen für deren Verwendung. *Deutsches Institut für Bautechnik (DIBt)*, (2020) Berlin.
- [40] Jung, A.; Weichold, O., Preparation and characterisation of highly alkaline hydrogels for the re-alkalisation of carbonated cementitious materials. *Soft Matter* (2018) 14, 8105-8111. <https://doi.org/10.1039/C8SM01158C>
- [41] Mrohs, T. B.; Weichold, O., Hydrolytic stability of crosslinked, highly alkaline Diallyldimethylammonium hydroxide hydrogels. *Gels* (2022) 8, 669. <https://doi.org/10.3390/gels8100669>
- [42] Merkel, M., Realkalisierungspotenzial von zementgebundenen Werkstoffen im Trinkwasserbereich. Ph.D. Thesis, Technische Universität Kaiserslautern, (2021) Kaiserslautern, 15.07.2021.
- [43] Merkel, M.; Breit, W.; Schulte-Holthausen, R.; Raupach, M., Realkalisierungspotenzial von Trinkwasserbehälterbeschichtungen. *Beton- und Stahlbetonbau* 114 (2019) 12, 919-928. <https://doi.org/10.1002/best.201900050>
- [44] Bier, T. A.; Hilsdorf, H. K.; Kropp, J., (1988) Karbonatisierung und Realkalisierung von Beton. *10. Internationale Baustoff- und Silikattagung - ibausil*. Weimar. 200-212.
- [45] Mattila, J.; Pentti, M., (1996) Realkalisation of carbonated concrete by cement-based coatings. In: *Corrosion of Reinforcement in Concrete Construction: 4th int. symposium, Robinson College, Cambridge, 1-4 July 1996 Special Publication*. 512-521.
- [46] Araujo, F., Estudo da repassivacao da armadura em concretos carbonatados atraves da tecnica de realcalinizacao quimica. Universidade de Sao Paulo, (2009) Sao Paulo,
- [47] Haardt, P.; Hilsdorf, H. K., (1993) Realkalisierung karbonatisierter Betonrandzonen durch großflächigen Auftrag zementgebundener Reparaturschichten. . *Internationales Kolloquium zum Thema Werkstoffwissenschaften und Bausanierung*. 666-684.
- [48] Bier, T. A.; Kropp, J.; Hilsdorf, H. K., Formation of silica gel during carbonation of cementitious systems containing slag cements. *ACI Symposium Publication* (1989) 114, <https://doi.org/10.14359/1817>

- [49] Guse, U.; Hilsdorf, H. K.; Haardt, P., Realkalisierung carbonatisierter Betonrandzonen durch den Auftrag zementgebundener Mörtel. *Kurzberichte aus der Bauforschung* (1994) 36,
- [50] Shah, V.; Scrivener, K.; Bhattacharjee, B.; Bishnoi, S., Changes in microstructure characteristics of cement paste on carbonation. *Cement and Concrete Research* (2018) 109, 184-197. <https://doi.org/10.1016/j.cemconres.2018.04.016>
- [51] Díaz-Díaz, F.; F. de Cano-Barrita, P.; Leon-Martinez, F. M.; Castellanos, F., Unilateral low-field magnetic resonance measurements of carbonation depth in unsaturated and saturated Portland cement mortars. *Cement and Concrete Research* (2020) Volume 138, 106237. <https://doi.org/10.1016/j.cemconres.2020.106237>
- [52] Villain, G.; Thiery, M., (2005) Impact of carbonation on microstructure and transport properties of concrete. *Proceedings of.* 1-8.
- [53] Boumaaza, M.; Turcry, P.; Huet, B.; Aït-Mokhtar, A., Influence of carbonation on the microstructure and the gas diffusivity of hardened cement pastes. *Construction and Building Materials* (2020) 253, 119227.
<https://doi.org/10.1016/j.conbuildmat.2020.119227>
- [54] Johannesson, B.; Utgenannt, P., Microstructural changes caused by carbonation of cement mortar. *Cement and Concrete Research* (2001) 31, 925-931.
[https://doi.org/10.1016/S0008-8846\(01\)00498-7](https://doi.org/10.1016/S0008-8846(01)00498-7)
- [55] Sevelsted, T. F.; Skibsted, J., Carbonation of C-S-H and C-A-S-H samples studied by ¹³C, ²⁷Al and ²⁹Si MAS NMR spectroscopy. *Cement and Concrete Research* (2015) 71, 56-65.
<https://doi.org/10.1016/j.cemconres.2015.01.019>
- [56] Castellote, M.; Fernandez, L.; Andrade, C.; Alonso, C., Chemical changes and phase analysis of OPC pastes carbonated at different CO₂ concentrations. *Materials and Structures* (2009) 42, 515-525. <https://doi.org/10.1617/s11527-008-9399-1>
- [57] Morandea, A. E.; White, C. E., In situ X-ray pair distribution function analysis of accelerated carbonation of a synthetic calcium-silicate-hydrate gel. *Journal of Materials Chemistry A* (2015) 3, 8597-8605. <https://doi.org/10.1039/C5TA00348B>
- [58] Zajac, M.; Skibsted, J.; Skocek, J.; Durdzinski, P.; Bullerjahn, F.; Haha, M. B., Phase assemblage and microstructure of cement paste subjected to enforced, wet carbonation. *Cement and Concrete Research* (2020) 130, 105990.
<https://doi.org/10.1016/j.cemconres.2020.105990>
- [59] Lu, B.; Shi, C.; Zhang, J.; Wang, J., Effects of carbonated hardened cement paste powder on hydration and microstructure of Portland cement. *Construction and Building Materials* (2018) 186, 699-708. <https://doi.org/10.1016/j.conbuildmat.2018.07.159>

- [60] Zajac, M.; Irbe, L.; Bullerjahn, F.; Hilbig, H.; Haha, M. B., Mechanisms of carbonation hydration hardening in Portland cements. *Cement and Concrete Research* (2022) 152, 106687. <https://doi.org/10.1016/j.cemconres.2021.106687>
- [61] Zajac, M.; Skibsted, J.; Durdzinski, P.; Bullerjahn, F.; Skocek, J.; Haha, M. B., Kinetics of enforced carbonation of cement paste. *Cement and Concrete Research* (2020) 131, 106013. <https://doi.org/10.1016/j.cemconres.2020.106013>
- [62] Rucker-Gramm, P.; Beddoe, R. E., Effect of moisture content of concrete on water uptake. *Cement and Concrete Research* (2010) 40, pp. 102-108. <https://doi.org/10.1016/j.cemconres.2009.09.001>
- [63] Krus, M., (1995) Feuchtetransport-und Speicherkoeffizienten poröser mineralischer Baustoffe: theoretische Grundlagen und neue Meßtechniken.
- [64] Vollpracht, A.; Lothenbach, B.; Snellings, R.; Haufe, J., The pore solution of blended cements: a review. *Materials and Structures* (2016) 49, 3341-3367. <https://doi.org/10.1617/s11527-015-0724-1>
- [65] Bier, T. A.; Kropp, J.; Hilsdorf, H., Carbonation and realcalinisation of concrete and hydrated cement paste. *Durability of construction materials* (1987) 3, 927-934.
- [66] Deutscher Ausschuss für Stahlbeton (DAfStb) DAfStb-Richtlinie Herstellung und Verwendung von zementgebundenem Vergussbeton und Vergussmörtel. *Beuth*, (2011) Berlin.
- [67] DIN 1045-2: Tragwerke aus Beton, Stahlbeton und Spannbeton – Teil 2: Beton – Festlegung, Eigenschaften, Herstellung und Konformität – Anwendungsregeln zu DIN EN 206-1. *Beuth*, (2023) Berlin.
- [68] DIN 18551: Spritzbeton–Nationale Anwendungsregeln zur Reihe DIN EN 14487 und Regeln für die Bemessung von Spritzbetonkonstruktionen. *Beuth*, (2014) Berlin.
- [69] DIN EN 206-1 Beton – Festlegung, Eigenschaften, Herstellung und Konformität. *Beuth*, (2021) Berlin.
- [70] DIN EN 14487-01: Spritzbeton–Teil 1: Begriffe, Festlegungen und Konformität. *Beuth*, (2023) Berlin.
- [71] DIN EN 1992-1-1: 2011-01 Eurocode 2: Bemessung und Konstruktion von Stahlbeton- und Spannbetontragwerken - Teil 1-1: Allgemeine Regeln und Regeln für Hochbauten, Brücken und Ingenieurbauwerke; Deutsche Fassung EN 1992-1-1:2023. *Beuth*, (2025) Berlin.
- [72] DIN EN 12390-10: 2019-08 Testing of hardened concrete-Part 10: Determination of carbonation resistance of concrete at atmospheric concentration of carbon dioxide. *Beuth*, (2019) Berlin.

- [73] Chinchón-Payá, S.; Andrade, C.; Chinchón, S., Indicator of carbonation front in concrete as substitute to phenolphthalein. *Cement and Concrete Research* (2016) 82, 87-91. <https://doi.org/10.1016/j.cemconres.2015.12.010>
- [74] Vogler, N.; Lindemann, M.; Drabetzki, P.; Kühne, H.-C., Alternative pH-indicators for determination of carbonation depth on cement-based concretes. *Cement and Concrete Composites* (2020) 109, 103565. <https://doi.org/10.1016/j.cemconcomp.2020.103565>

4. MULTI-TECHNIQUE CHARACTERIZATION OF THE CARBONATION AFFECTED ZONE INCLUDING NON-DESTRUCTIVE SINGLE SIDED ^1H NMR

4.1 ABSTRACT

Carbonation of cement-based building materials is not only a frequent trigger for corrosion of the reinforcement, but also causes various significant property changes in the carbonated layer. In addition to the decrease in the pH of the pore solution, carbonation is accompanied by a modification in the pore structure due to dissolution and precipitation reactions. The progress of carbonation is currently commonly measured by the phenolphthalein test. In this study, the non-destructive unilateral hydrogen nuclear magnetic resonance (^1H NMR) was used to determine the carbonation progress of mortars as well as changes in the pore structure. The ^1H NMR results were correlated and validated with known methods for characterizing the carbonation progress, including the carbonation depths, but also other structural and mineralogical changes. These results serve as a proof-of-concept which gives reason to apply this non-destructive method to further building materials, especially new environmentally-friendly binders.

4.2 INTRODUCTION

The carbonation of concrete plays an important role both in the field of low CO_2 construction and in the preservation of structures. On the one hand, concrete has the ability to bind CO_2 from the atmosphere, which, in case of Portland cement, can result in reduced porosity while increasing strength. On the other hand, the transformation of the hydrate phases to form calcium carbonate (CaCO_3) leads to a lower pH of the pore solution in the carbonated area [1, 2]. The pH reduction due to carbonation has a negative effect on the durability of reinforced concrete by causing a depassivation of the steel reinforcement and, later on, cracks and spalling on the component surface due to the increase in volume of the steel during corrosion. In contrast, the reduction of the total porosity causes a reduced moisture transport within the component and thus allows a reduction of the penetration of corrosion-promoting substances such as chlorides [3, 4]. Regardless of which of the above two carbonation-based processes is considered, the change in the transport properties of the carbonated area plays a fundamental role in the durability of the structure [5].

Currently, the carbonation depth is usually determined with the color indicator phenolphthalein ($\text{C}_{20}\text{H}_{14}\text{O}_4$) indicating the transition point of a pH value below 8.2 of the surfaces to which it is applied [6]. However, it should be noted, that the carbonation is not a process characterized by a

sharp boundary, but rather by a tortuous transition zone [7-9]. Starting from the high alkalinity of Portland cement ($\text{pH} \sim 13$), a pore solution with a pH of 11 already indicates a carbonation progress that would not be indicated with phenolphthalein [10]. Especially when alternative binders are used, the phenolphthalein test does not seem to be fully applicable when it comes to determining the real progress of the carbonation reaction [11]. Alternative binders, such as low-Calcium binders produced by supplementary cement materials (SCM) substitution using e.g. Metakaolin, seem to undergo a different carbonation process with respect to the development of the alkalinity of their pore solution, according to the current state of knowledge. Therefore, there is an additional need for new investigation methods for the carbonation of binders in the future. While many studies have been conducted on the repair of carbonated structures by surface treatments or by restoring the alkalinity of the pore solution of the concrete, e.g. [12-14], new approaches that link the change in porosity, the resulting transport properties and the evolution of the phase composition of the material are in need [15-17]. By linking these properties, an improved understanding of the carbonation process can be achieved and thus new conditions for repair measures can be formulated and the possible applications of new binders expanded. Complementary to the determination of carbonation depth by the phenolphthalein test, there are several methods to investigate the change of cement-based materials during the carbonation process, such as XRD, TGA and FTIR [18-20]. In addition to their destructive character, they are all based on the analysis of prepared powder samples, which are limited in their result's accuracy by the precision of the extraction and preparation process. This leads to the fact that in the research work carried out to date with the above-mentioned methods, often only an approximation is made to the processes under consideration.

Initial attempts have been made to characterize accelerated carbonated cement-based structures using hydrogen nuclear magnetic resonance (^1H NMR) [7, 21, 22]. The method has yielded very good results in the study of porous materials and polymers, making it a promising tool for in situ observation of building materials [23-30]. It was found that ^1H NMR offers a possibility to determine the carbonation depth of cement paste samples. In addition, ^1H NMR allows a more accurate characterization of the structural changes during the carbonation process with respect to the pore size distribution in water-saturated samples. As a result, the carbonated region of the studied system was divided into two layers, referred to as the carbonated layer and the transition zone [7]. The distinction of these zones is based on different relaxation times, which indicate a decrease in the total porosity in the carbonated layer, accompanied by a shift to larger pore sizes. In contrast to previous publications, this work focuses on complementing the existing methods, including the phenolphthalein test rather than classifying it as inaccurate for the determination of

the carbonation process. Using ^1H NMR, the present study aims to explain the carbonation depth given by the phenolphthalein test regarding the associated structural and mineralogical changes within the material during carbonation. This intends to associate the corrosion relevant turning point of the pore solution's pH value below 8.2 to an alteration process derived from the carbonation profile given by the ^1H NMR. Additionally, the potential of the ^1H NMR as a non-destructive method for the determination of the area affected by carbonation on various materials in the water saturated and non-saturated state is tested.

4.3 MATERIALS AND METHODS

In the first attempt to develop a suitable method, the choice of materials was intended to minimize the negative influences on the signal quality of the ^1H NMR. The measurement principle of ^1H NMR is based on the behavior of the hydrogen nuclei in the material under investigation as a result of an induced magnetic field. Therefore, it is important to minimize other magnetic influences, such as the iron content of the material to be measured [31]. Accordingly, a white Portland cement (WPC) of the cement type CEM I was chosen, which is characterized, among other things, by a low iron oxide content ($< 0.25\%$). The oxide composition obtained by XRF is shown in Table 4-1 as well as the phase composition, determined by XRD. The XRD measurement was carried out using a Panalytical X'Pert Pro X-Ray diffractometer equipped with a Panalytical X-Celerator detector. The analysis was done using the Bragg Brentano configuration and a X-ray tube ($\text{Cu K}\alpha$) at a voltage of 40 kV. The measurement range was 7 to 55 °. As an internal standard, the cement sample was mixed with rutile powder (4:1) with a crystalline proportion of 94.38 %. The diffractogram pattern was evaluated with rietveld analysis which results in a proportion of amorphous components of 3.3 %. The phase composition by XRD is given in Figure 4-1 Small amounts of Portlandite present in the raw cement can contribute to minor pre-hydration processes during the storage of the material before the preparation of the samples.

Table 4-1: Oxide and phase composition of the WPC used in this study.

Oxide	wt%	Phase	Proportion in %
CaO	68.10	Alite	72.4
SiO ₂	22.0	Belite	8.4
Al ₂ O ₃	4.77	Aluminate	5.3
Fe ₂ O ₃	0.22	Anhydrite	4.2
MgO	0.71	Bassanite	0.9
Na ₂ O	0.06	Portlandite	1.5
K ₂ O	0.74	Calcite	2.6
TiO ₂	0.12	Lime	0.6
		Amorphous	4.1

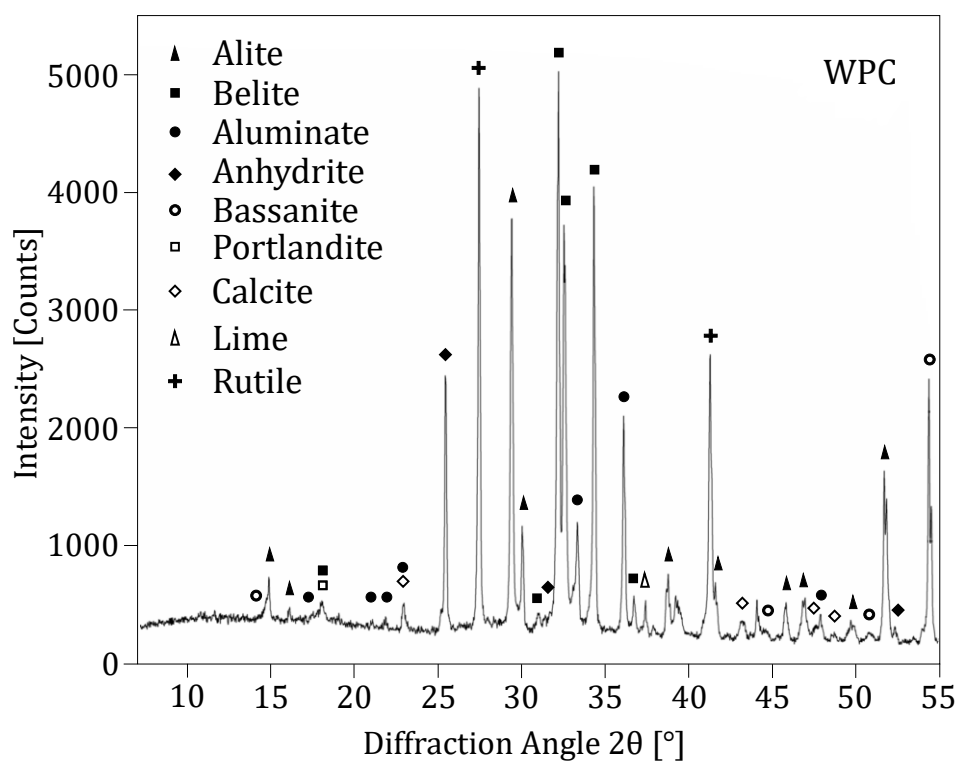


Figure 4-1: Results of XRD of the raw white Portland cement.

4.3.1 SAMPLE PREPARATION

Mortar samples containing aggregates in form of norm sand with a w/b ratio of 0.50 and a binder to aggregate ratio of 0.29 were produced in the form of standard prisms (dimensions $40 \times 40 \times 160 \text{ mm}^3$) and slabs (dimensions $300 \times 300 \times 40 \text{ mm}^3$). As a proof-of-concept, further ^1H NMR measurements were performed on two concretes following the concrete class A4 according to [32]. Table 4-2 comprises the formulations and strengths of the two concretes and the white cement mortar after 28 days.

Table 4-2: Composition and compressive strength after 28 days of the investigated samples

		WPC	MC040	MC040MK
w/b		0.50	0.40	
Type of binder		CEM I white cement	CEM I gray cement	
Cement		455	455	328.5
Metakaolin		-	-	136.5
Water	kg/m ³	228	182	
Aggregates (quarzitic)		1593	1771.5	1771.5
0.0-0.25 (quartz powder)		279.3	-	-
0.1-2.00		813.7	823.7	
2.0-16.00		-	947.8	4.1
$f_{c,28d}$	N/mm ²	52.0 ^{a)}	79.6 ^{b)}	82.3 ^{b)}

^{a)} Tested according to DIN EN 196-1:2016

^{b)} Tested according to DIN EN 12390-3:2009.

The specimens of the WPC were demolded 24 h after casting following storage under damp cloths and then stored in water for 6 days to ensure a proper curing of the sample, and avoid the creation of moisture gradients due to partial drying of the sample up to 7 days. It is assumed that the microstructure is mostly fixed at 7 days, even if the hydration continues slowly during the test. The water curing was followed by storage for 21 days at a relative humidity of 100 %.

Cores with a diameter of 50 mm and 100 mm and a height of 40 mm were extracted from the slabs by drilling and stored at a temperature of $(21 \pm 2) ^\circ\text{C}$ and a relative humidity of $(65 \pm 5) \%$ for natural carbonation (0.05 %) for 10 months. It should be noted that carbonation under accelerated conditions (CO_2 -Concentration $> 3 \%$) causes different changes in the microstructure and possibly different reaction products compared to natural carbonation [17, 33].

For the chemical investigations using Carbon-Sulfur Analysis (CSA – carbon and sulfur content quantification based on infrared analysis of volatiles after sample calcination) and Thermogravimetric Analysis (TGA), powder samples from a 100 mm diameter drill core were prepared and analyzed in 500 μm increments starting from the drill core surface to a depth of 5 mm. Figure 4-2 shows a schematic diagram of the sample preparation for CSA and TGA analysis. In order to exclude an influence of the carbonated marginal areas, the drill cores ($\varnothing = 100$ mm) were over-drilled with a diameter of 80 mm. Subsequently, the depth-graded powder samples with a fineness of 125 μm were obtained by partial grinding of the sample in 500 μm steps. In addition, thin sections were prepared covering the cross-section of the drill core with a diameter of 50 mm in 28 mm width and 48 mm depth starting from the specimen surface. The thin sections were embedded in fluorescent as well as non-pigmented epoxy resin and ground to a thickness of 25 μm , polished and covered.

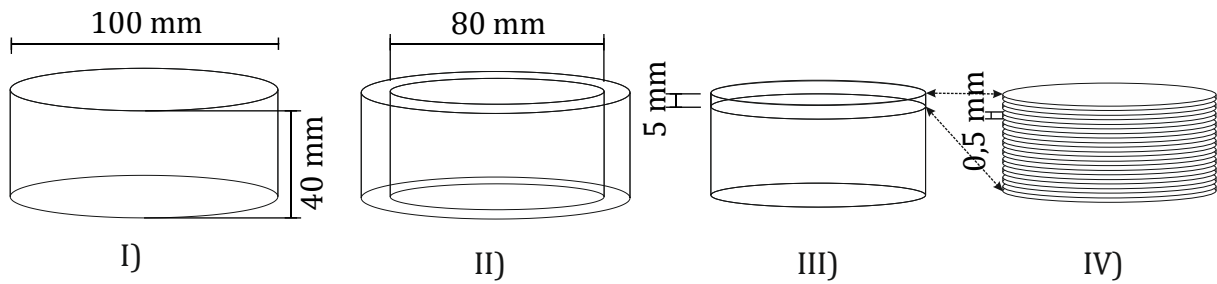


Figure 4-2: Scheme of the preparation of the TGA and XRD samples by over-drilling a disk of WPC (I) with a smaller diameter (II) followed by separating (III) and depth graded partial grinding in 500 μm steps (IV) of the first 5 mm of the sample surface.

For the Proof-of-concept, testing of the concrete specimens was reduced to ^1H NMR measurements and phenolphthalein tests to correlate the determined carbonation depth or area affected by carbonation respectively. The investigations of the concretes were carried out on slabs of $100 \times 100 \times 50 \text{ mm}^3$ which were stored under damped cloth for 24 h after fabrication followed by a water storage for further 6 days. After water storage the samples were dried at 60°C for 7 days. The accelerated carbonation was conducted at 3 %-CO₂-atmosphere at $(21 \pm 2)^\circ\text{C}$ and (65 ± 5) % relative humidity for 90 days.

4.3.2 METHODS

SINGLE-SIDED ^1H NMR MEASUREMENT

The relaxometry measurements were carried out using a single-sided ^1H NMR MOUSE from Magritek, which allows a maximum measurement depth of 25 mm and a radio-frequency (rf) of 13.12 MHz (see Figure 4-3 (a)) [34]. CPMG measurement sequence was selected for measurement by single-sided ^1H NMR, which allows the acquisition of a depth profile in specified step sizes. In the experiments, a total of 21 measuring depths were measured at a step size of 500 μm up to a measuring depth of 10 mm. Each of the 21 depths was measured using 1024 scans and a number of 200 echoes with an echo time of 0.158 ms and a recycle delay of 500 ms for a measurement time of 3 h. During the CPMG sequence the pulse length of the 90 as well as the 180-degree pulse was 10 μs to maintain the excited bandwidth and therefore the size of the sensitive volume while the amplitude of the pulses was changed by amplifying the 180 by 6 dB [35]. This measurement sequence was repeated 10 times per depth automatically instead of measuring one long experiment to minimize the risk of data loss. The same parameters were used for the measurement of the concrete samples.

The repetition of the measurement sequence allows a reduction of the scatter of the signal and results in an increased signal-to-noise ratio (S/N) from 45.7 to 237.7. The S/N was calculated by the amplitude of the first echo divided by the standard deviation of the last 20 echo amplitudes. Figure 4-3 (b) shows the difference of the measurement signal of a single measurement sequence compared to a signal, which was averaged from 10 measurement sequences. The magnified section of the raw data reveals the improvement of the data through averaging multiple experiments. With regard to the evaluation of the measurement signal with respect to the pore structure, which is based on a multi-exponential fit of the measurement signal, this methodology offers the possibility of a significantly more reliable result compared to a single measurement.

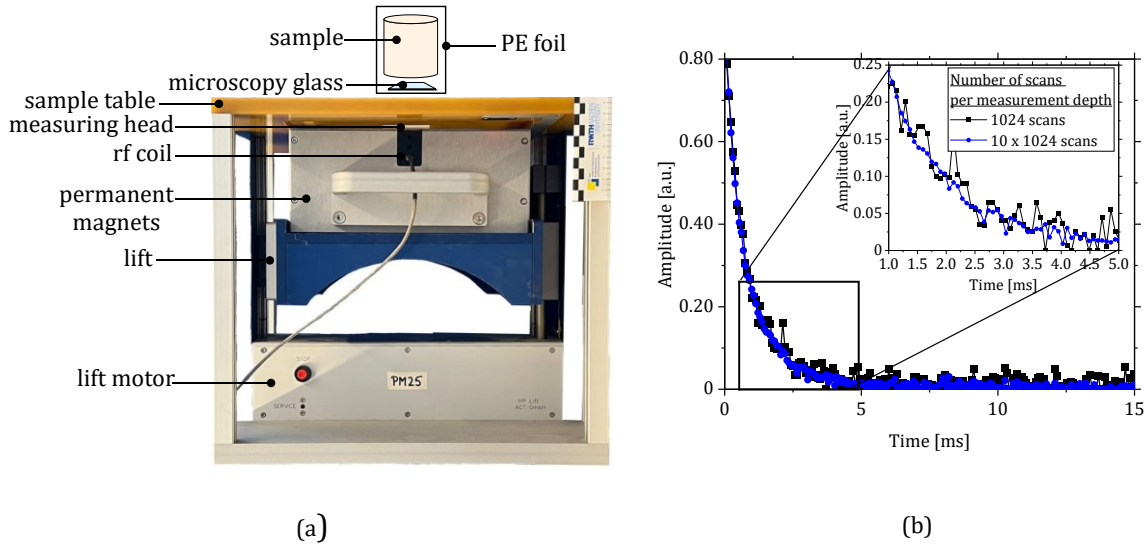


Figure 4-3: (a) Single-sided ^1H NMR MOUSE Type PM25 (Magritek) with a maximum measurement depth of 25 mm (b) improved Signal-to-Noise by averaging 10 experiments with 1024 scans each (right).

The averaged measurement signals of each measurement depth in the form of exponential decay curves were evaluated using the evaluation routine according to Schulte Holthausen, in which the signal is fitted using 4 individual exponential functions according to Equation 1

$$A(t) = \sum_{i=1}^4 A_j (e^{\frac{-t}{T_{2,i}}}) \quad (1)$$

where A corresponds to the amplitude of the signal and $T_{2,i}$ to the relaxation time of the corresponding mode [36]. The fit is obtained using a non-negative linear least-square algorithm. Another method for evaluating the data is the inverse Laplace transformation. However, this method requires a high quality of data, which is rarely the case in the case of CPMG measurements in an inhomogeneous magnetic field. According to Jennings and Muller et al., each of the four functions corresponds to one of the water classes interlayer, gel, interhydrate and capillary represented by four different relaxation times in the signal of the studied volume and provides information about the pore structure of the material [37-39]. The interlayer component allows a conclusion to be drawn about the proportion of the C-S-H phases by showing the amount of water in the interlayer of the phases which are assumed to have a layered silicate like structure [37]. The cylindrical sample of the WPC was measured in the dried and water saturated state, using the single-sided ^1H NMR. For the dried state, the sample was stored until equilibrium at 55 % RH. The

water saturation of the samples during the investigation is defined as the water storage up to constant mass under atmospheric pressure. The signal was evaluated with respect to the different T_2 water classes according to [37, 38]. To avoid overinterpreting the results due to the low S/N, fix T_2 were chosen for the analysis. Although it is expected to observe an evolution of the T_2 distribution, this approach allows us to more reliably analyze the relative distribution of the different pore classes. For the multiexponential fit in this study T_2 -values of 0.15, 1.0, 3.0 and 30.0 ms, respectively, were used to obtain the different water classes. The proportion of the different water classes in percent was calculated by normalizing the amplitudes of the different T_2 to the maximum amplitude of a measurement of pure water.

CHEMICAL ANALYSIS

For validation of the ^1H NMR method, further investigations were carried out to characterize the carbonation progress on naturally carbonated WPC. For the phenolphthalein test, the carbonation depth $d_{c,pH}$ was determined according to [6]. A naturally carbonated drill core was cracked in the middle and a 1 % phenolphthalein solution was applied on the fresh broken cross section. To obtain the carbonation depth, the thickness of the uncolored edge of the cross section was measured 24 h after the application of the phenolphthalein solution. The value for $d_{c,pH}$ was obtained by measuring the uncolored edge at three locations, according to the central points of the division of the edge length into quarters. The same procedure was carried out on the concrete samples after accelerated carbonation. To verify the standardized method for the determination of the carbonation depth of the mortar, the thickness of the uncolored edge was calculated in every point over the full length of the air side, which was also used for the measurement according to the standard. The thickness was calculated using the image analysis software ImageJ by tracing the outer edge and the edge of the uncolored edge in the direction of the sample core with a segmented line. The subtraction of the line's pixel coordinates yields the distance between the lines which then was converted into μm .

In case of the WPC and in addition to the phenolphthalein test, carbon-sulfur analysis (CSA) and thermogravimetry (TGA) were performed. Thermogravimetric analysis was carried out on the powder samples which were also used for the CSA in a depth-graded manner. The TGA was carried out using a METTLER TOLEDO TGA/DSC 1 Stare System thermo balance at a temperature range of 30 to 890 °C and a heating rate of 10 K/min in a nitrogen atmosphere. To calculate the proportion of the different phases, the mass loss in specific temperature ranges was assigned to different components of the sample based on [40]. From 0 to 400 °C the mass loss can be assigned to water bound in the C-S-H, AFm and AFt phases while the mass loss between 400 and 500 °C

results from the decomposition of Portlandite. In the range from 500 to 800 °C the carbonates are decomposed. No distinction between the different carbonate polymorphs was made. For the CSA, the Carbon-Sulfur Analyzer CS2000 manufactured by Eltra was used. The sample was heated up to 2000 °C in an induction stove to quantify the released carbon dioxide (CO_2) and sulfur (SO_3) using an infrared gas analyzer.

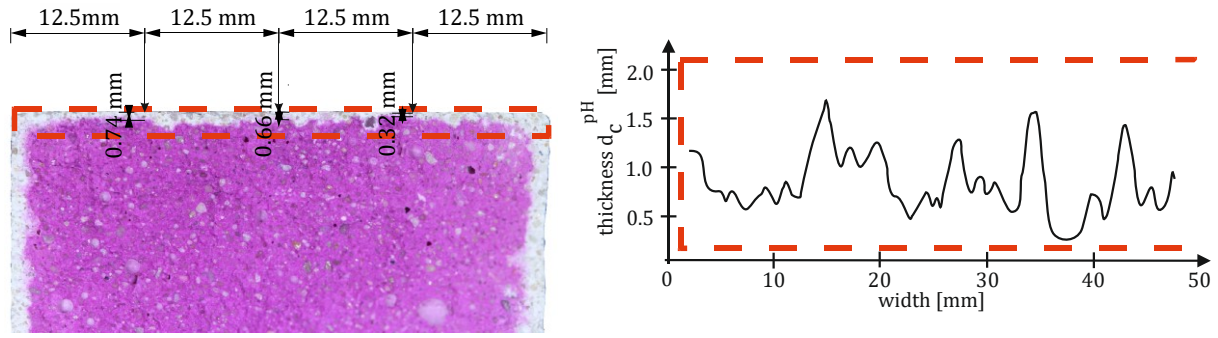
MICROSCOPY

The investigation of the thin sections of the WPC was carried out by light microscopy and scanning electron microscopy (SEM). For the SEM analysis, an uncovered thin section was coated with a 3 nm carbon layer under vacuum. The back scattered electron (BSE) images were taken, using a Zeiss Supra 55 scanning electron microscope. The working distance was set to 8.5 mm using an operating voltage of 15 kV. The used magnification was 100 x resulting in a resolution of 2048 x 1536 pixel. The covered thin section was examined using a light microscope Olympus BX 53 M equipped with an Olympus DP 23 camera and an automated table.

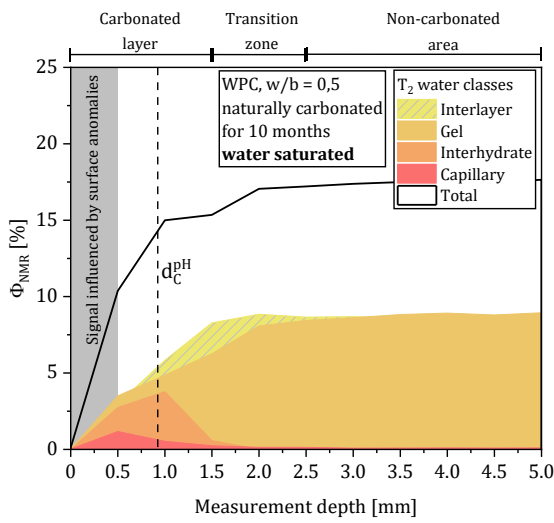
4.4 RESULTS

4.4.1 SUBDIVISION OF THE CARBONATED AREA BASED ON ^1H NMR

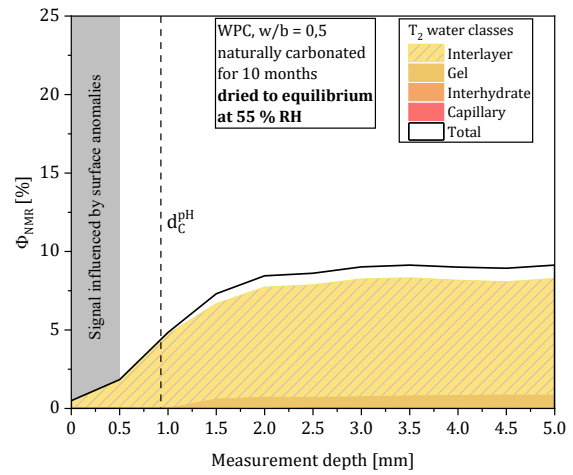
In the phenolphthalein test the naturally carbonated WPC sample which were measured with the single-sided ^1H NMR shows an uncolored edge, indicating carbonation in this area after natural carbonation. Starting from the surface, the carbonation depth $d_{c^{\text{pH}}}$ was 0.57 mm in the case of the WPC. This value was obtained by averaging the carbonation depth measured on three different locations as shown in Figure 4-4 (a), according to the standard [6]. The minimum carbonation depth is 0.32 mm and the maximum carbonation depth is 0.74 mm. The other three sides show a carbonation depth apparently twice as high as a result of the core drilling process. As comparison to the standard, the mean carbonation depth was calculated based on the penetration depth profile which is shown as an overlay on Figure 4-4 (a). The calculation results in a mean carbonation depth of 0.87 mm with a maximum at 1.73 mm and minimum at 0.32 mm.



(a)



(b)



(c)

Figure 4-4: a) Carbonation depth over the sample cross-section as an overlay compared to the measuring points to calculate the carbonation depth and the results of the Single-Sided ^1H NMR on naturally carbonated WPC sample in the dried (b) and water saturated state (c).

The results of the ^1H NMR in Figure 4-4 (b) and (c) show the resulting distribution of the different modes of the measured water in %, referred to as water classes, as a function of the measurement depth, for a dried sample (Figure 4-4 (b)) and re-saturated (Figure 4-4 (c)). Starting from the sample surface, the first 0.5 mm give a mixed signal due to irregularities at the surface of the sample. Apart from the deviating signal of the first 0.5 mm, the overall signal, referred to as total, represents the amount of water present in the measurement volume. The total curve shows a lower water content up to a measurement depth of 2.5 mm which was assigned to the *NMR carbonated Zone A*, including d_C^{pH} . The *Zone A* based on ^1H NMR is connected to the structurally

non-altered area referred to as *NMR non-carbonated Zone B* which is characterized by a higher water content and by the uniform total signal, which can be assumed to represent the bulk structure of the sample.

In addition to the total water content, the ^1H NMR signal can be analyzed to determine the different water classes present in the sample. Based on the results of [23], four different classes can be distinguished. It must be clarified that only some bound water can be measured by ^1H NMR using CPMG, which is based on the fact that the relaxation times (T_2) of crystalline bound water for most minerals (e.g. Portlandite, Ettringite) are too short to be detected. For this reason, previous research often refers to the different water classes as pore types of increasing size [23, 28] according to the order of their appearance in Figure 4-4.

As seen in Figure 4-4 (c) in the NMR non-carbonated Zone B (> 3 mm deep), the water detected is mainly present in the gel class, followed by the interlayer class, which refers to the space between the layers of calcium silicate hydrates (C-S-H). The interhydrate and capillary classes were not detected in Zone B of the sample. In comparison, the NMR carbonated Zone A, is dominated by a coarser structure. The coarser structure results from the detected classes referred to as interhydrate and capillary describing larger pores.

The measurement of the dried sample shows that the measurable water is mainly present in the interlayer. The interhydrate and capillary component is not measurable which indicates that this type of pore is mostly dry in this system. Compared to the water saturated sample, the total signal of the dried sample also shows a characteristic progression of the curve regarding the carbonation depth. Also, the proportion of the water present in the C-S-H in the dried state allows the distinction of Zone A and Zone B. As shown in the chemical analysis, the change in the NMR signal is assigned to carbonation rather than only drying due to the significant correlations between the depth at which chemical and physical changes typically attributed to carbonation were observed. Some of these changes are also due to the inherent drying that occurs during carbonation as shown in previous publications [20, 41, 42]. The boundary of Zone A to Zone B was set in the area that shows a change in the finer structure (gel) without simultaneously coarsening of the structure.

For the application of the single-sided ^1H NMR as a non-destructive method for measuring the carbonation depth on buildings, the ability to measure non-water-saturated samples is a requirement, since building components cannot be guaranteed to be saturated.

4.4.2 CHARACTERIZATION OF THE AREAS

NMR CARBONATED ZONE AND NMR NON-CARBONATED ZONE

The NMR carbonated Zone A is characterized by a coarser structure as observed in the ^1H NMR results and confirmed by microscopy. A darker colored cement paste can be observed in Zone A of the thin sections in Figure 4-5. This is due to the precipitation of carbonates as a result of carbonation, which is accompanied by a decrease in the overall porosity that leads to a reduction of the transmitted light. In the SEM-BSE image (Figure 4-5 (b)), the cement paste matrix in Zone A shows a more homogenous matrix compared to the NMR non-carbonated Zone B which consists of less dense components to a higher proportion, represented by lower gray values.

Figure 4-6 and Figure 4-7 present the results from the chemical analysis. In both the TGA and the CSA measurements, we can observe that the amounts of carbonates (or total CO_2) decrease as a function of the depth. In particular, two observations are significant: 1) the content of carbonates is not constant in Zone A, indicating that the carbonation process is still ongoing; and 2) the content of carbonates is not constant in Zone B indicating that CO_2 penetrated further than the carbonation depth $d_{c^{\text{pH}}}$. Similarly, the portlandite content determined by TGA increases in Zone B. Although it is almost constant in Zone A. On the other hand, the bound water up to 400°C is decreasing in Zone A, but near-constant at maximum value in Zone B. This indicates that in Zone B, the portlandite is the main buffering phase but in Zone A, the other hydrates (C-S-H-, AFm, Aft) are carbonating even though Portlandite is not fully depleted. This analysis is confirmed by the NMR results showing a depletion of the C-S-H interlayer in Zone A. The sulfate content is also decreasing (Figure 4-7) in this layer. It is consistent with the results of [8, 40] which shows a similar segregation of sulfate and was related to the carbonation of ettringite. The SO_3 peak in Zone A could be attributed to excess ettringite precipitation near the carbonation front [8]: From this interpretation, it is logical that the phenolphthalein front is present in Zone A as it requires most cement hydrates to be carbonated to reach a $\text{pH} < 9$ [40].

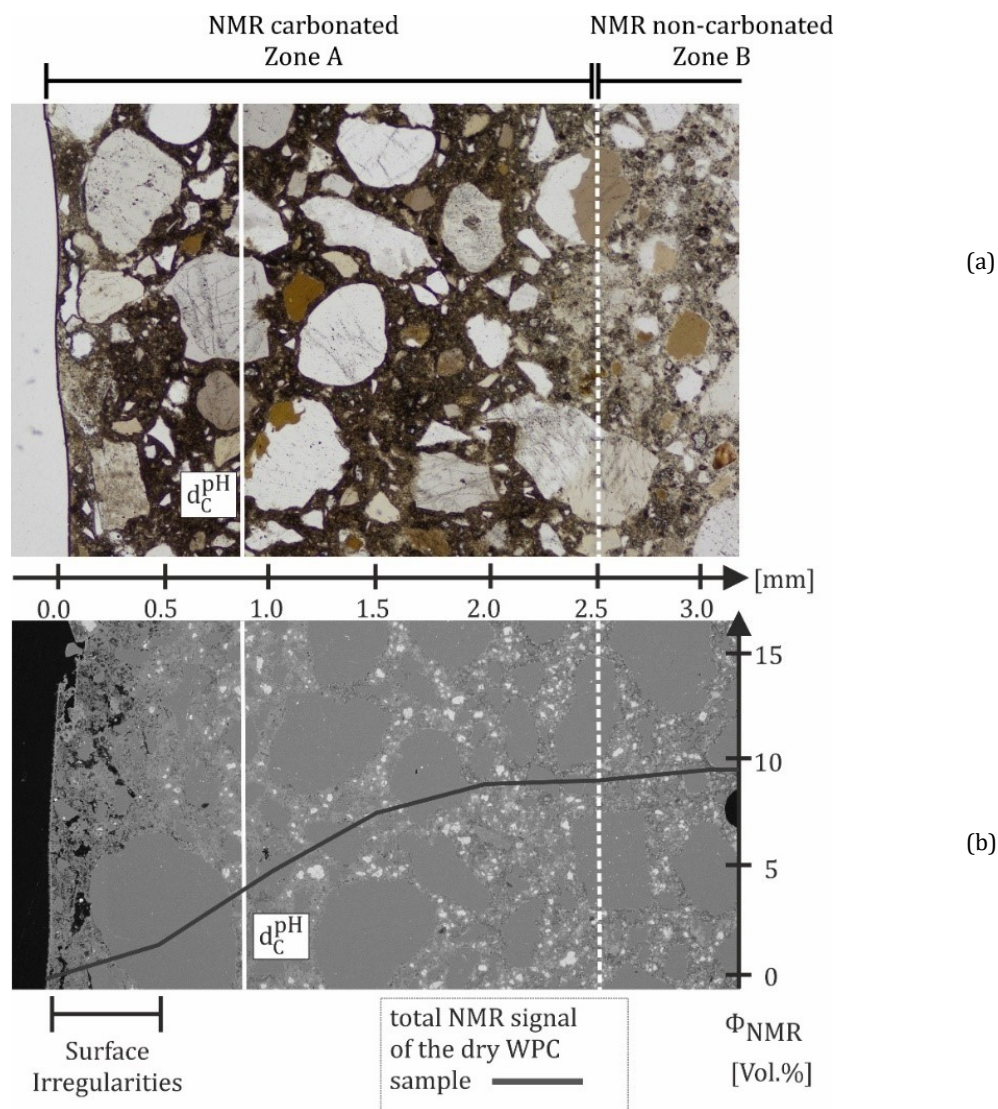


Figure 4-5: Overview images taken by light microscopy (a) and SEM-BSE (b) showing the cross section of the naturally carbonated WPC with highlighted subdivision of Zone A and Zone B area and the area of surface irregularities based on the NMR results as well as the carbonation depth by phenolphthalein.

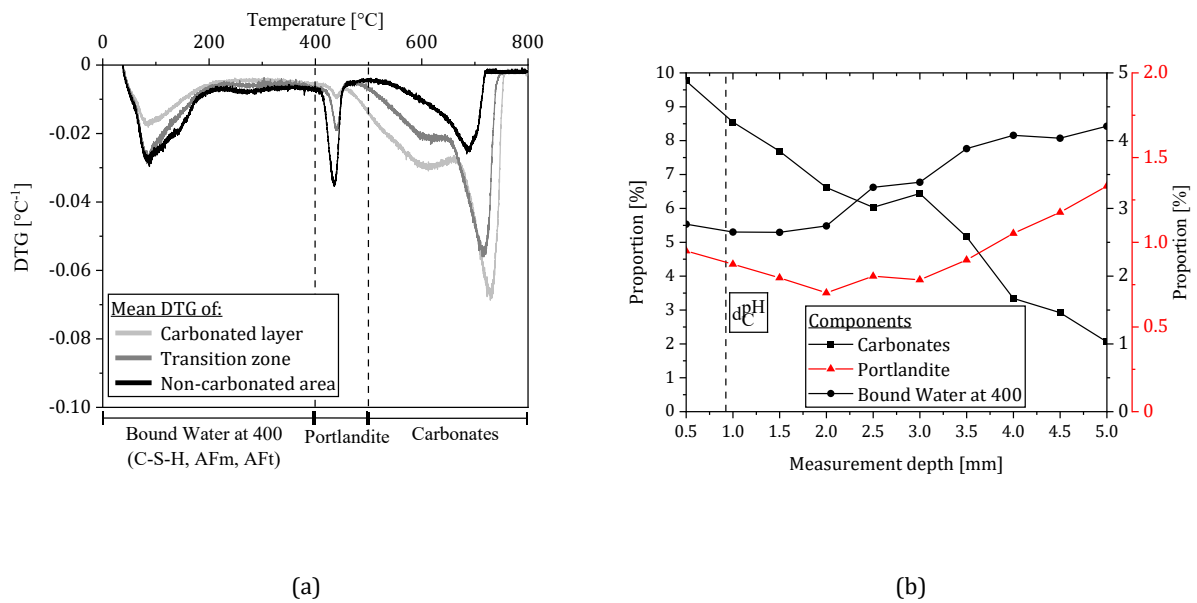


Figure 4-6: (a) Results of the TGA and (b) the derived proportion of the different components.

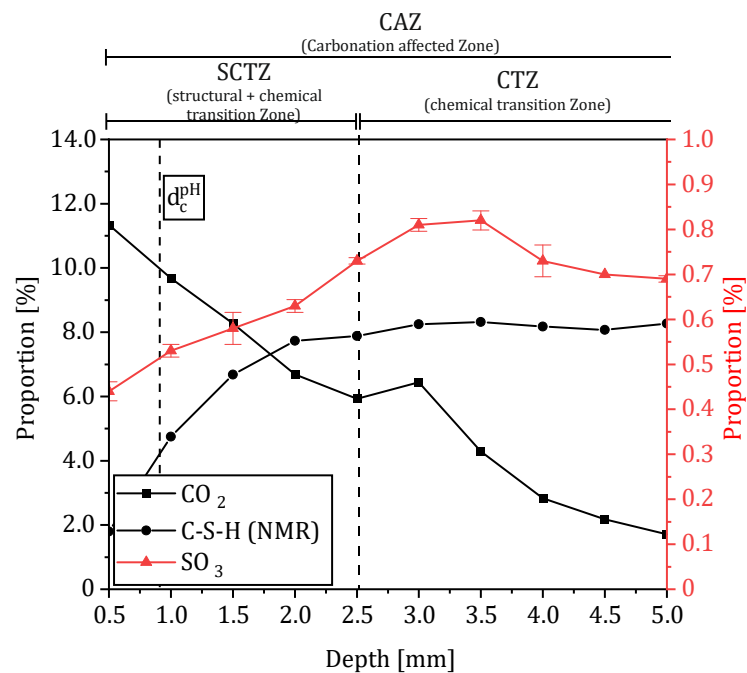


Figure 4-7: CO_2 and SO_3 profiles measured by CSA with indicated carbonation depth by phenolphthalein test and C-S-H profile by ^1H NMR measurement in the dried state.

Based on the additional, chemical characterization by TGA and CSA the width of the NMR carbonated Zone A was enlarged by combining both zones, giving the *carbonation affected zone (CAZ)*. The NMR MOUSE can only detect large structural changes, and therefore, some early carbonation are not detected, even though they can be measured by chemical analysis. This is due to the varying content of the different components at depths higher than the first assumed boundary of Zone A and Zone B. Further, the CAZ, which now at least extends to a depth of 5 mm of the investigated sample, is divided in two separate zones, a chemical transition zone (CTZ) and a *chemical/structural transition zone (SCTZ)*. The chemical transition zone is characterized by a constant distribution of the different water classes by ^1H NMR and a varying distribution of the different components given by TGA and CSA. The chemical/structural transition zone shows a varying structure as well as a varying distribution of the different phases. Overall, the results of the chemical and the structural analysis give reason to define a fully carbonated area. In the first assumption, this would be characterized by a constant structure and by constant ratios of the individual phases. However, this is not the case in any of the samples examined.

TRANSITION BETWEEN CTZ AND SCTZ

The additional subdivision of the CAZ into two separate Zones represents the different phases of the carbonation process. From the ^1H NMR results (Figure 4-4) the transition of the CTZ to the SCTZ is related to the apparition of interhydrate and capillary pores, and the decrease in the gel pore and interlayer volume. It can also be observed in the optical microscopy results (Figure 4-5) with a gradual shift towards a darker color. According to our interpretation of the CTZ and SCTZ, this transition corresponds to the area where portlandite finishes carbonation while the other hydrates (C-S-H, AFm and Aft) starts carbonating. The length of this area is attributed to the heterogeneity observed in Figure 4-5 as well as the low water content as observed by NMR (Figure 4-4).

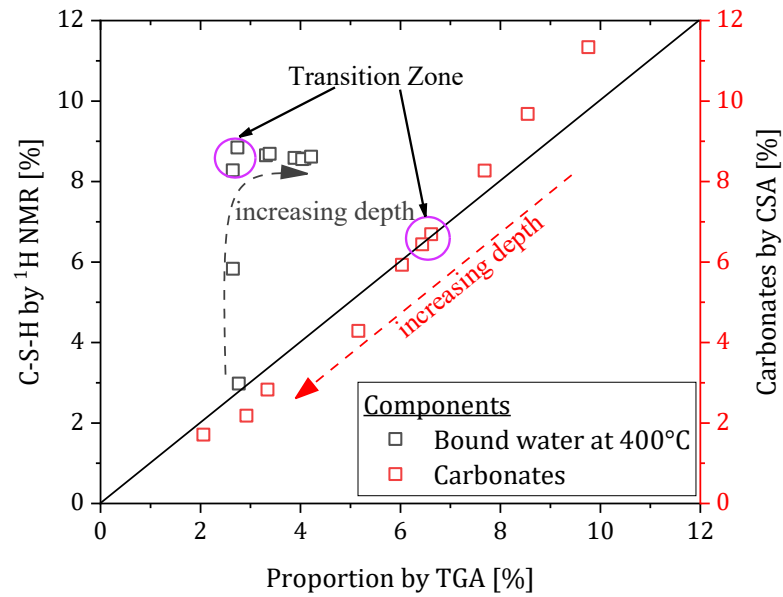


Figure 4-8: Correlation of the phase proportions resulting from the different analysis showing the sensitivity of the different methods regarding structural and mineralogical phases through carbonation.

The comparison of ^1H NMR and TGA results can be used to investigate in more details the order of carbonation. Figure 4-8 presents the correlation between the ^1H NMR, the TGA and the CSA results. The carbonate content by CSA and TGA agrees well. However, ^1H NMR and TGA results deviate significantly in the SCTZ. Figure 4-7 also indicates that SO_3 decrease significantly in this layer. This would indicate that after portlandite, the main phase to carbonate is the ettringite (initial ettringite, and secondary ettringite from the excess sulfates in the non-carbonated layer).

4.5 MEASUREMENTS ON CONCRETE SAMPLES

For checking whether the results of the investigation of the carbonated WPC can be transferred to other cement-based building materials, ^1H NMR measurements were conducted on accelerated carbonated concretes.

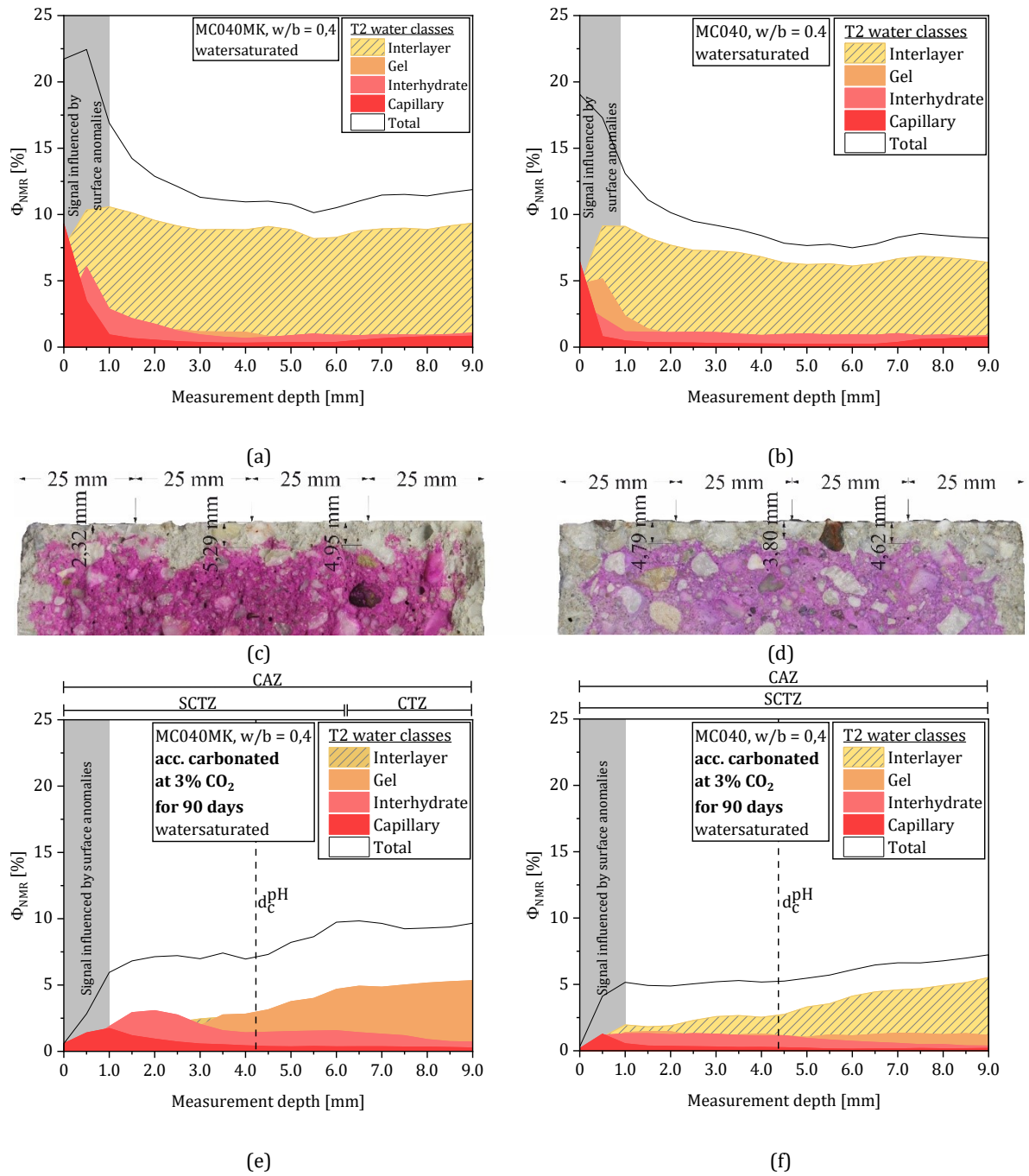


Figure 4-9: Results of the Phenolphthalein test (c) + (d) and ^1H NMR measurements on non-carbonated concretes (a) + (b) and the same concretes carbonated under accelerated conditions (3 % CO_2) for 90 days (e) + (f).

The two concretes were measured before and after accelerated carbonation after water-saturation. The derived Φ_{NMR} signals as a function of depth are shown in Figure 4-9. The assumptions derived from the investigations of the WPC can be applied to the two concrete types. Although the aggregate grain size causes a coarsening of the overall structure, the decrease in porosity with a simultaneous increase in larger pores resulting from the carbonation process in the hardened cement paste can be understood from the ^1H NMR results. The superposition of the results of the phenolphthalein test with the results of the depth-graded ^1H NMR measurements on the two concretes before and after accelerated carbonation shows the characteristic course of the change in microstructure as a function of depth derived from Figure 4-10. Both concretes show a decrease of the total porosity in the SCTZ, which is accompanied by a decrease of the interlayer signal assigned to the C-S-H phases.

At the same time, an increase in the interhydrate and capillary signals assigned to the larger pores was observed. These results agree with the results of the ^1H NMR measurements on the carbonated WPC. Likewise, a transition from CTZ to SCTZ could be determined for both concretes, which, in the case of the MC040 concrete, exceeds the maximum measurement depth of the single-sided ^1H NMR and a measurement of the CTZ area was not possible. Compared to this, the concrete with a 30 % substitution of the cement with metakaolin (MC040MK) after accelerated carbonation for 90 days, shows a curve characterized by two plateaus. The plateaus represent the SCTZ in the near-surface region up to a depth of 4 mm and, on the other hand, the CTZ area from a depth of 6.5 mm. A comparison of the different signal components also shows a shift towards a coarser microstructure in the SCTZ, which is mainly characterized by an increase in the measured signals of the interhydrate and capillary components. At the same time, there is a decrease in the water bound in the interlayer component, which represents the C-S-H phases in the microstructure. Overall, the ^1H NMR results of the carbonated concretes differ from the initial distribution of the water classes within

the maximum measurement depth before accelerated carbonation. Therefore, the transition from the CAZ to the Bulk was not determined.

The correlation of the ^1H NMR results with the phenolphthalein test also results in a deviation of the determined depth related progress of the carbonation. However, the difficulty of the determination of $d_{\text{c}^{\text{pH}}}$ due to the aggregate grain size should be taken into account here. It leads to a fuzzy boundary curve of the phenolphthalein test.

4.6 DISCUSSION

Understanding the structural and mineralogical changes through carbonation is fundamental to optimize the choice of repair measure to prevent corrosion of the steel reinforcement. This paper provides insights into the carbonation process using the non-destructive method single-sided ^1H NMR validated by further chemical and mineralogical investigation techniques.

4.6.1 COMPARISON OF THE CARBONATION PROGRESS BY ^1H NMR AND PHENOLPHTHALEIN

From the ^1H NMR measurements on white cement mortar (Figure 4-4) and the two different concretes (Figure 4-9) it can be observed that single-sided ^1H NMR yields a carbonation profile while phenolphthalein gives you the state of carbonation at a certain point ($d_{c^{\text{pH}}}$, $\text{pH} < 9$). The carbonation profile by ^1H NMR is divided into the areas: 1) Carbonation affected Zone (CAZ) and 2) Bulk while the CAZ is subdivided into a Zone of a) chemical transition (CTZ) and b) structural and chemical transition (SCTZ). In the present study $d_{c^{\text{pH}}}$ mainly lies within the SCTZ layer while the CTZ is not always included in the measured carbonation depth by phenolphthalein. Furthermore, the determination of $d_{c^{\text{pH}}}$ is limited in its points which can be avoided by measuring $d_{c^{\text{pH}}}$ using image analysis as shown in Figure 4-4 a). The impression that the carbonation depth by phenolphthalein underestimates the progression of the carbonation

should not be generated by these results. In case of steel reinforced structures, the phenolphthalein test enables the detection of the depth in which the pH of the pore solution is lower than the value needed for the passivation of the steel reinforcement. Based on this depth, the progression of the carbonation can be calculated to remaining useful life of a building structure. However, the results by single-sided ^1H NMR yield further information about the structural changes by carbonation not only at $d_{c^{\text{pH}}}$ but also at higher depth. With it, the course of the carbonation reaction leading to the drop in $\text{pH} < 9$ of the respective material can be determined. In case of the investigated materials, this drop lies in the area where the coarsening of the structure begins at the boundary of the CTZ to the SCTZ. Here, the structural change during carbonation of the investigated materials causes a shift in pore sizes towards larger pores with a simultaneous decrease in the overall porosity (Φ_{NMR}). These results are consistent with those of [20, 22] where an increase in larger pores as a result of carbonation of cement-based materials was observed by ^1H NMR and mercury porosimetry (MIP). To yield a more precise characterization of the reactions leading to the drop of $\text{pH} < 9$, samples of one material with different carbonation depth can be analyzed.

4.6.2 STRUCTURAL AND MINERALOGICAL CHANGES THROUGH CARBONATION BY DIFFERENT TECHNIQUES

Next to ^1H NMR and phenolphthalein, the carbonation progress of the white cement mortar was investigated using chemical analysis like CSA and TGA. Figure 4-10 comprises the results of the different techniques. Accordingly, there is a certain amount of CO_2 which can be bound in form of carbonates in the sample before the C-S-H of the cement paste gets decomposed through decalcification. By this decalcification, the concentration gradient between the hardened cement paste and the pore solution resulting from the depletion of calcium, is counteracted. This reaction is accompanied by the release of water and a decrease in the volume of the reaction product, which leads to an increase in the larger pore sizes. The overall decrease in pore space is a result of the precipitation processes of CaCO_3 during the carbonation reaction, which settles in the space between the hydration products of the cement.

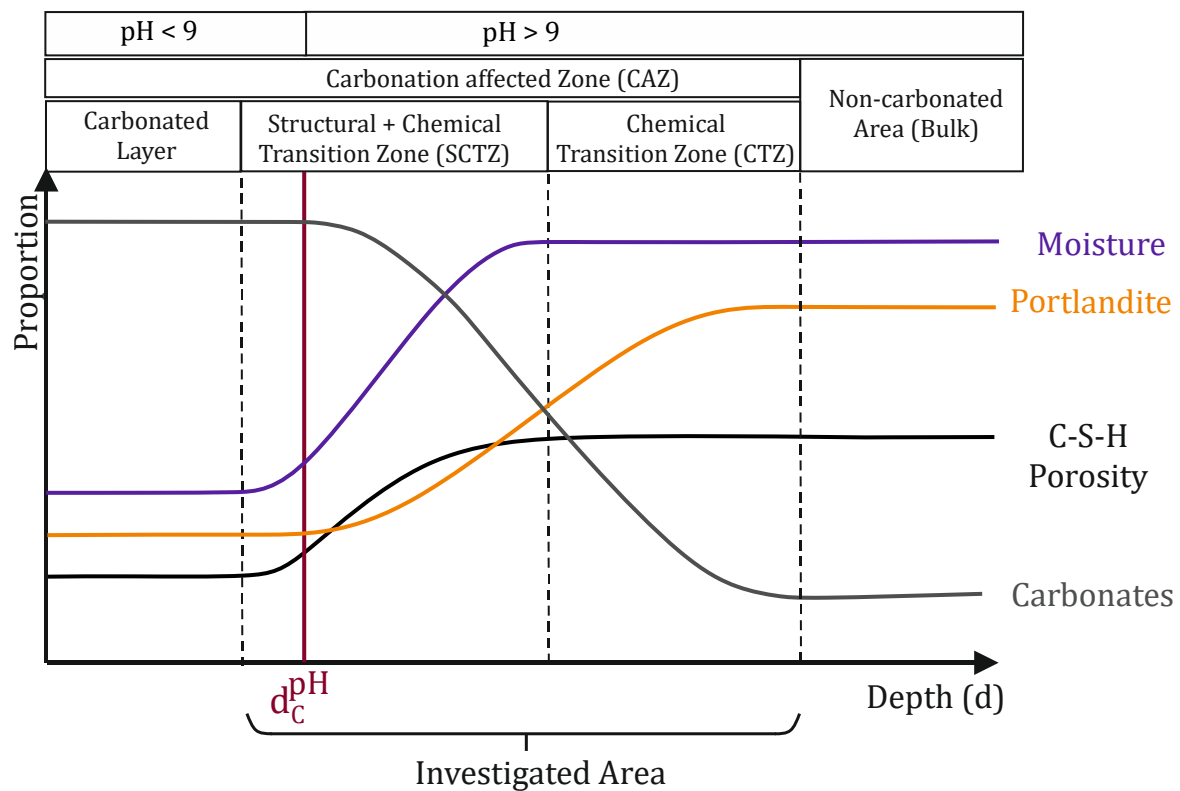


Figure 4-10: Comparison of the effects of carbonation on the different structures in cement-based materials derived from different analysis methods.

Based on the observation by ^1H NMR, that the carbonated layer is characterized by a coarsening of the structure due to the degradation of the C-S-H and thus a shift in the proportion of semi-crystalline bound to free and physically bound water, the interface between the transition zone and the carbonated layer can be understood as a drying front. This drying front at around 1.5 mm is created by the release of the capillary water until the water vapor pressure is minimized. Therefore, a higher proportion of larger pores results in a lower water content in an environment characterized by humidity below the water vapor capacity of the air. The lower water content in this area as measured with ^1H NMR result in a non-local equilibrium carbonation front which is shown by the diffusive carbonation front. This assumption is confirmed by the results of ^1H NMR measurements on a dried sample, also shown in Figure 4-4, which were conditioned in the same way as the samples measured in the water saturated state during the manufacturing process. The measurement shows that the total signal consists mainly of the signal of the water semi-crystalline bound in the interlayer-space. The change in the slope of the total signal agrees with that of the total signal of the water saturated samples. This agreement leads to the assumption that the carbonation depth could be measured on dried samples, which is important for the application of the ^1H NMR on site.

4.6.3 REQUIREMENTS AND LIMITS OF MEASURING CARBONATION BY SINGLE-SIDED ^1H NMR

Requirement for the application of the single-sided ^1H NMR as a nondestructive tool for measuring the Carbonation affected Zone (CAZ) on site is that the carbonation depth lies within the maximum measurement depth of the NMR device. In this study, the NMR MOUSE PM25 enables a measurement up to a depth of 25 mm. According to [43], the concrete cover of steel reinforced components varies dependent on the exposure class and can be up to 50 mm. Although a detailed characterization of the structure based on the different types of bound water is not possible on dried samples, the CAZ could be determined in a non-destructive way using the total water content.

4.7 CONCLUSION

It is the aim of this paper to give further insight into the carbonation process of cement-based materials by the combination of different investigation techniques. For that, the single-sided ^1H NMR was tested as a non-destructive method to determine the carbonation progress. A comparison of the results of the different techniques among each other allows a deeper understanding of the results.

The described investigations and the listed results show that with the help of single-sided ^1H NMR, the CAZ can be determined nondestructively. The following results can be summarized:

- The ^1H NMR offers the possibility to determine not only the depths but also the structural and mineralogical changes as a result of carbonation.
- The progress of the carbonation could be measured on water saturated samples as well as on dried samples.
- A comparison of the results with the currently used, destructive method of the phenolphthalein test for determining the carbonation depth showed that the structural changes as a result of carbonation do not follow a sharp boundary, as the phenolphthalein test suggests. The Phenolphthalein test therefore shows one point on the carbonation profile given by the ^1H NMR.
- With the aid of ^1H NMR, the decrease in the C-S-H phases with a simultaneous increase in the carbonates and an associated reduction in the overall porosity and coarsening of the pore structure as a result of carbonation were measured for the binders investigated.
- Materials containing alternative binders such as metakaolin could also be investigated by ^1H NMR with respect to their microstructure and the changes caused by carbonation.
- Combining ^1H NMR with other techniques (such as TGA, CSA and phenolphthalein) allows to obtain the carbonation order of the hydrates. In particular, in this system (WPC) it was observed that Portlandite carbonates first, then Ettringite and C-S-H.
- The results obtained showed a very diffusive carbonation front. It is assumed that the large heterogeneities in addition to a kinetic inhibition by low moisture content is responsible for the non-local equilibrium carbonation front. The use of ^1H NMR allows to better characterize the moisture content and can help better analyze the shape of the carbonation front.

4.8 OUTLOOK

Based on the results, the different states of the carbonation process can be investigated using ^1H NMR. For the possibility of optimizing the repair measures of carbonated concrete, the influence of the different carbonation states on the efficiency of the repair measures should be analyzed. For example, a dense structure as a result of carbonation prevents the introduction of hydroxide ions to restore alkalinity in the concrete which makes the determination of porosity limits interesting.

Further, the non-destructive determination of the carbonation depth $d_{\text{C}^{\text{pH}}}$ by ^1H NMR is of interest. A requirement for this is the direct correlation of the structural change within the carbonation

and the associated changes in the pore solution. For this purpose, carbonation progresses of varying degrees can be generated on a material and measured using ^1H NMR and pH indicators.

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4.9 REFERENCES

- [1] Groves, G.; Rodway, D.; Richardson, I., The carbonation of hardened cement pastes. *Advances in Cement research* (**1990**) 3, 117-125.
<https://doi.org/10.1680/adcr.1990.3.11.117>
- [2] Houst, Y. F.; Wittmann, F. H., Depth profiles of carbonates formed during natural carbonation. *Cement and concrete research* (**2002**) 32, 1923-1930.
[https://doi.org/10.1016/S0008-8846\(02\)00908-0](https://doi.org/10.1016/S0008-8846(02)00908-0)
- [3] Bier, T. A., Influence of type of cement and curing on carbonation progress and pore structure of hydrated cement pastes. *MRS Online Proceedings Library (OPL)* (**1986**) 85, 123.
- [4] Johannesson, B.; Utgenannt, P., Microstructural changes caused by carbonation of cement mortar. *Cement and Concrete Research* (**2001**) 31, 925-931.
[https://doi.org/10.1016/S0008-8846\(01\)00498-7](https://doi.org/10.1016/S0008-8846(01)00498-7)
- [5] Kropp, J., Karbonatisierung und Transportvorgänge in Zementstein. Ph.D. Thesis, Universität Karlsruhe, (**1983**)
- [6] DIN EN 12390-10: 2019-08 Testing of hardened concrete-Part 10: Determination of carbonation resistance of concrete at atmospheric concentration of carbon dioxide. *Beuth*, (**2019**) Berlin.
- [7] Díaz-Díaz, F.; F. de Cano-Barrita, P.; Leon-Martinez, F. M.; Castellanos, F., Unilateral low-field magnetic resonance measurements of carbonation depth in unsaturated and saturated Portland cement mortars. *Cement and Concrete Research* (**2020**) Volume 138, 106237. <https://doi.org/10.1016/j.cemconres.2020.106237>

- [8] Georget, F.; Soja, W.; Louise Scrivener, K., Characteristic lengths of the carbonation front in naturally carbonated cement pastes: Implications for reactive transport models. *Cement and Concrete Research* (2020) 134, 106080.
<https://doi.org/10.1016/j.cemconres.2020.106080>
- [9] Cheng-Feng, C.; Jing-Wen, C., The experimental investigation of concrete carbonation depth. *Cement and Concrete Research* (2006) 36, 1760-1767.
<https://doi.org/10.1016/j.cemconres.2004.07.025>
- [10] McPolin, D. O.; Basheer, P. A.; Long, A. E., Carbonation and pH in mortars manufactured with supplementary cementitious materials. *Journal of Materials in Civil Engineering* (2009) 21, 217-225. [https://doi.org/10.1061/\(ASCE\)0899-1561\(2009\)21:5\(217\)](https://doi.org/10.1061/(ASCE)0899-1561(2009)21:5(217))
- [11] Kraft, B.; Achenbach, R.; Ludwig, H.-M.; Raupach, M., Hydration and Carbonation of Alternative Binders. *Corrosion and Materials Degradation* (2022) Volume 3, 19-52.
<https://doi.org/10.3390/cmd3010003>
- [12] Merah, A., Concrete anti-carbonation coatings: a review. *Journal of Adhesion Science and Technology* (2021) 35, <https://doi.org/10.1080/01694243.2020.1803594>
- [13] Réus, G. C.; Medeiros, M. H. F., Chemical realkalization for carbonated concrete treatment: Alkaline solutions and application methods. *Construction and Building Materials* (2020) 262, 120880. <https://doi.org/10.1016/j.conbuildmat.2020.120880>
- [14] Schulte Holthausen, R.; Merkel, M.; Breit, W.; Raupach, M., Monitoring the microstructural deterioration of concrete exposed to leaching in purified water. *Civil Engineering Design* (2022) 4, 99-109. <https://doi.org/10.1002/cend.202100051>
- [15] Auroy, M.; Poyet, S.; Le Bescop, P.; Torrenti, J.-M.; Charpentier, T.; Moskura, M.; Bourbon, X., Impact of carbonation on unsaturated water transport properties of cement-based materials. *Cement and concrete research* (2015) 74, 44-58.
<https://doi.org/10.1016/j.cemconres.2015.04.002>
- [16] Auroy, M.; Poyet, S.; Le Bescop, P.; Torrenti, J., (2013) Impact of carbonation on the durability of cementitious materials: water transport properties characterization. *EPJ Web of Conferences*. 01008. <https://doi.org/10.1051/epjconf/20135601008>
- [17] Auroy M.; Poyet S.; Le Bescop P.; Torrenti J. M.; Charpentier T.; Moskura M.; Bourbon X., Comparison between natural and accelerated carbonation (3% CO_2): Impact on mineralogy, microstructure, water retention and cracking. *Cement and Concrete Research* (2018) 109, 64-80.
- [18] Thiel, C.; Beddoe, R.; Lowke, D.; Gehlen, C., (2014) Accelerated carbonation: changes in water transport, porosity and phases of mortart due to different pressures. *10th fib International PhD Symposium in Civil Engineering*. Québec, Canada. pp. 217-222.

- [19] Morandeau, A.; Thiéry, M.; Dangla, P., Impact of accelerated carbonation on OPC cement paste blended with fly ash. *Cement and Concrete Research* (2015) 67, 226-236. <https://doi.org/10.1016/j.cemconres.2014.10.003>
- [20] Soja, W.; Maraghechi, H.; Georget, F.; Scrivener, K., (2018) Changes of microstructure and diffusivity in blended cement pastes exposed to natural carbonation. *MATEC Web of Conferences*. 02009. <https://doi.org/10.1051/mateconf/201819902009>
- [21] Thiel, C.; Beddoe, R.; Lowke, D.; Gehlen, C., (2016) Investigating the role of moisture on concrete carbonation using single-sided ^1H -NMR. International RILEM Conference on Materials, Systems and Structures in Civil Engineering Conference segment on Moisture in Materials and Structures. Technical University of Denmark, Lyngby, Denmark. pp. 261-268.
- [22] F. de J. Cano-Barrita, P.; Balcom, B. J.; Castellanos, F., Carbonation front in cement paste detected by T_2 NMR measurements using a low field unilateral magnet. *Materials and Structures* (2017) <https://doi.org/10.1617/s11527-017-1019-5>
- [23] McDonald, P. J.; Korb, J.-P.; Mitchell, J.; Monteilhet, L., Surface relaxation and chemical exchange in hydrating cement pastes: a two-dimensional NMR relaxation study. *Physical Review E* (2005) 72, 011409. <https://doi.org/10.1103/PhysRevE.72.011409>
- [24] Nagel, S. M.; Strangfeld, C.; Kruschwitz, S., Application of ^1H proton NMR relaxometry to building materials—A review. *Journal of magnetic resonance open* (2021) Volume 6, 100012. <https://doi.org/10.1016/j.jmro.2021.100012>
- [25] Zhao, H.; Wu, X.; Huang, Y.; Zhang, P.; Tian, Q.; Liu, J., Investigation of moisture transport in cement-based materials using low-field nuclear magnetic resonance imaging. *Magazine of Concrete Research* (2021) 73, 252-270. <https://doi.org/10.1680/jmacr.19.00211>
- [26] Blümich, B.; Anders, J., When the MOUSE leaves the house. *Magnetic Resonance* (2021) 2, 149-160. <https://doi.org/10.5194/mr-2-149-2021>
- [27] Valori, A., Characterisation of cementitious materials by ^1H NMR. Ph.D. Thesis, University of Surrey (United Kingdom), (2009)
- [28] Song, Y.-Q., Magnetic resonance of porous media (MRPM): A perspective. *Journal of Magnetic Resonance* (2013) 229, 12-24. <https://doi.org/10.1016/j.jmr.2012.11.010>
- [29] Keil, A.; Orlowsky, J.; Raupach, M., Use of a mobile NMR sensor as a non-destructive measurement system in building preservation. *Bautechnik* (2011) 88, 741-748. <https://doi.org/10.1002/bate.201101499>
- [30] Schulte-Holthausen, R.; Raupach, M.; Merkel, M.; Breit, W., Non-destructive determination of the leaching of concrete using unilateral hydrogen nuclear magnetic resonance. *Bautechnik* (2020) 97, 679-687. <https://doi.org/10.1002/bate.202010081>

- [31] Schulte-Holthausen, R.; Raupach, M., A phenomenological approach on the influence of paramagnetic iron in cement stone on 2D T_1 - T_2 relaxation in single-sided ^1H nuclear magnetic resonance. *Cement and Concrete Research* (2019) 120, 279-293.
<https://doi.org/10.1016/j.cemconres.2019.03.027>
- [32] Bundesanstalt für Wasserbau, BAWRecommendation Repair Products-Instructions for the Expert Planner on Structure-Related Product Characteristics and Test Methods. Edition 2019. (2019)
- [33] Castellote, M.; Fernandez, L.; Andrade, C.; Alonso, C., Chemical changes and phase analysis of OPC pastes carbonated at different CO_2 concentrations. *Materials and Structures* (2009) 42, 515-525. <https://doi.org/10.1617/s11527-008-9399-1>
- [34] Blümich, B.; Perlo, J.; Casanova, F., Mobile single-sided NMR. *Progress in Nuclear Magnetic Resonance Spectroscopy* (2008) 52, 197-269.
<https://doi.org/10.1016/j.pnmrs.2007.10.002>
- [35] Casanova, F.; Perlo, J.; Blümich, B., (2011) Single-sided NMR. *Springer*.
- [36] Schulte-Holthausen, R., Evaluation of the pore structure of concrete using single-sided ^1H nuclear magnetic resonance relaxometry. Ph.D. Thesis, RWTH Aachen, (2019)
- [37] Jennings, H. M., Refinements to colloid model of CSH in cement: CM-II. *Cement and Concrete Research* (2008) 38, 275-289. <https://doi.org/10.1016/j.cemconres.2007.10.006>
- [38] Jennings, H. M., A model for the microstructure of calcium silicate hydrate in cement paste. *Cement and concrete research* (2000) Volume 30, pp. 101-116.
[https://doi.org/10.1016/S0008-8846\(99\)00209-4](https://doi.org/10.1016/S0008-8846(99)00209-4)
- [39] Muller, A. C. A.; Scrivener, K. L.; Gajewicz, A. M.; McDonald, P. J., Densification of C-S-H measured by ^1H NMR relaxometry. *The Journal of Physical Chemistry C* (2013) 117, 403-412. <https://doi.org/10.1021/jp3102964>
- [40] Shi, Z.; Lothenbach, B.; Geiker, M. R.; Kaufmann, J.; Leemann, A.; Ferreira, S.; Skibsted, J., Experimental studies and thermodynamic modeling of the carbonation of Portland cement, metakaolin and limestone mortars. *Cement and Concrete Research* (2016) 88, 60-72. <https://doi.org/10.1016/j.cemconres.2016.06.006>
- [41] McDonald, P. J.; Istok, O.; Janota, M.; Gajewicz-Jaromin, A. M.; Faux, D. A., Sorption, anomalous water transport and dynamic porosity in cement paste: A spatially localised ^1H NMR relaxation study and a proposed mechanism. *Cement and Concrete Research* (2020) 133, 106045. <https://doi.org/10.1016/j.cemconres.2020.106045>
- [42] Georget, F.; Prévost, J. H.; Huet, B., Impact of the microstructure model on coupled simulation of drying and accelerated carbonation. *Cement and concrete research* (2018) 104, 1-12. <https://doi.org/10.1016/j.cemconres.2017.11.008>

- [43] DIN EN 1992-1-1: 2011-01 Eurocode 2: Bemessung und Konstruktion von Stahlbeton- und Spannbetontragwerken - Teil 1-1: Allgemeine Regeln und Regeln für Hochbauten, Brücken und Ingenieurbauwerke; Deutsche Fassung EN 1992-1-1:2023. *Beuth*, (2025) Berlin.

5. APPLICATION OF HYBRID ALKALI-ACTIVATED BINDERS FOR CHEMICAL RE-ALKALIZATION

5.1 ABSTRACT

The repair of reinforced concrete structures affected by carbonation-induced corrosion is essential for the preservation of existing buildings. The chemical re-alkalization, using cementitious layers applied to the surface of carbonated concrete is a commonly used method to restore the passivity of the embedded steel reinforcement. Despite its practical relevance and low implementation effort, the mechanisms contributing to the re-alkalization process, especially when using low-CO₂ binders, remain insufficiently understood. In the present study, the applicability of hybrid alkaline-activated binders (HAAB), which enable a reduction of the clinker content while simultaneously adding additional alkaline components through alkaline activation, is investigated. Under defined exposure conditions, re-alkalization depths of up to 30 mm were achieved using HAAB. The application of alternative pH indicators allows a more precise analysis of the spatial and temporal evolution of the re-alkalized area, highlighting the critical role of the initial suction phase. The results provide new insights into the interaction between the binder chemistry and the re-alkalization effectiveness as well as the importance of the availability of alkalis.

5.2 INTRODUCTION

With an increasing number of existing concrete buildings, the maintenance of steel reinforced concrete structures gains further relevance as these structures often suffer from durability-reducing processes such as concrete carbonation.

Carbonation is one of the causes of damage of concrete structures as it decreases the alkalinity of the concrete's pore solution leading to the depassivation of the embedded steel reinforcement. In case the protective passive layer of the reinforcement gets dissolved, the steel becomes susceptible to corrosion, which is mainly promoted by the presence of oxygen and moisture. In addition to carbonation, chloride-induced corrosion can occur which is often the case in presence of de-icing salts or marine environments, leading to localized pitting corrosion. If the penetration of corrosion-promoting substances such as CO₂ and chloride is not prevented and sufficient oxygen and water are available, electrochemical corrosion of the steel reinforcement will occur which will massively reduce the durability of the concrete component in the further course [1].

There are different approaches to repair concrete structures which suffer from carbonation that can be referred to as methods to maintain or restore passivity [2]. More precisely, to maintain or

rebuild the alkalinity of the concrete, an alkaline mortar can be applied onto the concrete surface, which is called chemical re-alkalization (CRA), referred to as procedure 7.4 “Realkalization of carbonated concrete by diffusion to maintain or rebuild the passivity.” (compare Figure 5-1) [2].

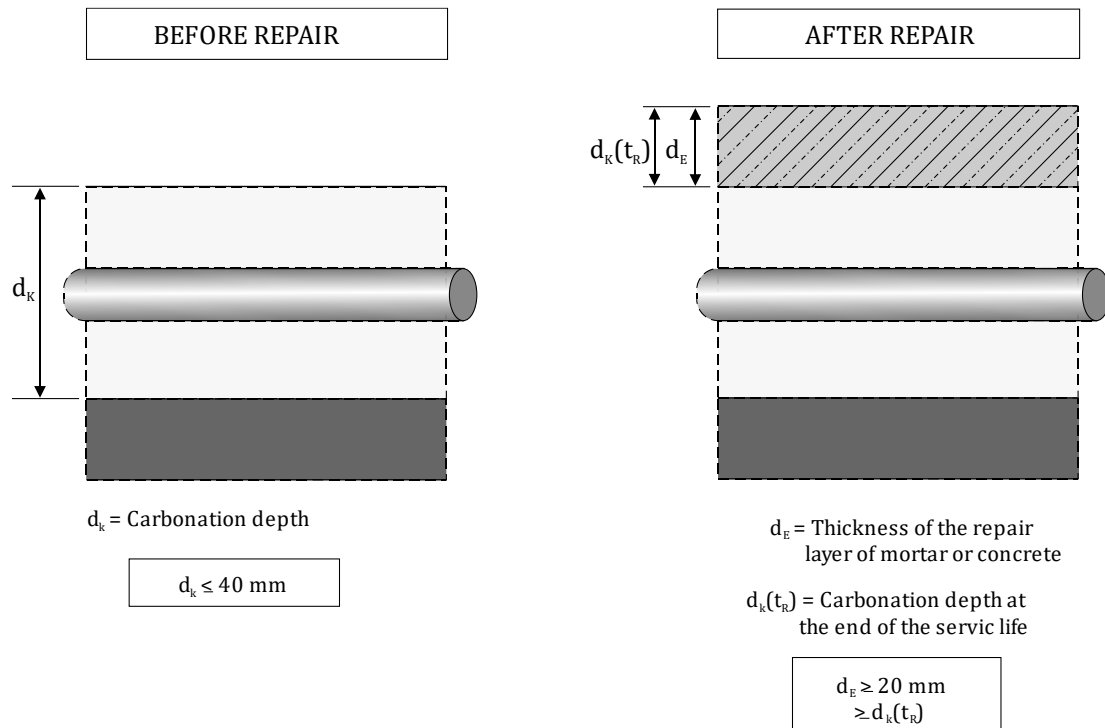


Figure 5-1: Excerpt from the technical rule for maintenance illustrating the repair method called chemical re-alkalization (procedure 7.4) [2].

Depending on the exposure conditions, the layer thickness of the applied repair mortar is varied between 20 and 25 mm to ensure a protection of the concrete against re-carbonation within the planned remaining service-life of the component. This means that until the end of the remaining service-life (t_R), the carbonation depth (d_k) of the repair layer must not be higher than the layer thickness, which results in specific requirements regarding the carbonation resistance of the repair material. The method can be used in case of a carbonation depth that has advanced to the reinforcement to re-passivate the embedded steel in case of slight corrosion. In the same way, the procedure can act as a preventative method to inhibit the progression of the carbonation towards the reinforcement Figure 5-2.

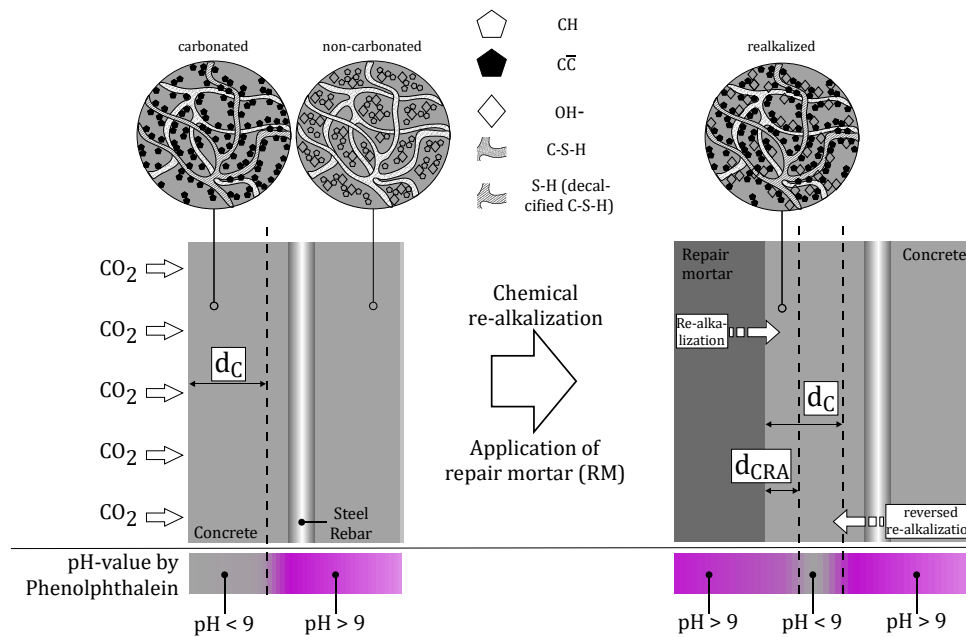


Figure 5-2: Schematic representation of the principle of CRA with d_C = carbonation depth, d_{CRA} = re-alkalization depth, reversed re-alkalization = rear-side re-alkalization, CH = $\text{Ca}(\text{OH})_2$, CC = CaCO_3 , OH = hydroxides, C-S-H = Calcium-Silicate-Hydrates, S-H = Silicate-Hydrates [3].

Although CRA has been the subject of several scientific studies, the results have so far only been published in two papers in indexed journals [3, 4]. Glawe et al. provide a comprehensive summary of the literature on CRA, which clearly shows that a large part of the fundamental work on CRA can also be found in non-indexed publications [3]. While most papers demonstrate the potential of this method, there is a lack of the investigation of current application-related materials such as clinker-reduced binders. Compared to the electrochemical re-alkalization (ERA), which is an active re-alkalization principle due to the current-induced transport of the alkalis from an alkaline electrolyte into the carbonated concrete, the transport of the alkalis during CRA is based on the concentration gradient between the repair layer and the carbonated concrete as well as moisture-based piggyback transport [5, 6].

Using this repair method which is regulated in [7, 8], the pH of the concrete's pore solution can be increased to values above 9 to prevent the depassivation process of the steel reinforcement as a result of carbonation [9]. Usually the method of CRA is implemented using mortars which are based on ordinary Portland cement (OPC) due to its highly alkaline pore solution and high carbonation resistance. Both properties are mainly ensured by the cement's component

portlandite ($\text{Ca}(\text{OH})_2$) which forms during the hydration process of OPC and can be present in dissolved form in the pore solution or crystalline form in the binder matrix [10]. This hydrate phase acts as a chemical buffer against carbonation as it reacts with the penetrating CO_2 to form CaCO_3 . In hardened concrete, an initial equilibrium exists between dissolved and bound portlandite. Carbonation leads to a depletion of the portlandite in the pore solution through the formation of carbonates. This is counteracted by the dissolution of the crystalline portlandite until no more portlandite can dissolve as a buffer [11]. As a result of ongoing carbonation, all portlandite gets consumed which means that the carbonation depth progresses further in direction of the steel reinforcement. Even though the application of OPC-based repair mortars is state of the art for the CRA, some researches show that these mortars are not suitable to enable re-alkalization depths higher than 14 mm [12, 13]. However, in drinking water environments, additional requirements for repair mortars must be considered such as hygiene and material compatibility. For the CRA in such environments, specific regulations can be found in the DVGW Bulletin W300, the content of which was recently updated based on investigations of mortars based on calcium aluminates or other pozzolanic additives [14].

Regarding the re-alkalization method as represented in Figure 5-2, it is assumed that the re-alkalization also comes from the non-carbonated concrete which is called rear-side re-alkalization. Assuming this already progressed behind the reinforcement, should be able to be re-alkalized [2]. It remains to be verified whether the interaction of the two directions of re-alkalization leads to a possible re-alkalization depth of 40 mm as one condition is sufficient moisture in this depth of the carbonated concrete.

In addition to mortars, investigations into the CRA using alkaline solutions have been conducted which show the potential of introducing these solutions into the concrete directly to achieve an increase of the pH-value in the carbonated area [4, 15]. However, these solutions do not offer any additional protection against carbonation as they cannot act as barrier themselves against CO_2 penetrating into the concrete.

The possibility to combine the characteristics of OPC-based mortars and alkaline solutions is given by hybrid alkali-activated binders (HAAB) [16, 17]. These materials consist of a mixture of OPC and supplementary cementitious materials (SCM) using substitution rates similar to composite cements enabling a reduction of the clinker content by up to 50 % [18]. To ensure a sufficient activation of the SCM like e.g. calcined clay, the binder additionally is activated using activator solutions such as potassium or sodium hydroxide (KOH, NaOH). While alkali-activated materials are said to have a pore solution of high pH [19, 20], the lower carbonation resistance of these

materials is often mentioned as a disadvantage when it comes to the durability. However, this can be counteracted by using OPC as part of the hybrid binder to ensure carbonation resistance [21]. Another aspect to consider when researching potential repair materials is workability on the construction site. In this case, the additional alkaline activation caused by the use of highly alkaline solutions poses a hazard to the person performing the work. For alkali-activated binders, alternative manufacturing processes are already being researched to avoid the handling of such alkaline solutions. One widely used approach is to produce the mortar as a one-part material, with the alkaline activator in powder form added to the dry mix and then mixed with water [22]. Explicit studies on the behavior of HAAB as one-part mixtures are currently not available. The research presented in this paper provides a first proof-of-concept for the application of HAAB as re-alkalization materials with high substitution rates up to 50% using calcined clays. Deeper insight into the processes during CRA is given by time-resolved analysis of the re-alkalization processes using methods such as pH-indicators which enable a classification of the tested materials including research results from the literature regarding their re-alkalization potential.

5.3 MATERIALS AND METHODS

The entire investigation process is shown in Figure 5-3. In order to meet the basic requirement of a sufficient bond between the substrate concrete and the applied repair mortar as required in [2, 7, 23], the adaption of the investigated repair materials to the carbonated concrete was included.

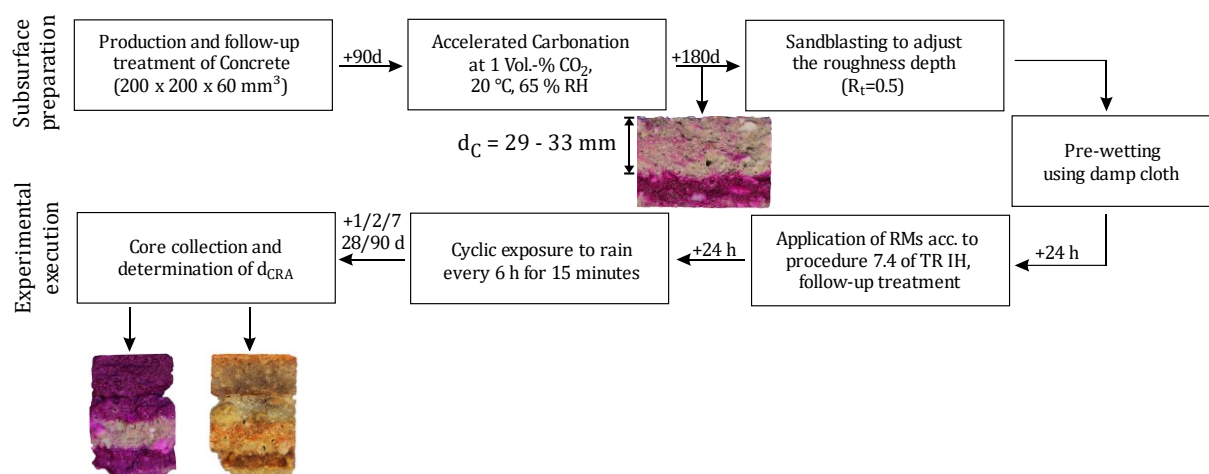


Figure 5-3: Schematic overview of the experimental procedure.

For this, the influence of the substitution rate of calcined clay (C) on the compressive strength of a binary binder consisting of cement and calcined clay as well as HAAB was investigated systematically. In particular, a substitution rate above 25 % should be investigated, as this represents the current recommended limit of substitution with calcined clays without loss of mortar performance and durability, based on a combination of scientific studies and technical recommendations [24, 25].

The concrete mixture which was used in the present work, corresponds to the German concrete class A2 according to [2] and represents concrete of poor quality. The mixture of the concrete based on the cement type CEM I 32.5 R (see Table 5-1) with a water to binder ratio (w/b) of 0.89 is given in Table 5-2. It is characterized by a high porosity accompanied with a low compressive strength which makes it susceptible to the penetration of CO₂ enhancing the risk of carbonation-induced corrosion. The mixture is not a concrete composition as used according to German building standards, but merely a model recipe to recreate the conditions of older existing structures in the laboratory.

Table 5-1: Oxide composition of the used binders.

Component	Unit	CEM I 32.5 R	Metakaolin
SiO ₂		20.88	60.97
Al ₂ O ₃		5.61	35.01
Fe ₂ O ₃		2.53	1.26
MnO		0.057	0.00
TiO ₂		0.333	1.63
P ₂ O ₅		0.113	0.04
CaO	wt%	64.62	0.24
MgO		1.61	0.13
K ₂ O		0.90	0.51
Na ₂ O		0.12	0.06
SO ₃		2.78	0.04
Sum		99.55	99.92
LOI		1.97	1.03

The concrete was produced in form of slabs with the dimensions of 200 mm x 200 mm x 50 mm. After production, the slabs were stored under damp cloths for 48 h before they were taken out of the formwork and stored in water for 6 days. Afterwards, the slabs were stored at $(23 \pm 3)^\circ\text{C}$ and $(55 \pm 5)^\circ\text{C}$ for additional 81 days. Before accelerated carbonation, the plates were sealed with wax on all sides except the filling side, to ensure one-sided carbonation. At the age of 90 days, the slabs were carbonated under accelerated conditions using 1 Vol.-% CO_2 and 65 % relative humidity at 20°C in a CO_2 chamber. The carbonation depth of the concrete substrates ranged between 29 to 33 mm. Following accelerated carbonation for 6 months, the slabs were sandblasted using quartz particles up to a roughness of 1.0 mm, to ensure a sufficient bond between the concrete and the mortars that were subsequently applied to the concrete slabs. The roughness was measured using the sand patch test according to [26].

Table 5-2: Overview of the investigated mixtures for the repair mortars and the substrate concrete

		A2 Concrete	Ref.	25C	50C	25C0.05	50C0.05	25C0.3	50C0.3
w/b Binder		0.89	0.43	0.51	0.58	0.51	0.58	0.51	0.58
CEM I gray cement 32.5 R									
Cement		180	505.3	364.2	235.6	363.2	228.9	363.1	227.1
Metakaolin		-	-	121.4	235.6	121.0	228.9	121.1	227.1
Water		160.2	218.8	247.6	275.2	240.9	255.9	210.6	136.2
KOH _{sol}			-			12.1	22.9	72.6	136.2
KOH/C			-			0.05	0.05	0.3	0.3
Aggregates (quarzitic)	kg/m ³	2008.4	1515.9	1456.8	1413.6	1452.7	1373.4	1452.6	1362.5
0.0-0.25		-	266.0	255.7	248.1	255.0	241.0	254.9	239.1
0.1-2.00		843.5	1249.9	1204.1	1165.5	1197.8	1132.4	1197.6	1123.4
2.0-8.00		883.7				-			
8.0-16.00		482.0				-			
Slump	mm	-	111.6	113.0	114.7	109.6	102.8	101.6	109.3
f _{c,28d}	N/mm ²	15.4	29.8	20.4	11.9	28.0	19.1	16.5	12.9
GWP (CO ₂) ¹⁾	kg/m ²		8.2	6.9	5.8	7.1	6.1	8.3	8.3

¹⁾ The mass of CO₂ related to the amount of mortar used to apply a 20 mm thick layer per m² of concrete

5.3.1 DEVELOPMENT OF MORTAR MIXTURES WITH HIGH SUBSTITUTION RATES

The substitution rate of the basic mixture (Ref.) was gradually changed from 0 % up to 90 % of calcined clay. The mixtures were produced in the form of standard prisms ($40 \times 40 \times 160 \text{ mm}^3$). After production, the samples of all mixtures were treated the same way by storing the formwork under damp cloths with an additional cover using a plastic tarp for 24 h. Afterwards, the samples were taken out of the formwork and stored at 23°C and 50 % relative humidity for 7 and 35 days, respectively. Before testing the compressive strength according to [27], each prism was cut into three cubes ($40 \times 40 \times 40 \text{ mm}^3$). The results of the compressive strength in Figure 5-4 show the decreasing compressive strength with an increasing substitution rate as well as sample age. While the decrease in the compressive strength at higher sample age is in contradiction with [28], it can be explained by the deviating storage conditions of the prisms. After demolding, the prisms were stored at lower humidity than is normally required for the hydration of clinker-containing binders. This can lead to structural damage in the form of micro- and shrinkage cracks which then can result in poor strength development. Nevertheless, the comparatively dry storage was chosen primarily to counteract the leaching and dilution of the alkalis of the mortar during early curing.

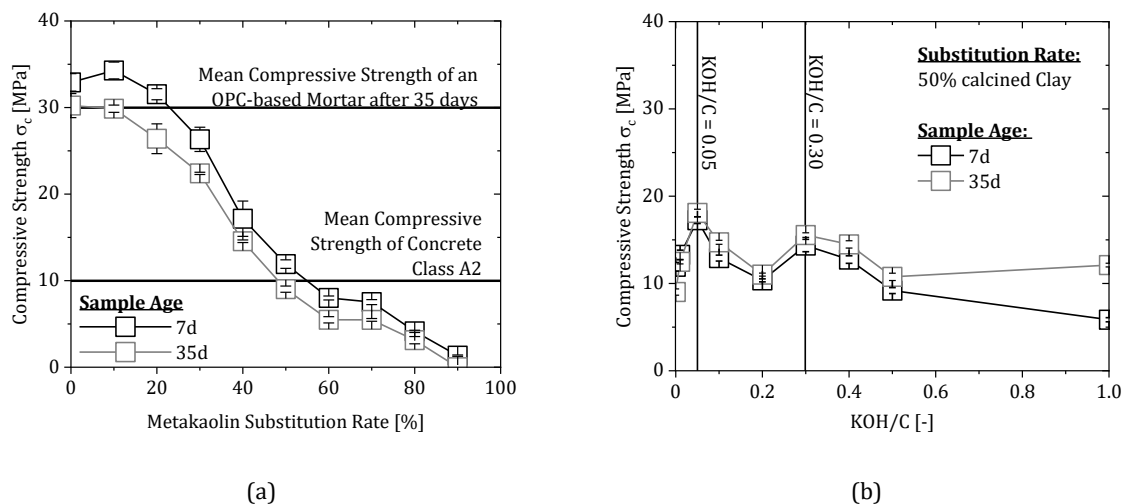


Figure 5-4: Influence of a) the substitution rate and b) the potassium hydroxide to calcined clay ratio (KOH/C) on the compressive strength

To counteract the strong decrease of the compressive strength of the mixture with a substitution rate of 50 %, this mixture was supplemented with a 50 % potassium hydroxide (KOH) solution systematically, by using different ratios of the calcined clay (C) and the potassium hydroxide in the activation solution (KOH/C). Given by Figure 5-4, two sweet-spots were determined at

KOH/C = 0.05 and 0.3, showing an increase in the compressive strength of up to 50 % by alkali-activation. The w/b was adjusted to ensure suitable workability and consistency of the mortar based on the slump of the reference mixture (compare Table 5-2). The w/b includes the water of the activator solution as well as the additional water which was calculated for a sufficient cement hydration.

As a result of the preliminary tests, seven different mixtures were investigated regarding their re-alkalization potential which are summarized in Table 5-2. The composition of the mixtures enables the analysis of the influence of first, the substitution rate and second, the alkali-activation on the potential to rebuild the alkalinity in carbonated concrete. Table 5-2 also contains the global warming potential (GWP) of the various mortars, which was calculated based on the amount of mortar to be applied per m² of concrete. A mortar layer thickness of 20 mm was assumed. The following GWP-values (kg CO₂/ kg) for the production of the different components were taken from the literature: Cement – 0.81; Metakaolin— 0.42; 50 % KOH-solution – 0.98 [29-31]. Based on the calculation, the maximum GWP of the different mixtures corresponds approximately to the GWP of the cement-based mortar which was used as a reference. Compared to the mixtures used in this study, the production of cement-free, alkali-activated binders often requires additional components to achieve sufficient performance, which in turn can lead to an increased GWP compared to a conventional Portland cement-based mortar.

5.3.2 APPLICATION OF THE MORTAR SYSTEMS ON THE CARBONATED CONCRETE

Before the mortar systems were applied on to the carbonated concrete slabs, the concrete was pre-wetted using damp cloths for 24 h which results in a slightly shiny concrete surface. This preparation of the substrate is intended to counteract the absorption behavior of the previously dry concrete substrate so that the mixing water of the mortar is not excessively absorbed into the substrate. If the concrete is not pre-wetted, a changed w/b value of the mortar can occur in the bonding zone, which means that the strength of the mortar can no longer be guaranteed. It must be noted, that the absorption of the mixing water after application of the mortar to the concrete cannot be completely avoided. However, this is in favor of CRA, the extent of which is initially determined primarily by the piggyback transport of alkalis based on the moisture gradient between mortar and concrete [3]. To facilitate the even application of the mortar systems at a thickness of 20 mm, the concrete substrates were installed in formwork whose frame height was 20 mm above the slab surface.

The mortars were applied in two layers directly on the pre-wetted concrete as shown in Figure 5-5 (a) to (f). After the application of the first layer, the composite system was clamped on a shaking

table and was shaken according to [27] for 120 s at a frequency and at an amplitude of 0.75, which defines the movement of the table from the starting position in mm. The same procedure was done after applying the second layer with additional stripping of the surface using a manual tamper.

The produced composite systems were stored under damp cloths again and taken out of the formwork after 24 h.

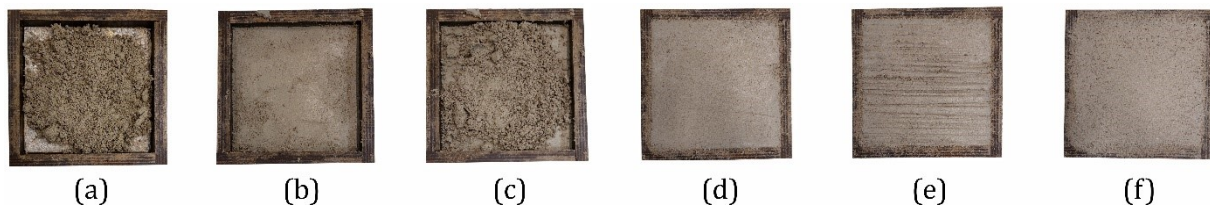


Figure 5-5: Sequence of steps during the application of the repair mortars in the production of the composite systems: a filling the first layer of repair mortar b distributing and compacting the material c application of the second layer of the repair mortar d compacting the second layer e and f peel off to smoothen the surface

5.3.3 STORAGE OF THE COMPOSITE SYSTEMS DURING RE-ALKALIZATION

Previous studies show that the driving force of re-alkalization is, in addition to the concentration gradient between carbonated concrete and repair material, also the availability of moisture as a transport medium for the alkalis [4]. To simulate a cyclic irrigation of a concrete structure as is the case for components exposed to the elements, the composite systems were stored in an irrigation system which enables watering of the surface in specific time intervals. The selected exposure is based on exposure class XC4, which defines alternating wet and dry periods that may be exposed to carbonation-based corrosion according to [32].

Before storing the composite systems in the irrigation system, all side surfaces of the samples were coated with a silicone-based sealing material. The lateral penetration of moisture into the test specimen should therefore be prevented in order to enable one-sided water exposure. The seven composite systems were stored in the irrigation system for 90 days and watering was taking place for a duration of 15 min every 6 h. The composite systems were inclined by positioning them on PVC strips on one side to ensure that excess water could run off.

5.3.4 DETERMINATION OF THE RE-ALKALIZATION DEPTH

To determine the re-alkalization potential of the different mortars, the re-alkalization depth of the composite systems was determined.

For that, the samples were taken out of the irrigation system after 1, 2, 7, 28 and 90 days. A drill core with a diameter of 50 mm was taken from each composite system after the different durations of irrigation. In total, 5 drill cores were taken from each composite system. The surface of the remaining hole in the composite system were sealed with the silicone-based material to prevent the moisture ingress through the drilled holes.

The drill cores then were split using a hydraulic press. The two resulting gap surfaces were sprayed with an indicator solution immediately after splitting. Two different indicators were applied to each sample which compositions are given in Table 5-3. The first indicator Phenolphthalein ($C_{20}H_{14}O_4$) is primarily used in the investigation of the carbonation of cement-based materials [33]. Using the color change point of the indicator, an area with a pH greater than 9 (purple coloring) can be distinguished from an area with a pH value less than 9 (no coloring) [34, 35].

Conversely, this indicator can be used to identify the area that, as a result of re-alkalization, has achieved an increase in the pH value in the carbonated area to a value above 9. The thickness of the re-alkalized area by CRA is referred to re-alkalization depth (d_{CRA}). In Table 5-4 the results of the Phenolphthalein test on one of the composite systems is shown at different times after spraying the indicator on the sample surface. The results of the indicator at the different times show a strong dependence on the duration after which d_{CRA} is determined. Only looking at the result 30 s after spraying the indicator on the surface, a clear re-alkalization depth can be recognized.

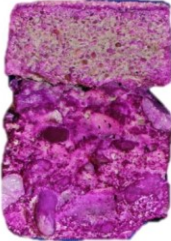
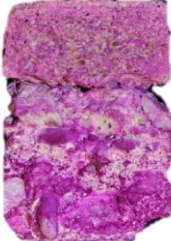
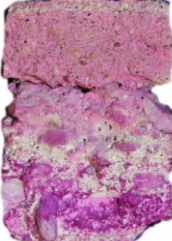
In addition, a second indicator was used to check the possibility of a less time sensitive method compared to the Phenolphthalein test. The second indicator is called Mordant Orange 1 ($C_{13}H_8N_3NaO_5$), also known as Alizarin Yellow R, and its composition is given in Table 5-3 together with the composition of the Phenolphthalein indicator. Compared to Phenolphthalein which is classified as carcinogenic, none of the components of Mordant Orange 1 are identified as a known carcinogen [36].

Table 5-3: Composition of the indicator solutions.

Name	Color Change	Composition	Chemical Formula
Phenolphthalein	colorless - magenta	1 g indicator powder, 70 ml ethanol, 30 ml demineralized water	$C_{20}H_{14}O_4$
Mordant Orange 1	light yellow - brown		$C_{13}H_8N_3NaO_5$

Based on the photographic documentation of the indicator tests, it was determined that the depth of re-alkalization delivers the clearest results after 30 s in case of Phenolphthalein and after 24 h in the case of Mordant Orange 1. Since Mordant Orange 1 obviously produces less time-sensitive results, the correspondence of the realization depths using the two indicators was checked using the correlation Figure 5-6. Based on the correlation of d_{CRA} given by the two indicators, the re-alkalization depth then was obtained by calculating the mean value of the two depths. Through this, the errors caused by the time sensitivity of the Phenolphthalein test were minimized.

Table 5-4: Results of the indicator tests at the different times after spraying the indicator on the sample surface.

System 50C 0.3 after 7 days of cyclic irrigation				
Time after indicator spraying	30 seconds	1 hour	3 hours	24 hours
Phenolphthalein				
Mordant Orange				

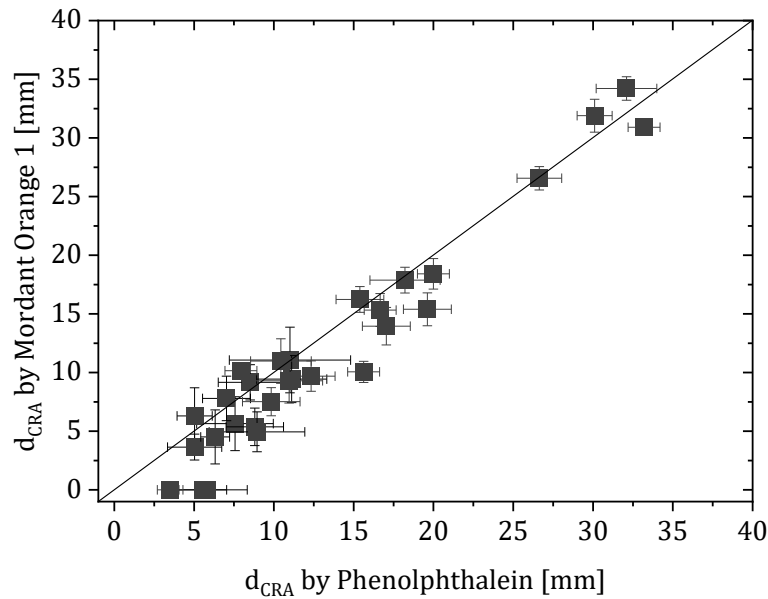


Figure 5-6: Correlation of the values for d_{CRA} obtained by the different indicators Phenolphthalein and Mordant Orange 1.

Further, the range of the displayed pH-values of the different areas of the sample were simulated by calibration solutions with known pH values. The solutions were produced by mixing different amounts of the 50 % KOH activator solution, which was used for the alkali activation, with water. The pH-value was measured using a digital pH-electrode. Figure 5-7- shows the color range of the two indicators according to the different pH values of the calibration solutions.

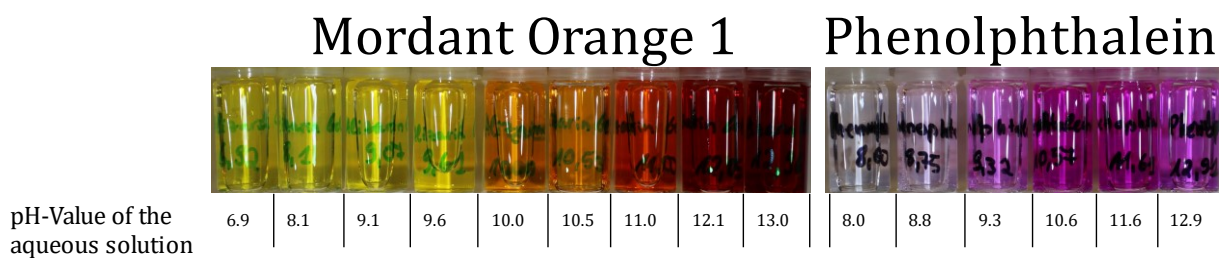


Figure 5-7: Calibration solutions for checking the color change points of the indicators.

In addition to the Phenolphthalein test which shows a first color change from colorless to violet when the pH changes from 8.8 to 9.3 and a second one between a pH-value of 9.3 to 10.6, the indicator Mordant Orange 1 shows two color-based turning points from yellow to orange (9.6 to 10.0) and orange to red (10.5 to 11). Both indicators are similar in that the higher the pH value, the more intense the coloring on the sprayed sample surface becomes.

In comparison to the colors of the calibration solutions, Mordant Orange shows a varying color on the surface of the alkali-activated repair material. For further evaluation of the determined re-alkalization depths, the grayish-brown color was interpreted as an interaction of the solid material with the indicator—as discussed later—but was still evaluated as a pH-value higher than 11.

The re-alkalization depth was determined as shown in Figure 5-8 using the image analysis program JMicrovision. The software enables the measurement of the re-alkalization depth in each point along the re-alkalization front. The final re-alkalization depth was then obtained by calculating the mean value of all data points of one sample [37].

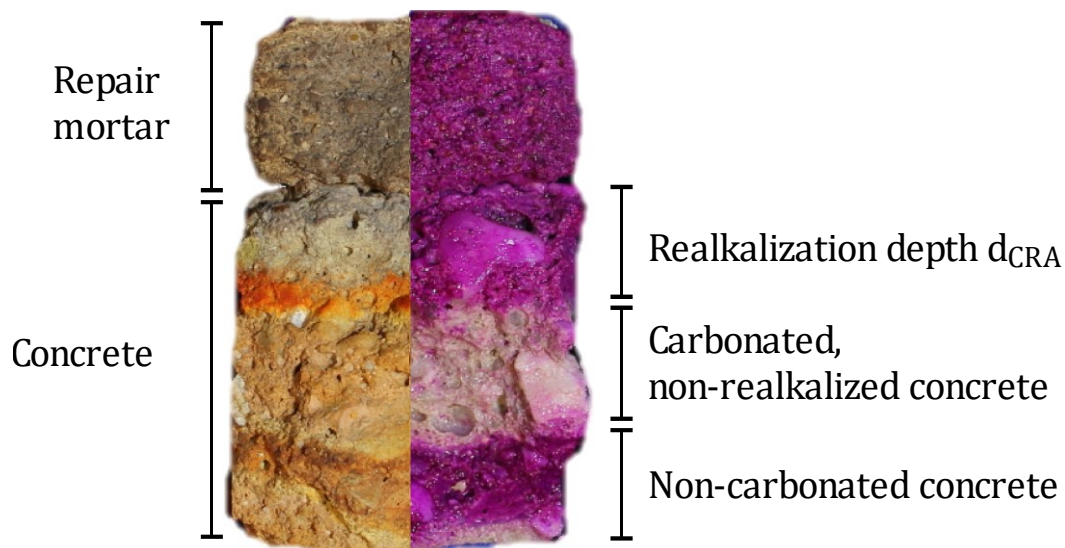


Figure 5-8: Definition of the different areas as a result of CRA (rear-side re-alkalization was not visible on these samples)

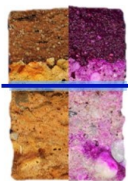
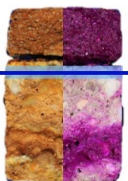
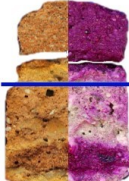
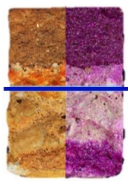
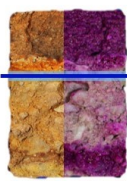
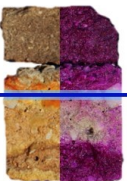
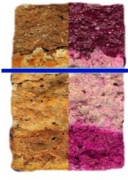
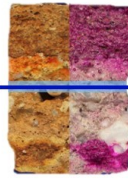
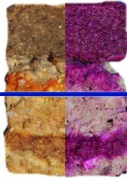
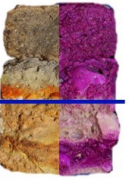
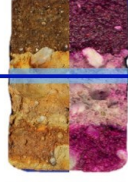
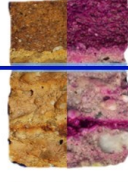
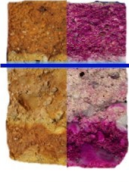
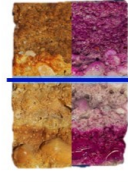
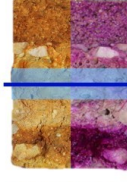
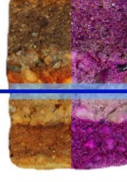
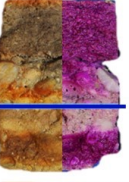
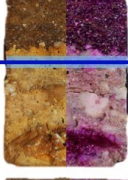
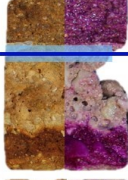
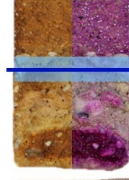
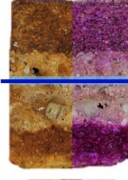
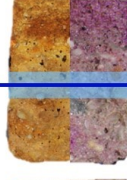
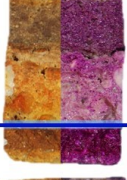
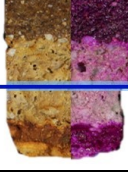
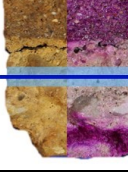
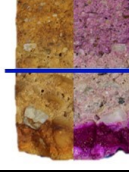
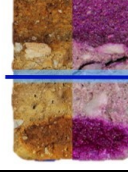
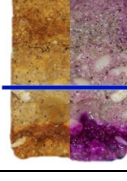
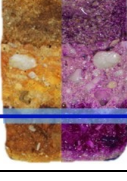
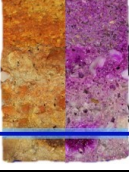
5.4 RESULTS

5.4.1 PROGRESSION OF THE CRA OVER TIME

The process of CRA is based on the transport of hydroxide ions through the pore system of the repair layer and the concrete which makes the depth of re-alkalization (d_{CRA}) achieved a time-dependent variable. In order to determine whether this process comprises different phases, as described by Merkel et al. [12], for example, the re-alkalization depth was determined at different points in time after the application of the repair material onto the concrete substrate. The value for d_{CRA} was obtained by averaging the re-alkalization depth given by Phenolphthalein and Mordant Orange 1. Table 5-5 shows the results of the indicator tests of the different composite systems over time. The pictures which show the indicator result of Mordant Orange 1 were taken 1 day after spraying the indicator solution on the sample surface while the pictures of the Phenolphthalein test were taken 30 s after spraying. In some cases, the splitting of the drill cores resulted in the separation of the repair layer and the concrete substrate. However, during the re-alkalization time of 90 days the adhesion of all repair layers were sufficient enough to maintain a continuous bond of the composite systems.

By looking at the pictures it already becomes clear that there are systems which are not able to develop a steadily increasing re-alkalization depth over time. Compared to the composite system Ref., the mixtures 25C and 50C show less progress in the re-alkalization depth over time. More specifically, the increased substitution rate leads to decreasing CRA. While both systems show initial re-alkalization of the area directly at the interface of the repair layer and the concrete, the pH value in this area appears to decrease again over time, so that the Phenolphthalein test no longer shows a color change. This contrasts with the re-alkalization progress of the mortars, which were additionally alkali-activated and show an increasing re-alkalization depth over the 90 days. Although the substitution rate was also varied here, no clear inhibition of the progress of re-alkalization was seen as the proportion of metakaolin increased. Rather, the progress of re-alkalization increases with an increased KOH/C ratio, regardless of the substitution rate. This means that the mortars with a KOH/C = 0.3 achieved complete re-alkalization of the carbonation depth of approximately 30 mm after just 28 days.

Table 5-5: Overview of the results of the indicator tests of all composite system at the different times after application of the repair mortar (blue line marks the mean re-alkalization depth with the standard deviation in light blue).

Time after mortar application in days	Composite Systems						
	Ref.	25C	50C	25C 0.05	50C 0.05	25C 0.3	50C 0.3
1							
2							
7							
28							
90							

In some cases, the determination of d_{CRA} was difficult because no clear front which could be interpreted as the re-alkalization depth was visible. Especially the results of the indicator tests of the system 50C 0.05 after 28 and 90 days showed a very pale coloring of the entire cross section. Even though a re-alkalized area could not be determined as clearly as after 7 days, a value was determined for the re-alkalization depth of 28 and 90 days that at least corresponds to the re-alkalization value after 7 days. This assumption was made because the investigations cannot yet

rule out the possibility that a paler coloring did not nevertheless lead to sufficient re-alkalization. Possible reasons for the pale coloring will be discussed later. In comparison to the non-activated system (50C), also the alkali-activated system with lower KOH/C (50C 0.05) showed only a pale color due to the indicator in the area of the repair mortar. This suggests that the alkalinity in the entire system is at the limit of the indicator test transition point. As a result, adequate re-alkalization cannot therefore be guaranteed without proper alkali-activation when the substitution rate exceeds 50 %. This is confirmed by the results of the systems 25C 0.3 and 50C 0.3 which both show a clear coloring of the repair mortar even after 90 days, regardless of the level of the substitution rate.

Comparing these results with the initial determination of the suitable KOH/C for an appropriate compressive strength of the repair mortar, the established sweet spots for KOH/C do not necessarily correlate with a sufficient CRA by the respective material. It appears that sufficient alkali-activation of the metakaolin can be achieved using KOH/C ratio of 0.05, but this results in there no longer being sufficient alkalis available for transport during the re-alkalization process. This means, that only a limited amount of alkalis enters the carbonated concrete and are redistributed during further storage in the concrete in such a way that the concentration gradient between mortar and concrete is balanced as much as possible. This results in an overall increasing pH-value in the carbonated area, which, however, is not sufficient enough to achieve a pH value greater than the transition point of the indicators. Conversely, the absorption of alkalis at an early stage of hydration can hinder the hardening and strength development of the mortar, since the KOH/C ratio is reduced by a depletion of alkalis, including potassium. When determining the KOH/C value, it is important to ensure that a buffer of KOH is considered in order not to significantly impede the strength development of the mortar.

5.4.2 DIFFERENTIATION OF THE PHASES DURING RE-ALKALIZATION

The results presented in Figure 5-9 summarize the re-alkalization depths of all seven composite systems as a function of the time after the application which also corresponds to the storage of the systems in the irrigation system. The final re-alkalization depth was achieved when the original carbonation depth was reached. Because of the maximum aggregate size of 16 mm within the concrete, the carbonation depths varied between 29 to 33 mm. From the results, a strong dependence of the maximum achievable re-alkalization depth from the applied mortar can be recognized. As a reference, the re-alkalization depth of a mortar containing ordinary Portland cement according to [27] exclusively was determined. Only the alkali-activated repair mortars with a higher proportion of KOH (0.3) show a full re-alkalization of the carbonated concrete.

Further, the evolution of the re-alkalization shows different phases which are characterized by varying slopes of the progression curve of d_{CRA} . To be more precise, the re-alkalization process within the first day shows a significantly greater increase regarding d_{CRA} than during the rest of the investigations up to 90 days. In addition, the non-activated systems show a decrease of the re-alkalization depth following the strong increase in the beginning. However, two of the non-activated systems (Ref., 25C) manage to reach the d_{CRA} of the alkali-activated systems with lower KOH/C. The exception is the non-activated system with a substitution of 50 % metakaolin, whose maximum re-alkalization depth corresponds to the depth that was already reached within the first two days.

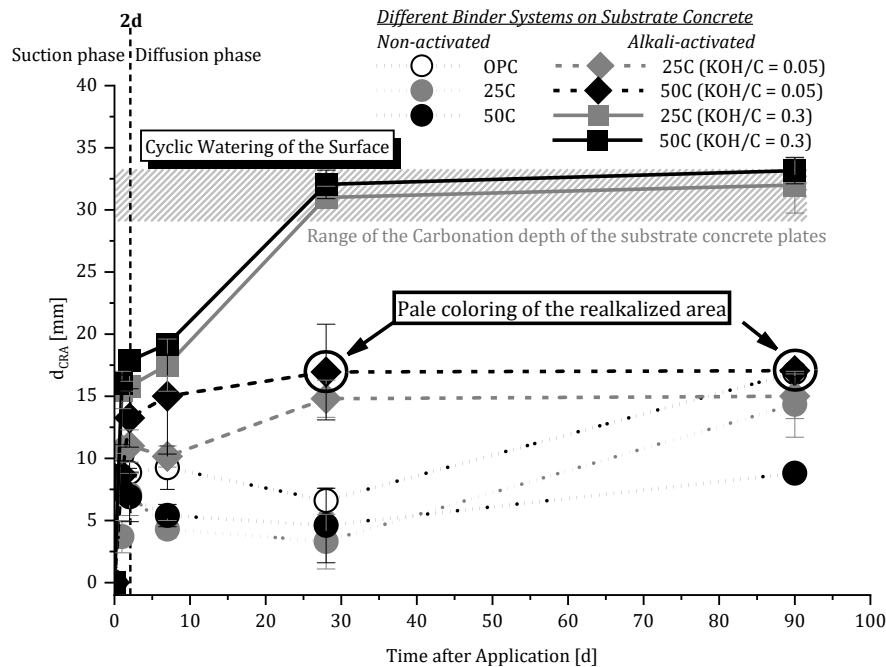


Figure 5-9: Evolution of d_{CRA} of the different composite systems over time under cyclic watering.

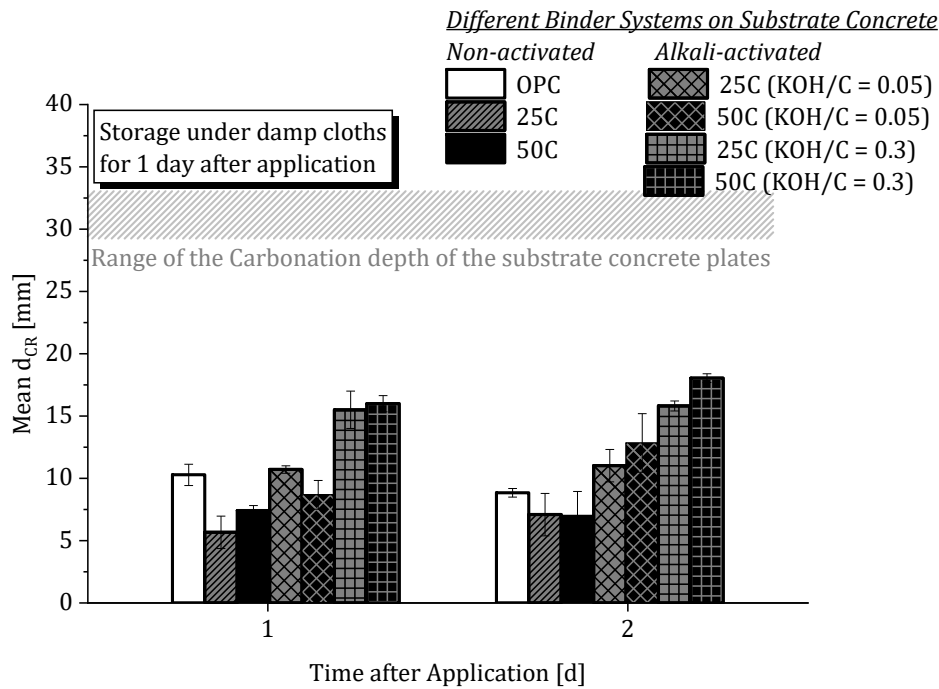


Figure 5-10: Evolution of d_{CRA} of the composite systems during the suction phase.

Based on the results, the re-alkalization process of the present systems could be divided into the suction and diffusion phase [12]. The suction phase which takes place directly after the application of the repair mortar and extends up to a time between the second and the seventh day based on the present data. Within this time, the re-alkalization depth is displayed by a sharp colored transition from the re-alkalized to the non-re-alkalized area representing the front-like progression of the mainly capillary driven transport. The diffusion phase describes the re-alkalization progress

until the maximum re-alkalization depth is reached. Compared to the re-alkalization depth during the suction phase, only a blurred re-alkalization front is visible, which only partially allows the determination of an exact re-alkalization depth. The weaker definition of the two areas is representative of the diffusion-controlled processes during the diffusion phase, which do not follow a clear penetration front. Although the suction phase appears to follow a linear progression based on the present data, it should be noted that the first value for d_{CRA} was determined after 24 h which is assumed to be the end of the suction phase. As Merkel has demonstrated, the progression of d_{CRA} within the first day can already exhibit non-linear behavior [38]. Therefore, a linear interpretation of the progression of the chemical re-alkalization during the suction phase may be misleading. The resolution of the progression of d_{CRA} is subject to the application limits of the

investigation methods of CRA. The extend of the suction phase is shown in more detail in Figure 5-10 which includes d_{CRA} of the first two days separately. It becomes clear, that a at least 50% of the maximum d_{CRA} is reached within the suction phase in the presented experiments. Regarding the alkali-activated systems with $KOH/C = 0.3$, d_{CRA} is doubled during the diffusion phase while all other systems show only minimal further progression within this phase.

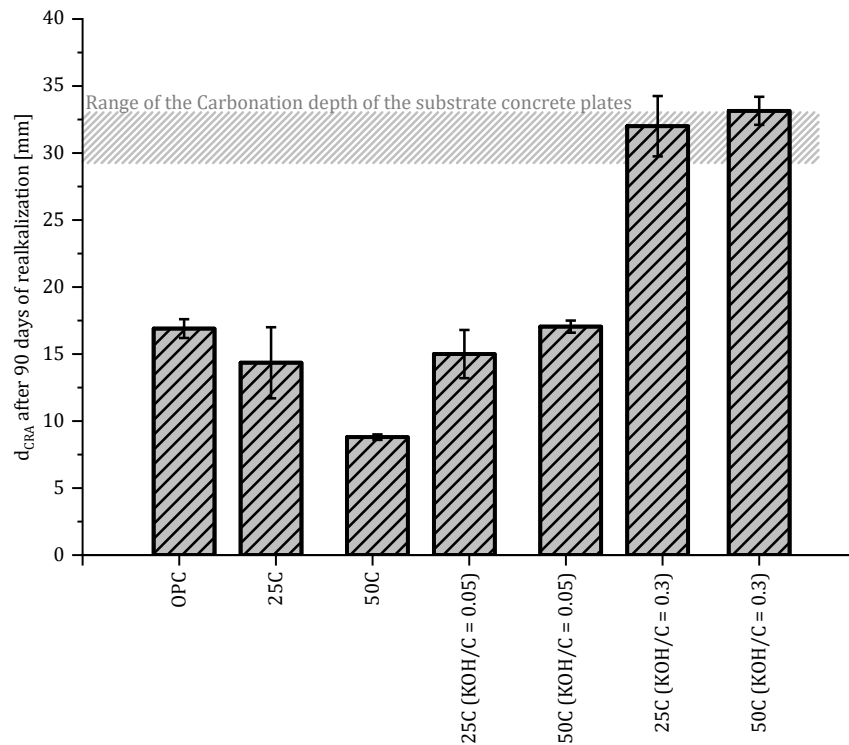


Figure 5-11: Maximum re-alkalization depths reached by the different repair mortars after 90 days.

As a summary, Figure 5-11 shows the maximum re-alkalization depth achieved by the various composite systems after 90 days of cyclical watering of the surface. A comparison of the mortars based on the re-alkalization coefficient was omitted at this point, which will be discussed later. Regarding the maximum re-alkalization depth, the same trend in the re-alkalization progress is evident as during the suction phase. The mortars with $KOH/C = 0.3$ show the highest re-alkalization depth after 90 days and enable complete re-alkalization of the carbonation depth. All other systems show a relatively small increase of the re-alkalization depth during the diffusion phase compared to the re-alkalization depth after the suction phase. This makes clear that the

suction phase is decisive for the maximum achievable re-alkalization depth, but that this also depends on the binder used.

5.5 DISCUSSION

The process of the chemical re-alkalization is influenced by multiple factors which can originate from the repair material, the concrete substrate as well as the environmental conditions. This paper focused on the influence of the repair material by not varying the concrete substrate and also setting the environmental conditions to constant cyclic irrigation. For the investigation of the influences caused by the repair material, seven different materials were used for the chemical re-alkalization of carbonated concrete. The present results provide insights into the different phases of the chemical re-alkalization process as well as the potential of hybrid alkali-activated mortars to be used as a repair material.

5.5.1 INFLUENCE OF THE ALKALI-ACTIVATION ON THE RE-ALKALIZATION PROCESS

Based on the results of this study, the decrease of the poor maximum achievable d_{CRA} through the application of mortars with substitution rates $\geq 25\%$ of calcined clay can be counteracted by alkali-activation using Potassium hydroxide solutions. In concrete terms, a re-alkalization depth of up to 33 mm can be achieved with the help of alkali-activation depending on the KOH/C ratio. It is important to note that the alkali-activation also influences the compressive strength of the mortar, which means that an arbitrarily high ratio of KOH/C cannot be selected.

In particular, alkali-activation appears to have an influence on the extent of chemical re-alkalization within the suction phase. Here the mortars with the high KOH/C ratio show the greatest progress in the first two days which is also independent of the substitution rate. It can be assumed that there is a quantity of KOH that is required to activate the metakaolin in order to achieve sufficient compressive strength. The KOH, which is not incorporated into the structure of the material, is then available for CRA and can be transported into the underlying concrete.

Taking a look at the non-activated mortars, the maximum CRA possible is up to half the carbonation depth of the concrete. This maximum re-alkalization depth is in agreement with the results by Bier who demonstrated a maximum achievable re-alkalization depth of 14 mm using cement-based mortars [13]. Interestingly, here too the maximum re-alkalization depth of the non-activated mortars ends with d_{CRA} of the mixtures with KOH/C = 0.05, even if these mortars show a higher re-alkalization depth during the suction phase than the non-activated mortars. It can be assumed that due to the lower proportion of KOH in the activator solution, fewer alkalis remain mobile as a result of the activation and hardening of the material. Why the mixture 25C 0.05 and 50C 0.05 achieve at most the same depth of re-alkalization as the cement-based reference mixture,

despite the additional addition of alkalis in the activator solution, cannot be explained based on the results.

Overall, the strong dependence of the re-alkalization rate during the suction phase on the applied repair material and the associated varying concentration gradient between the repair layer and the concrete suggests a concentration-based transport during the suction phase. According to Merkel, alkali transport during the suction phase is mainly based on the moisture gradient between the two layers, resulting in a piggy pack-transport of the alkalis [38]. In the present study, this assumption would lead to a similar re-alkalization rate during the suction phase for all repair materials, since the concrete substrate was prepared in the same way for all composite systems. This preparation included pre-wetting of the concrete for 24 h before the application of the mortar to ensure a wet near-surface area of the concrete which at the time inhibits capillary suction. Based on the present data, the transport within the suction phase is assumed to be strongly driven by the concentration gradient which decreases further during the whole re-alkalization process. The different behavior of the mortars during the suction phase can also be explained by the fact that the transport processes are influenced by the ions present in the pore solution such as potassium and calcium. While the high ionic diffusivity of potassium can enhance the mobility of the hydroxides, the tendency of calcium to interact with the pore walls and to form precipitation products may counteract the transport of the hydroxides [39].

5.5.2 APPLICATION OF ALTERNATIVE INDICATORS TO INVESTIGATE THE PROGRESS OF CHEMICAL RE-ALKALIZATION

This study presents the application of an alternative indicator to measure the re-alkalization depth. The approach is based on the fact that the conventionally applied indicator Phenolphthalein shows a strong time-sensitivity which can strongly influence the resulting value for the re-alkalization depth d_{CRA} . In comparison, the introduced indicator Mordant Orange 1 shows a more stable result which shows no variation within the first 24 h after spraying the indicator on the sample surface. The strong time-sensitivity of phenolphthalein is known to be based on the combination of CO_2 -sensitivity of the indicator and the reversible properties of the color change process by opening of the ring structure which is unstable in the presence of atmospheric CO_2 as it lowers the local pH and causes the molecule to return to its original, colorless structure. In comparison, Mordant Orange 1 changes color through a simple acid-base reaction during which it loses or gains a proton depending on the pH present in the pore solution, while its molecular structure remains unchanged. Because this protonation-deprotonation process is less sensitive to small pH changes caused by CO_2 from the air, the color of Mordant Orange remains stable over time under atmospheric exposure [40]. Additionally, the correlation

of the d_{CRA} given by Mordant Orange 1 and Phenolphthalein shows that Phenolphthalein displays a different pH value than the previously assumed value of 9 when it is sprayed on a concrete surface. This can also be validated by the coloring of the calibration solutions in Figure 5-7 which show a clear color change at a pH of 10.6 which also corresponds to the color change of Mordant Orange 1 at a pH over 10.5. Further, the correlation of the values for d_{CRA} given by both indicators are in good agreement which makes Mordant Orange 1 a suitable, less time-sensitive alternative for phenolphthalein.

Based on the results of this study, Mordant Orange 1 seems to show more than only two different pH ranges. By looking at the results of the indicator test of the composite systems with $KOH/C = 0.3$ at day 1 to day 7, the re-alkalization front is characterized by a dark orange area followed by a grayish-brown area towards the repair material. Of particular interest is the different gray-brown coloration of the mortar layer and the re-alkalized area as this color was not produced using the calibration solutions. In addition to a very high pH value above the calibration solutions, the gray-brown coloration could also be due to an interaction with the solid matrix. Since the alkalinity of the pore solution in the mortar and re-alkalized area is mainly caused by dissolved potassium hydroxide, the pore solution differs from that of the carbonated and non-carbonated concrete, where the pH value of the pore solution is mainly generated by dissolved calcium hydroxide. In addition to the pH-value of the pore solution, also the components present in the solution seem to influence the performance of the indicator.

Regarding the corresponding pH-value given by the calibration solution, the re-alkalized area can be divided into different zones with reference to their alkalinity. Therefore, the re-alkalization front is characterized by lower pH value compared to the rest of the re-alkalized area. This could mean that the re-alkalization takes place in several steps and that the pH value within the area of the carbonation front only increases further as the re-alkalization progresses. In order to test this assumption, further investigations into the course of the pH value in the re-alkalized area should be carried out. Especially since the clear re-alkalization front and the subsequent brownish coloring, which could represent an even higher pH-value due to the darker color, can no longer be seen on the 14th and 28th days of the test. With the help of further investigations into the existing pH values, it could also be checked whether the re-alkalization front will dissipate as the re-alkalization progresses further. The dissipation of the front could be accompanied by an equalization of the pH value in the entire re-alkalized area, which is confirmed by the uniform coloring using the indicator test.

The equalization of the pH value can also be caused by the reaction of alkaline components with the carbonated concrete, gradually leading to pH neutralization. Carbonation and the associated

decalcification of the C-S-H phases in the concrete result in the formation of an amorphous silica gel with pozzolanic reactivity [41]. In contact with alkaline components such as dissolved Portlandite, it leads to the formation of secondary, solid C-S-H phases, which decreases the concentration of alkalis in the pore solution [42-45].

Whether the final overall pH value is sufficient enough to rebuild the alkalinity in the carbonated concrete resulting in the re-passivation of the steel reinforcement should be addressed in future research.

5.5.3 APPLICABILITY OF THE RE-ALKALIZATION COEFFICIENT

As already pointed out, the re-alkalization process is a combination of different phases during which the rate of re-alkalization varies over time. As the described studies show, after an initially high re-alkalization rate, the re-alkalization rate decreases at the transition from the suction phase to the diffusion phase. While the course can still be approximated to be linear within the first two days of the suction phase, the re-alkalization then follows a non-linear course. Fitting the data of both phases using the root-time law to obtain the re-alkalization coefficient as a material parameter as described in [4] would result in an overestimation of the maximum achievable re-alkalization depth. By applying the law to re-alkalization data, a linear progression of the re-alkalization depth is assumed as well as an infinite carbonation depth. Further, an infinite alkali depot of the repair mortar is required to maintain a constantly increasing re-alkalization depth. This is counteracted by the consumption of the available mobile alkalis for diffusion due to carbonation of the repair mortar as well as the re-alkalization process itself. Therefore, the root-time law is only applicable on the data obtained during the suction phase. However, the studies showed that a high re-alkalization rate during the suction phase does not necessarily lead to an equally high maximum re-alkalization depth. A comparison of materials based on the coefficient calculated on the basis of the suction phase would therefore be misleading. To compare the materials studied with results from other research, a model should be used that considers the above-mentioned deviations from the square root-time law which will be the subject of further research.

5.6 CONCLUSION

The present study serves as a proof-of-concept for the application of hybrid alkali-activated binders as repair mortars for the chemical re-alkalization of carbonated concrete. Further, the analyses were dedicated to get a better understanding of the re-alkalization process itself. For this purpose, new investigation techniques were conducted which enable a concretization of the

various processes within the chemical re-alkalization. Based on the investigations, the following conclusions can be drawn:

- Using hybrid alkali-activated binders, a maximum re-alkalization depth of up to 33 mm can be achieved, in other words a doubling of the previously possible re-alkalization depth when using conventional repair mortars for the chemical re-alkalization.
- The pH indicator Mordant Orange 1 presents a less time-sensitive method for the determination of the re-alkalization depth compared to the standard method using Phenolphthalein.
- The re-alkalization process can be divided into two different phases, the suction phase and the diffusion phase which are characterized by varying velocity of the progression of the re-alkalization.
- The initial suction phase is particularly important for the extent of the chemical re-alkalization, which, according to this study, takes place within the first two days after application of the mortar and is driven by a combination of the concentration and moisture gradient between mortar and concrete.
- The rear-side re-alkalization could not be observed under the conditions described.

5.7 OUTLOOK

With the help of the present work, the influence of hybrid alkali-activated binders on the chemical re-alkalization could be investigated. For this purpose, only the binders used were varied and the properties of the carbonated concrete and the storage during re-alkalization were kept constant. Future work should therefore include the variation of the carbonated concrete based on composite cements as well as the variation of the environmental conditions after the application of the mortars. Regarding the repair mortars additional activation solutions could be tested as well as cement-free alkali-activated binders. Also, the transport processes during the suction phase and the correlation between the re-alkalization depth and the present moisture of the composite systems within the first two days should be resolved more precisely. Electrochemical measurements should also be carried out on embedded reinforcement in order to verify that the chemical re-alkalization ultimately also leads to re-passivation of the steel reinforcement. Finally, the carbonation resistance of the repair mortars should be investigated to ensure the applicability of the materials.

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Michael Raupach (Supervisor)

5.8 REFERENCES

- [1] Papadakis, V. G.; Vayenas, C. G.; Fardis, M. N., Fundamental Modeling and Experimental Investigation of Concrete Carbonation. *ACI materials journal* (1991) 88,
- [2] Deutsches Institut für Bautechnik (DIBt) Technische Regel - Instandhaltung von Betonbauwerken (TR Instandhaltung) - Teil 1: Anwendungsbereich und Planung der Instandhaltung. *Deutsches Institut für Bautechnik (DIBt)*, (2020) Berlin.
- [3] Glawe, C.; Raupach, M., Basics and new opportunities for chemical re-alkalisation of carbonated concrete, including alkali-activated binders. *Magazine of Concrete Research* (2024) 76, 1185-1197. <https://dx.doi.org/10.1680/jmacr.24.00026>
- [4] Réus, G. C.; Medeiros, M. H. F., Chemical realkalization for carbonated concrete treatment: Alkaline solutions and application methods. *Construction and Building Materials* (2020) 262, 120880. <https://doi.org/10.1016/j.conbuildmat.2020.120880>
- [5] González, J. A.; Cobo, A.; González, M. N.; Otero, E., On the effectiveness of realkalisation as a rehabilitation method for corroded reinforced concrete structures. *Materials and Corrosion* (2000) 51, 97-103.
[https://doi.org/10.1002/\(SICI\)1521-4176\(200002\)51:2<97::AID-MAC097>3.0.CO;2-3](https://doi.org/10.1002/(SICI)1521-4176(200002)51:2<97::AID-MAC097>3.0.CO;2-3)
- [6] González, F.; Fajardo, G.; Arliguie, G.; Juárez, C.; Escadeillas, G., Electrochemical realkalisation of carbonated concrete: An alternative approach to prevention of reinforcing steel corrosion. *International Journal of Electrochemical Science* (2011) 6, 6332-6349. [https://doi.org/10.1016/S1452-3981\(23\)19684-2](https://doi.org/10.1016/S1452-3981(23)19684-2)
- [7] Deutsches Institut für Bautechnik (DIBt) Technische Regel - Instandhaltung von Betonbauwerken (TR Instandhaltung) - Teil 2: Merkmale von Produkten oder Systemen für die Instandsetzung und Regelungen für deren Verwendung. *Deutsches Institut für Bautechnik (DIBt)*, (2020) Berlin.
- [8] DIN EN 1504-9:2008. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 9: General Principles for the Use of Products and Systems. *Beuth*, (2008) Berlin.
- [9] Mietz, J., Electrochemical realkalisation for rehabilitation of reinforced concrete structures. *Materials and Corrosion* (1995) 46, 527-533.
<https://doi.org/10.1002/maco.19950460904>
- [10] Lothenbach, B.; Scrivener, K.; Hooton, R., Supplementary cementitious materials. *Cement and Concrete Research* (2011) 41, 1244-1256.

- <https://doi.org/10.1016/j.cemconres.2010.12.001>
- [11] Groves, G.; Rodway, D.; Richardson, I., The carbonation of hardened cement pastes. *Advances in Cement research* (**1990**) 3, 117-125.
<https://doi.org/10.1680/adcr.1990.3.11.117>
- [12] Merkel, M.; Breit, W.; Schulte-Holthausen, R.; Raupach, M., Realkalisierungspotenzial von Trinkwasserbehälterbeschichtungen. *Beton- und Stahlbetonbau* 114 (**2019**) 12, 919-928.
<https://doi.org/10.1002/best.201900050>
- [13] Bier, T. A., Carbonation and realkalization of cement paste and concrete. Ph.D. Thesis, Universität Fridericiana zu Karlsruhe, (**1988**) Karlsruhe, 23.12.1987.
- [14] DVGW W 300-5:2020-08 Drinking water container - Part 5: Assessment of the usability of construction products for lining and coating systems. (**2020**)
- [15] Moraes, M. C. d.; Cascudo, O.; Oliveira, A. M. d.; Carasek, H., Realcalinização do concreto sujeito à carbonatação: Revisão sistemática da literatura sobre os métodos de tratamento, eficácia e mecanismos da reação. *Matéria (Rio de Janeiro)* (**2024**) 29,
- [16] García-Lodeiro, I.; Fernández-Jiménez, A.; Palomo, A., Variation in hybrid cements over time. Alkaline activation of fly ash–portland cement blends. *Cement and Concrete Research* (**2013**) 52, 112-122. <https://doi.org/10.1016/j.cemconres.2013.03.022>
- [17] Detphan, S.; Hanjitsuwan, S.; Pangdaeng, S.; Phoo-ngernkham, T.; Damrongwiriyanupap, N.; Wongsas, A.; Sukontasukkul, P.; Chindaprasirt, P., Hybrid alkali-activated fly ash-Portland cement binders with modified polymer as patch repair. *Construction and Building Materials* (**2024**) 436, 136776. <https://doi.org/10.1016/j.conbuildmat.2024.136776>
- [18] DIN EN 197-5: 2021-6 Zement–Teil 5: Portlandkompositzement CEM II/CM und Kompositzement CEM VI. *Berlin: Beuth*, (**2021**)
- [19] Kraft, B.; Achenbach, R.; Ludwig, H.-M.; Raupach, M., Hydration and Carbonation of Alternative Binders. *Corrosion and Materials Degradation* (**2022**) Volume 3, 19-52.
<https://doi.org/10.3390/cmd3010003>
- [20] Bernal, S. A., Effect of the activator dose on the compressive strength and accelerated carbonation resistance of alkali silicate-activated slag/metakaolin blended materials. *Construction and Building Materials* (**2015**) 98, 217-226.
<https://doi.org/10.1016/j.conbuildmat.2015.08.013>
- [21] Carvalho, M.; Meira, G.; Ferreira, P.; Medeiros, M., Study of the effectiveness of realkalisation treatment on reinforcement repassivation by using simulated concrete pore solution. *Construction and Building Materials* (**2022**) 321, 126318.
<https://doi.org/10.1016/j.conbuildmat.2022.126318>
- [22] Segura, I. P.; Luukkonen, T.; Yliniemi, J.; Sreenivasan, H.; Damø, A. J.; Jensen, L. S.; Canut, M.; Kantola, A. M.; Telkki, V.-V.; Jensen, P. A., Comparison of one-part and two-part alkali-

- activated metakaolin and blast furnace slag. *Journal of Sustainable Metallurgy* (2022) 8, 1816-1830. <https://doi.org/10.1007/s40831-022-00606-9>
- [23] DIN EN 1504-7:2006. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 7: Reinforcement Corrosion Protection. *Beuth*, (2006) Berlin.
- [24] Scrivener, K. L.; John, V. M.; Gartner, E. M., Eco-efficient cements: Potential economically viable solutions for a low-CO₂ cement-based materials industry. *Cement and Concrete Research* (2018) 114, 2-26. <https://doi.org/10.1016/j.cemconres.2018.03.015>
- [25] Ahmed Ali Almatrar, M.; Saad Abdul-Mughni, H.; Ismail Al-Safi, S., Effect of Metakaolin on strength and durability of concrete. *JES. Journal of Engineering Sciences* (2009) 37, 1389-1405. <https://doi.org/10.21608/jesaun.2009.128522>
- [26] DIN EN 1766: 2017 Products and systems for the protection and repair of concrete structures–Test methods–Reference concretes for testing; German version EN 1766: 2017.
- [27] DIN EN 196-1 Prüfverfahren für Zement–Teil 1: Bestimmung der Festigkeit. (2005)
- [28] Bredy, P.; Chabannet, M.; Pera, J., Microstructure and Porosity of Metakaolin Blended Cements. *MRS Proceedings* (1988) 136, 275. <https://doi.org/10.1557/PROC-136-275>
- [29] Habert, G., (2013) Environmental impact of Portland cement production. *Woodhead Publishing*. <https://doi.org/10.1533/9780857098993.1.3>
- [30] Heath, A.; Paine, K.; McManus, M., Minimising the global warming potential of clay based geopolymers. *Journal of Cleaner Production* (2014) 78, 75-83. <https://doi.org/10.1016/j.jclepro.2014.04.046>
- [31] ISCC System GmbH, (2021) ISCC EU 205 Greenhouse Gas Emissions, version 4.0
- [32] DIN EN 206-1 Beton – Festlegung, Eigenschaften, Herstellung und Konformität. *Beuth*, (2021) Berlin.
- [33] DIN EN 12390-10: 2019-08 Testing of hardened concrete-Part 10: Determination of carbonation resistance of concrete at atmospheric concentration of carbon dioxide. *Beuth*, (2019) Berlin.
- [34] CPC 18 Measurement of hardened concrete carbonation depth, 1988. *RILEM Recommendations for the Testing and Use of Construction Materials. e* (1994) 56-58. <https://doi.org/10.1007/BF02472327>
- [35] Vogler, N.; Lindemann, M.; Drabetzki, P.; Kühne, H.-C., Alternative pH-indicators for determination of carbonation depth on cement-based concretes. *Cement and Concrete Composites* (2020) 109, 103565. <https://doi.org/10.1016/j.cemconcomp.2020.103565>
- [36] Ward's Science, (2018) Alizarin Yellow R, 0.1% pH indicator solution. Safety Data Sheet (SDS).

- [37] Glawe, C.; Georget, F.; Raupach, M.; Matschei, T., Multi technique characterization of the carbonation affected zone uncluding non-destructive sindle sided ^1H NMR *Cement and Concrete Research* (2024) 178, 107438.
<https://doi.org/10.1016/j.cemconres.2024.107438>
- [38] Merkel, M., Realkalisierungspotenzial von zementgebundenen Werkstoffen im Trinkwasserbereich. Ph.D. Thesis, Technische Universität Kaiserslautern, (2021) Kaiserslautern, 15.07.2021.
- [39] Appelo, C. A. J., Solute transport solved with the Nernst-Planck equation for concrete pores with 'free' water and a double layer. *Cement and Concrete Research* (2017) 101, 102-113.
<https://doi.org/10.1016/j.cemconres.2017.08.030>
- [40] Bishop, E., (2013) Indicators: international series of monographs in analytical chemistry. Elsevier.
- [41] Sevelsted, T. F.; Skibsted, J., Carbonation of C-S-H and C-A-S-H samples studied by ^{13}C , ^{27}Al and ^{29}Si MAS NMR spectroscopy. *Cement and Concrete Research* (2015) 71, 56-65.
<https://doi.org/10.1016/j.cemconres.2015.01.019>
- [42] Lu, B.; Shi, C.; Zhang, J.; Wang, J., Effects of carbonated hardened cement paste powder on hydration and microstructure of Portland cement. *Construction and Building Materials* (2018) 186, 699-708. <https://doi.org/10.1016/j.conbuildmat.2018.07.159>
- [43] Zajac, M.; Skibsted, J.; Skocek, J.; Durdzinski, P.; Bullerjahn, F.; Haha, M. B., Phase assemblage and microstructure of cement paste subjected to enforced, wet carbonation. *Cement and Concrete Research* (2020) 130, 105990.
<https://doi.org/10.1016/j.cemconres.2020.105990>
- [44] Zajac, M.; Irbe, L.; Bullerjahn, F.; Hilbig, H.; Haha, M. B., Mechanisms of carbonation hydration hardening in Portland cements. *Cement and Concrete Research* (2022) 152, 106687. <https://doi.org/10.1016/j.cemconres.2021.106687>
- [45] Zajac, M.; Skibsted, J.; Durdzinski, P.; Bullerjahn, F.; Skocek, J.; Haha, M. B., Kinetics of enforced carbonation of cement paste. *Cement and Concrete Research* (2020) 131, 106013. <https://doi.org/10.1016/j.cemconres.2020.106013>

6. QUANTITATIVE ANALYSIS OF THE ALKALI TRANSPORT DURING CHEMICAL RE-ALKALIZATION USING LASER-INDUCED BREAKDOWN SPECTROSCOPY

6.1 ABSTRACT

With the increasing number of existing buildings, the implementation of durability-preserving repair procedures is becoming increasingly important. The chemical re-alkalization (CRA) enables the protection of reinforced concrete structures exposed to carbonation by maintaining or restoring the alkalinity in the concrete through the application of an alkaline mortar, such as hybrid alkali-activated binders (HAABs). However, the process of CRA is still insufficiently understood, which means that the requirements for the repair mortars can only be roughly formulated. This paper therefore investigates the process of CRA using laser-induced breakdown spectroscopy (LIBS). Based on the quantitative results of potassium transport in the composite system, a time-dependent attenuation factor can be determined that allows for the adaptation of Fick's second law of diffusion previously used to predict CRA. The attenuation factor provides further insight into the course of potassium transport, which, based on the results, never follows an ideal diffusion process. Adjusting the diffusion law allows for an improved prediction of the maximum achievable re-alkalization depth depending on the repair mortar, where a potassium content of, e.g., 2.3 wt% leads to a complete re-alkalization of 16 mm. The present study demonstrates the potential of LIBS to quantitatively represent CRA for the first time thus providing new insights into potassium transport and the dynamics of the process.

6.2 INTRODUCTION

The steel reinforcement of concrete buildings often suffers from carbonation-induced corrosion which can reduce the durability of existing structures creating a need for options to counteract corrosion or carbonation of concrete. The focus is primarily on options preserving the existing building structures in order to promote the sustainability of the construction sector and to minimize repair costs. The protection of the steel reinforcement against carbonation-induced corrosion can be achieved by different methods which include the replacement of the carbonated concrete as well as the application of an alkaline mortar onto the carbonated concrete to restore a $\text{pH} > 9$ within the concrete by the diffusion of the alkaline components from the mortar into the underlying concrete. The latter is referred to as chemical re-alkalization (CRA) which acts as a principle to maintain or rebuild the alkalinity of the concrete [1, 2]. As an alternative to Portland cement-based repair mortars (RMs), other materials for chemical re-alkalization such as highly

alkaline hydrogels and various alkaline solutions have been tested in the past [3, 4]. Even though these materials represent a CO₂-reduced alternative to cements, they do not offer any additional protection against re-carbonation. There are different results regarding the resistance of the re-alkalized concrete to re-carbonation, when there is no additional protection against carbonation given by the re-alkalization material itself. In contrast, Mukhin was able to demonstrate a pH value of 10 ten years after re-alkalization using an alkaline solution without any additionally applied carbonation protection on the re-alkalized concrete [5]. On the other hand, this is contradicted by the fact that the evidence of re-alkalization using the phenolphthalein test on a fracture surface of re-alkalized concrete fades again after a short time upon contact with the atmosphere [6]. This would mean rapid re-carbonation of the re-alkalized area. Still, the use of alternative re-alkalization materials to Portland cement-based mortars offers the opportunity to redefine the performance of repair materials. Basis for the application of new materials to restore the alkalinity in the carbonated concrete is the fundamental understanding of the main processes during the chemical re-alkalization. A first investigation regarding the transport processes during the re-alkalization process was conducted by Merkel resulting in the assumption that the chemical re-alkalization can be divided into two different phases, the suction phase and the diffusion phase [7]. This differentiation is based on the rate the re-alkalization depth increases with over time. In the suction phase, Merkel observed a rapid, nearly linear progression of the re-alkalization depth within the first day after different cement-based repair mortars were applied on the concrete surface. During this phase, the re-alkalization is said to be primarily driven by the piggyback transport of the alkalis from the mortar into the concrete, due to a moisture gradient between the fresh mortar and the more or less dry concrete. Therefore, the extent of the re-alkalization is strongly influenced by the moisture present in the near-surface of the concrete. After one day, the re-alkalization rate changed into a non-linear progress which, according to Merkel, is mainly controlled by the ambient humidity. This transition is assumed to be due to the hardening of the repair mortar as well as the saturation of the pore structure of the concrete during the suction phase, resulting in a diffusion-based transport of the alkalis within the diffusion phase. A variation in the re-alkalization rate was also observed by Glawe et al. using hybrid alkali-activated binders (HAABs) as the re-alkalization material [6]. These HAABs consist of a combination of ordinary Portland cement (OPC) and calcined clay which additionally were alkali-activated by a potassium hydroxide solution. In case of the investigation by Glawe et al., the carbonated concrete was pre-wetted before the re-alkalization mortar was applied, leading to a wet concrete in the near-surface area [6]. A water-filled pore structure of the concrete results in a strong decrease in the capillary suction of the concrete from which it can be deduced that the high re-alkalization rate in the first

day after application of the mortar is not exclusively due to the suction-based absorptivity of the concrete. Still, the substrate concrete and more precisely the water-to-binder ratio (w/b) is shown to have an influence on the re-alkalization rate as it directly influences the porosity of the concrete [8]. A higher w/b therefore results in a coarser structure which leads to more pathways for fluids to be transported through the concrete. By comparing the data from Reus et al. and Glawe et al., the influence of the w/b of the concrete becomes clear as the HAABs show similar or even higher re-alkalization rates although the alkaline solutions provide more moisture for the alkali transport into the concrete (compare Figure 6-1) [3, 6, 7, 9, 10]. However, in the first approach Merkel and Réus et al. described the transport processes during the chemical re-alkalization using the root-time-law (compare Equation (1)) assuming a steady decrease in alkali ingress [3, 7]. This decrease is assumed to be higher than the progression of time. The course of the re-alkalization therefore only differs dependent on the used re-alkalization material. The different re-alkalization materials are characterized by the re-alkalization coefficient k_{CRA} .

$$d_{CRA} = k_{CRA} \cdot \sqrt{t} \quad (1)$$

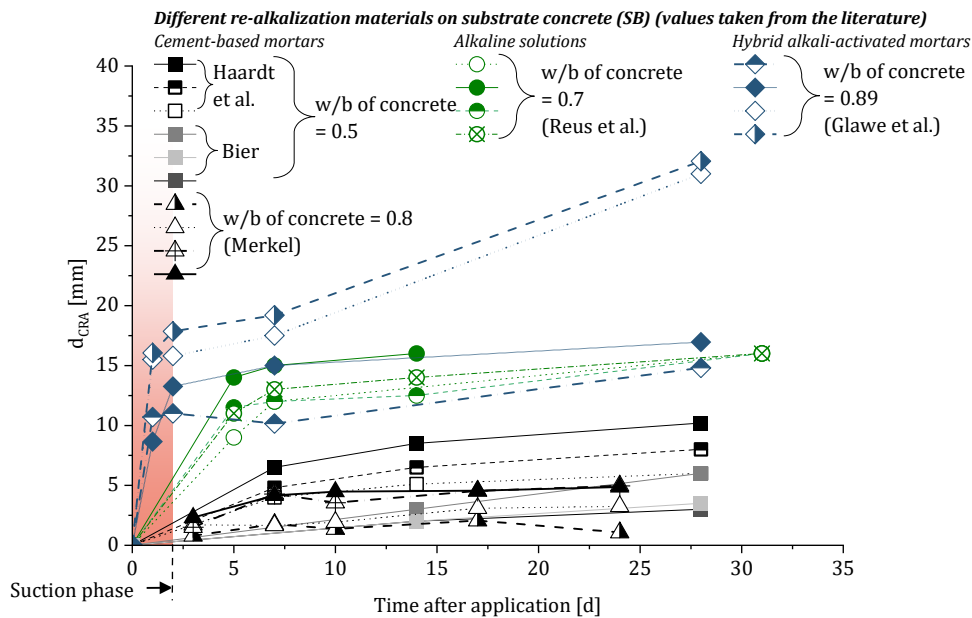


Figure 6-1: Summary of the progression of the CRA over time using different substrate concretes based on the literature [3, 6, 7, 9, 10].

Réus et al. used the re-alkalization coefficient, which is normally given in $\text{mm}/t^{0.5}$, to compare different alkaline solutions regarding their sufficiency as a re-alkalization material [3]. The comparison showed the highest re-alkalization coefficient for a potassium hydroxide solution. Also, Glawe et al. could correlate an increased re-alkalization rate with a higher amount of potassium hydroxide in the repair mortar [6]. However, it has to be taken into account that the calculation of the coefficient is based on the assumption that there are no different phases within the chemical re-alkalization and that the different re-alkalization materials have an unlimited alkali depot. These assumptions stand in contrast to the differentiation of the different phases during re-alkalization made by Merkel and result in an underestimation of the achieved re-alkalization depth during the suction phase and an overestimation of the maximum re-alkalization depth of the different re-alkalization materials. To fully understand the different phases of the chemical re-alkalization, further insight into the alkali transport and the changes in the alkali concentration of the repair mortar as well as the concrete is needed. Therefore, this paper aims to illustrate the alkali transport during the CRA using laser-induced breakdown spectroscopy (LIBS) which allows a quantification of the different components participating in the re-alkalization process. The advantages of LIBS over traditional methods to study the CRA are given in Table 6-1 [11-15]. Further, the alkali depletion of the re-alkalization material is analyzed to determine the material-specific, maximum expected re-alkalization depth in a specific amount of time. Using the collected data, a model is developed that takes into account the systematic deviation of the re-alkalization process from an ideal diffusion-based process using an attenuation factor.

Table 6-1 Comparison of LIBS with traditional analysis methods for chemical re-alkalization

Method		Measured Variable	Resolution	Sample Preparation	Qualitative Quantitative	Advantages of LIBS over this Method
LIBS (Laser-induced breakdown spectroscopy)		Elemental concentrations	Up to 100 μm	Sawed and dry surface	X	-
Chemical indicator spray (e.g., Phenolphthalein)		Visual pH threshold front	In mm range (depends on aggregate size)	Fresh fracture surface	X	LIBS gives quantitative element profiles instead of single pH threshold front; avoids dye kinetics and influence of timing.
Optical pH imaging/fluorescent imaging		pH maps or profiles	~100 to 500 μm (depending on pixel size)	Sawed, clean surface	X	LIBS measures elements directly; no dyes needed.
Pore solution expression	Fluid samples measured using ion chromatography	Composition of pore solution	No spatial resolution	Pressing out sample	X	LIBS enables spatial resolution; no influence of sample preparation (e.g., high pressure)
Cold-Water extraction				Crushing, sieving of sample and leaching of powder, filtering of fluid	X	LIBS avoids deviations through leaching; provides in situ profiles

6.3 MATERIALS AND METHODS

The investigation of the CRA is based on the analysis of the penetration behavior of alkaline components from a repair layer in the form of a mortar into the substrate concrete. In this study, a concrete based on CEM I 32.5 R cement was used, while the mortar was made from a mixture of metakaolin and CEM I 52.5 R cement. The oxide composition of the different materials is given in Table 6-2.

Table 6-2: Oxide composition of the used binders.

Component	Unit	CEM I 32.5 R	CEM I 52.5 R	Metakaolin
SiO ₂		20.88	20.21	60.97
Al ₂ O ₃		5.61	5.61	35.01
Fe ₂ O ₃		2.53	2.15	1.26
MnO		0.057	0.06	0.00
TiO ₂		0.333	0.33	1.63
P ₂ O ₅		0.113	0.28	0.04
CaO	wt-%	64.62	64.46	0.24
MgO		1.61	1.57	0.13
K ₂ O		0.90	1.00	0.51
Na ₂ O		0.12	0.11	0.06
SO ₃		2.78	3.85	0.04
Sum		99.55	99.63	99.92
LOI		1.97	2.60	1.03

6.3.1 PREPARATION OF THE CONCRETE

To investigate the penetration behavior of alkalis from the repair material into the concrete substrate, cylindrical samples were first prepared from a concrete class A2 according to TR IH [16]. This concrete class with a maximum grain size of 16 mm and very high w/b ratio of 0.89 is intended to represent particularly porous concretes susceptible to carbonation. In the first step, cylindrical samples of the A2 concrete with a diameter of 100 mm and a height of 200 mm and 300 mm, respectively, were produced using steel formworks. The concrete mixture is given in Table 6-3. The cylinders were stored under PE-foil for 48 h and were taken out of the formworks afterwards. Next, the concrete disks were stored in water up to a concrete age of 7 days. At a

concrete age of 7 days, each of the cylinders was then cut into 5 disks with a height of 55 mm. One front side was sandblasted to achieve a mean roughness (R_z) depth of 10 mm which ensures a sufficient bond between mortar and substrate concrete in the later process. For further hydration, the disks were then stored at 100 % relative humidity (RH) for additional 21 days. After overall 28 days of hydration, the disks were stored at 23 °C and 55 % RH as preparation for the following drying process which was started at a concrete age of 35 days. For curing, the concrete disks were stored in a chamber at 60 °C for 21 days until mass constancy. By drying the concrete disks, the aim was to accelerate the subsequent artificial carbonation, since the concrete moisture content has a significant influence on the carbonation rate [17]. Before transferring the concrete disks into the carbonation chamber, the lateral surfaces as well as the non-sandblasted surface was sealed in two layers using a 2-component epoxy resin. The application of the two layers was carried out with a delay of 24 h. Finally, the dried and sealed concrete disks were stored in the carbonation chamber at 1 Vol.-% CO₂ at 20 °C and 65 % RH for 15 weeks.

Table 6-3: Mixtures of the investigated substrate concrete and the repair mortars

	A2 Concrete	Ref.	50C	50C 0.5 KOH	50C 0.5 KOH-KWG	50C 0.5 KWG	50C 2.3 KOH	50C 2.3 KOH-KWG
w/b	0.89				0.58			
Binder	CEM I 32.5 R				CEM I 52.5 R			
Cement	180	491.75	225.26	223.00	222.70	222.39	212.35	210.68
Metakaolin	-	-	225.26	223.00	222.70	222.39	212.35	210.68
Aggregates (quarzitic)								
	kg/m ³							
0.0-0.25	-	376.98	355.47	341.19	340.73	340.26	324.90	322.34
0.1-2.00	841.06	1098.28	996.1	996.82	995.45	994.11	949.20	941.72
2.0-8.00	680.87				-			
8.0-16.00	480.61				-			
Water	160.20	287.18	263.11	255.83	255.18	254.53	221.52	218.20
KOH _{sol} (50%)	-	-	-	22.30	11.13	-	127.41	63.20
Potassium Waterglass (silicate modulus = 1.0)	-	-	-	-	14.84	29.63	-	84.21
Potassium in fresh mortar (calculated)	-	0.18	0.14	0.50	0.50	0.50	2.30	2.30
Potassium in fresh cement paste (calculated)	wt%	0.52	0.40	1.46	1.45	1.44	6.08	5.93

After the carbonation process, the disks were prepared for the application of the different repair materials. For the application, the disks were put into 3D-printed formworks which exceeded the heights of the disks for 20 mm to allow the application of a repair layer of 20 mm thickness. According to [2], a repair layer of 20 mm minimum should be applied to ensure a full chemical re-alkalization of the carbonation depth of up to 40 mm. However, the layer thickness can be adapted according to the exposure class of the carbonated concrete component.

PRE-WETTING OF THE CONCRETE

Before the repair layer was applied on top of the concrete, the sandblasted surface of the concrete disk was pre-wetted twice with a brush at intervals of ten minutes. This method was chosen because it was qualitatively observed in a preliminary test that excessive prewetting counteracts the initial suction phase within the chemical re-alkalization. The test was intended to investigate an approach for simplified substrate preparation for CRA. For the preliminary test, one concrete disk was pre-wetted by storage under water for 24 h and one disk was pre-wetted by brushing with water in two layers while a third disk was not pre-wetted. On top of each disk, a repair mortar was applied as a 20 mm thick layer which was enriched with the fluorescent substance Uranine [18]. After the application, the disks were stored under damp cloth for 24 h. Afterwards, each of the composite systems was split and the resulting cross-sectional area was photographed under UV light. The result is given in Figure 6-2. The Uranine enables the qualitative visualization of the moisture penetration from the repair layer into the concrete dependent on the pre-wetting method.

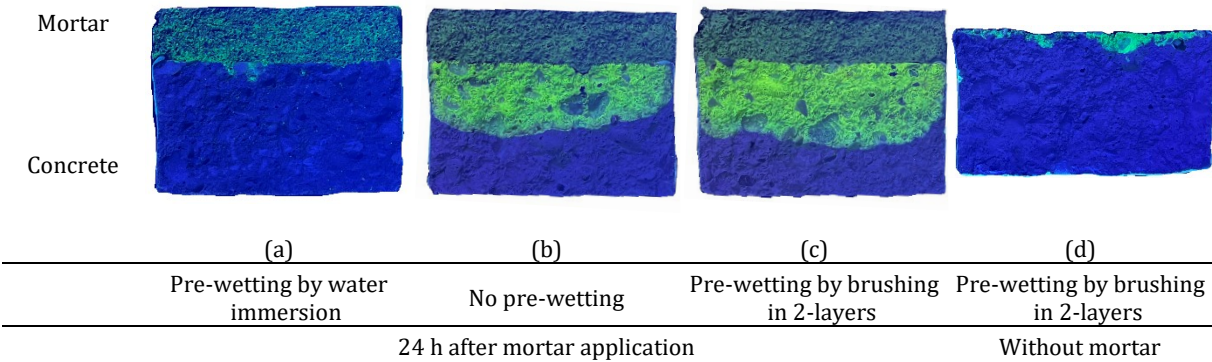


Figure 6-2: Results of the preliminary test to determine the influence of the pre-wetting method on the suction phase using repair mortars enriched with fluorescent Uranine.

It is clearly shown that the pre-wetting procedure of water storage leads to a low penetration of the moisture from the repair layer into the concrete compared to the prewetting by brushing. Interestingly, the brushing results in a similar penetration of moisture into the concrete as the non-pre-wetted concrete disks shows. However, pre-wetting of the concrete is essential to prevent excessive capillary suction of the concrete during the first hours after application as this can lead to weak bond behavior between repair layer and concrete and to a deviating w/b of the repair mortar near to the bonding area [19]. To ensure that the brushing is able to pre-wet the concrete in the near-surface area, an additional disk was pre-wetted with an Uranine solution, split and photographed under UV light. The result shows that the brushed solution penetrates into the near-surface area of the concrete and is assumed to act as a barrier against excessive capillary suction within the first hours after application of the repair layer.

6.3.2 APPLICATION OF THE REPAIR MORTAR

Before the application of the repair mortars, the concrete disks were put into 3Dprinted formworks and were pre-wetted using the brushing method. The mixtures of the repair mortars are given in Table 6-3. Except for the reference mixture (OPC), for all mortars, a substitution rate of 50 wt% was used which corresponds to the mixtures used in [6]. As activation solutions, a 50 % potassium solution (KOH) was used as well as potassium water glass (KWG) with a silicate modulus of 1.0. The values of 0.5 and 2.3 correspond to the calculated potassium solution in the fresh mortar. The mortars were mixed by first homogenizing the dry components consisting of Metakaolin and a CEM I 52.5 R and the wet components of water, KOH and KWG separately. The values for w/b were calculated by including the solid content of the activator solution to the proportion of the binder and were set to 0.58 for all mixtures. For homogenizing the wet components, the water and the activator solution were put in the mixing bowl and were mixed for 10 s. Before adding the dry components, the cement, metakaolin and sand were homogenized using a wood spatula. The dry components were then added to the mixing bowl followed by a mixing process of 2 min. After mixing, each mortar was applied on five concrete disks with a layer thickness of 20 mm. After the application, the composite systems were stored under damp cloths and PE-Foil for 24 h. Afterwards, the composite systems were taken out of the formwork and put into an irrigation system, except for one sample per variation, which was directly analyzed. The remaining four samples per variation were exposed to cyclic watering for 1 h with a delay of 23 h for 90 days in total.

6.3.3 ANALYSIS OF THE CRA

After the application of the mortar, the composite systems were stored in the irrigation system as described above. Except from the first sample, which was directly analyzed one day after the mortar application, the remaining samples were analyzed at 7, 28 and 90 days of cyclic watering, respectively. The analyses were conducted using the two indicator solutions Phenolphthalein and Mordant Orange 1 as described in [6]. Further, the samples were investigated using laser-induced-breakdown-spectroscopy (LIBS) after 1, 7, 28 and 90 days. The combination of both techniques is supposed to give insight into the alkali transport during the CRA as function of time and enables the correlation of the pH indicators with the quantified potassium concentration by LIBS in the cross-sectional area of the composite systems. To enable the implementation of both analysis techniques on one sample, the composite systems were cut in half using a saw which enables dry sawing by simultaneously monitoring the temperature of the saw blade. By this, a maximum temperature of 50 °C was maintained to minimize heat-related changes within the sample. When sawing, care was also taken to ensure that the sawing process was carried out from the direction of the concrete towards the applied mortar in order to avoid additional mortar material being introduced into the concrete.

INDICATOR TESTS

The indicator tests were conducted at five different times to analyze the progression of the re-alkalization depth (d_{CRA}) over time. As Glawe et al. characterized the indicator Mordant Orange 1 as a less time-sensitive alternative for Phenolphthalein, both indicators were used in the present study [6]. The characteristics of the indicators is given in Table 6-4.

Table 6-4: . Characteristics of the indicator solutions.

Name	Color Change	Composition	Chemical Formula
Phenolphthalein	colorless–magenta	1 g indicator powder, 70 mL ethanol, 30 mL demineralized water	$C_{20}H_{14}O_4$
Mordant Orange 1	light yellow–brown		$C_{13}H_9N_3O_5$

The indicators were both applied on the cross-sectional area of one half of the sawn composite system which enable a direct comparison of the displayed d_{CRA} . The values for d_{CRA} were obtained by measuring the thickness of the previously carbonated area that has been colored as a result of the spraying of the indicator, indicating an increase in the pH of the concrete in this area of at least above 9. Although the phenolphthalein test usually indicates a clear turning point, there may still

be deviations from the actual pH profile in the samples, which can be determined using optical pH methods, for example [13]. The transition range of the indicator in particular can lead to an underestimation of the CRA as a result of flat pH profiles, as weak coloring occurs in this range. At the same time, interactions between the indicator and the sample can lead to leaching processes, which cause the pH value to rise in the area close to the surface and thus lead to an overestimation of the alkalinity [12]. The measurements were carried out using photographs taken 30 s after spraying the indicator solutions and then processed using the JMicrovision software (version 1.3.4). The software enables the measurement of the d_{CRA} in each point of the re-alkalization front and the calculation of d_{CRA} of each composite system by averaging all data points after the different storage times, respectively [20]. In the first approach, an attempt was made to calculate the average of the results of the two indicators to determine d_{CRA} , in accordance with the studies by Glawe et al. [6]. However, when using Mordant Orange 1, a very slightly visible re-alkalized area was observed in most cases. Furthermore, the different colors of the re-alkalized zone, as observed by Glawe et al., could not be detected [6]. Therefore, the d_{CRA} values were determined exclusively based on the results of the indicator phenolphthalein. Still, the use of Mordant Orange 1 enables the identification of another process resulting from the cyclical irrigation during storage. With increasing storage time, a lighter-colored zone became apparent in the near-surface area of the repair mortar. This is assumed to be a hydroxide-depleted zone, resulting from leaching processes caused by regular irrigation of the sample. This zone will be referred to as the depleted zone. Some samples exhibited a depleted zone near the surface of the lateral surfaces. The depletion with increasing storage time can be explained by the unsealed lateral surfaces of the mortar, which were also in contact with water during the cyclic irrigation. To exclude the influence of this areas on the determined re-alkalization depths, a 15 mm edge area was excluded from the evaluation as shown in Figure 6-3.

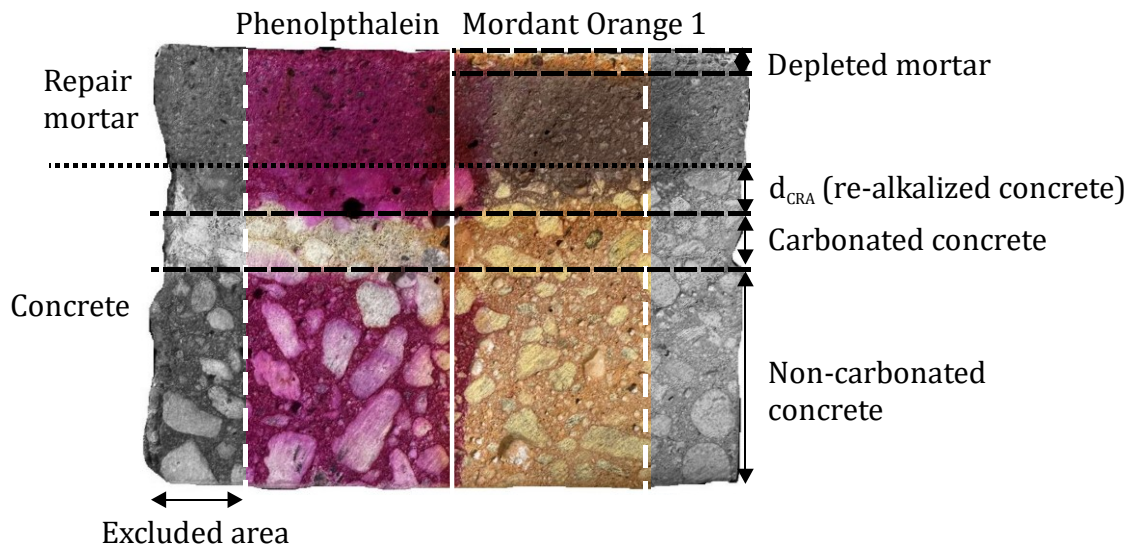


Figure 6-3: Representation of the definition of the different areas displayed by the indicator solutions Phenol-phthalein and Mordant Orange 1.

Based on the values for d_{CRA} , the re-alkalization coefficient k_{CRA} was determined according to the root-time law as described in the Introduction section. Although the root-time law assumes that there is an infinite alkali buffer within the repair material, which is demonstrated to not be the case later on, the obtained values allow us to roughly compare the different repair materials of this study.

LASER-INDICED-BREAKDOWN SPECTROSCOPY

In addition to the indicator tests, the second half of each composite system were analyzed using laser-induced-breakdown-spectroscopy (LIBS) to quantify the potassium ingress in the cross-sectional area of the samples. The focus was on the potassium concentration because potassium was assumed to act as the main active constituent for the CRA using the HAABs of this study which were alkali-activated using a potassium hydroxide solution and potassium water glass. As LIBS is often used to determine the penetration of chloride into concrete, a calibration method was developed to quantify the potassium concentration in the investigated area [11, 21]. The following measurements were conducted using equipment by SECOPTA (Teltow, Germany), Model: FiberLIBSlab after 1, 7, 28 and 90 days of storing the composite systems in the irrigation system. For the calibration to quantify the potassium concentration, calibration mixtures were prepared that gradually cover the potassium content of the materials to be tested Figure 6-4. The potassium contents were selected based on the μ XRF analysis and the calculated potassium contents of the activator solutions (compare Table 6-5).

Table 6-5: Potassium content of the used components.

	CEM I 32.5 R	CEM I 52.5 R	Metakaolin	KOH _{sol} (50 %)	KWG (Silicate Modulus = 1.0)
	wt%				
K	0.75	0.83	0.42	34.84	26.15

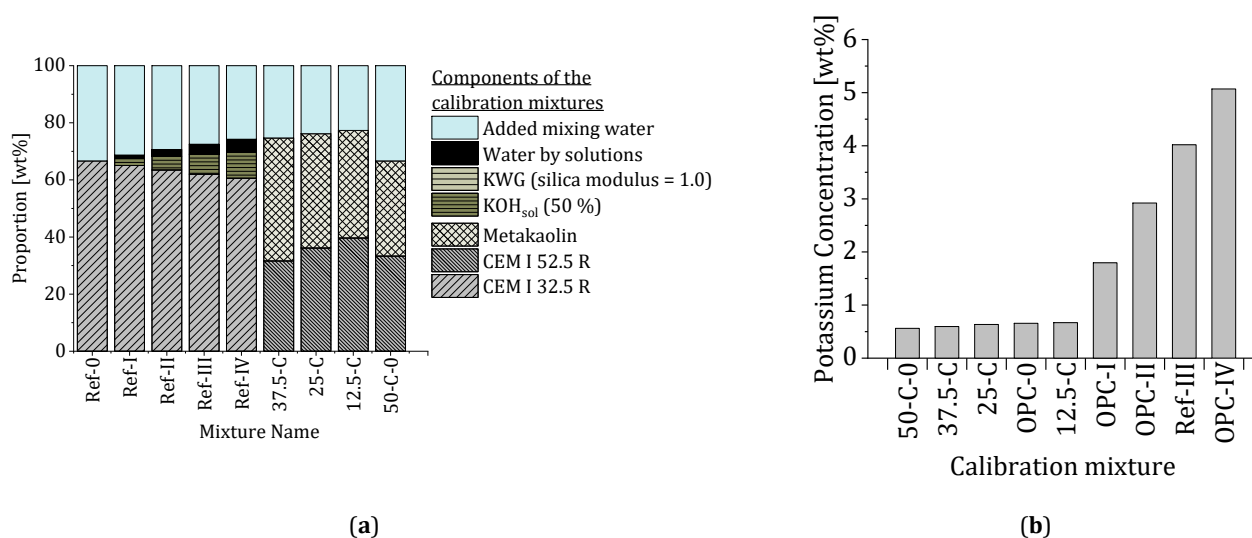


Figure 6-4: (a) Composition of the calibration mixtures and (b) range of potassium concentrations (mixtures were sorted in order of the potassium concentration for visualization).

The calibration mixtures were produced by mixing the components in a sealed plastic bag and let them cure for 7 days. After curing, the mixtures were dried in a beaker glass at 105 °C until constant mass was reached. The dried mixtures were crushed using a mortar and then ground in a ball mill for 5 min at 400 turns per minute. The mill was cleaned after each mixture by grinding quartz sand and cleaning with isopropanol. The powder samples were pressed into tablets using a press with a load of 25 tons. Each tablet was put into a sealed plastic bag and stored in a container over silica gel beads to prevent water absorption. The calibration tablets were measured at each measuring time of the composite systems to take into account any influences of the measuring equipment. For the measurement, the tablets were installed in the LIBS chamber as shown in Figure 6-5. During the measurement, each measuring point was burst four times. The first burst was discarded to exclude any surface anomalies which could have evolved during the storage of the tablets. The generated spectra of the other three bursts were averaged.

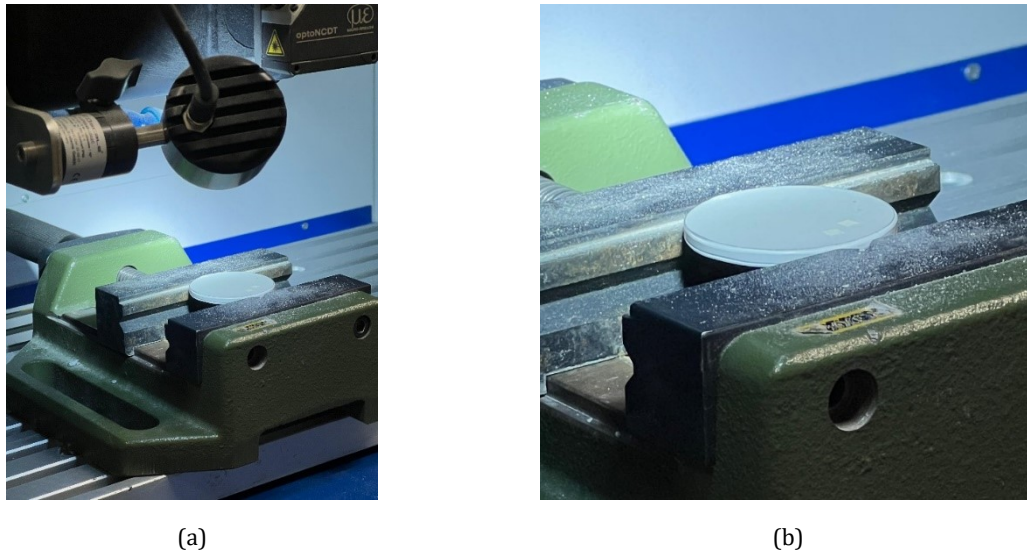


Figure 6-5: (a) Installed calibration tablet in the LIBS chamber and (b) magnification of the measuring field.

For the evaluation of the spectra, a differentiation was made depending on the existing potassium concentration. For concentrations up to 3 wt% the characteristic potassium band at 769.896 nm wavelength was analyzed while the quantification of concentrations of 3.0 – 5.0 wt%, the potassium band at 693.8 nm was analyzed, which is a common procedure as described in [22]. The described evaluation procedure was also applied on the LIBS measurements of the composite systems which enables a quantification of the potassium concentration in wt% relative to the cement content. To analyze the penetration behavior of potassium in the cross-section of the composite systems, 2D measurements were generated using the LIBS device. The entire measurement field extended to 30 mm width and 75 mm length with a resolution of 0.4 mm per measurement point (compare Figure 6-6). The width of 30 mm was chosen according to the maximum grain size of the concrete of 16 mm. The measuring field was set individually for each sample to ensure the highest possible proportion of cement matrix within the measurement field. At the same time, the LIBS measurements, as well as the indicator evaluation, did not cover the edge area to exclude any anomalies in the area of the lateral surfaces. In addition to visualizing the potassium distribution in the cross-section of the samples, the LIBS data were analyzed to depict depth profiles of potassium concentration following the extraction of the aggregates [23]. After applying the calibration method on the LIBS Data, the data gives the potassium concentration in wt% relative to the cement. As described above, the potassium concentration was then averaged for each measuring depth to obtain depth profiles of the cross-sectional area

of each composite system. The profiles were further evaluated by determining the penetration depth of potassium at the different measuring times of 1, 7, 28 and 90. For reference, the maximum potassium content in the carbonated concrete was determined using LIBS on a sample to which no repair mortar was applied. The maximum potassium content of the carbonated concrete was determined to be 0.57 wt% relative to the cement. A measured content above this value was assigned to potassium ingress as a result of CRA which enables the determination of the penetration depth of potassium from the repair mortar into the concrete.

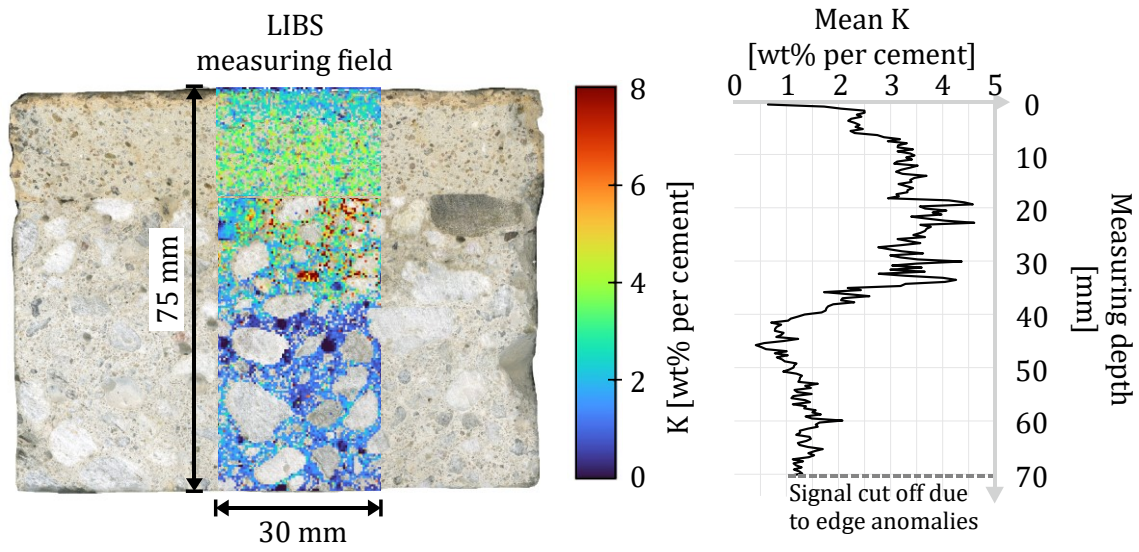


Figure 6-6: Exemplary representation of the measuring field of the LIBS measurement with excluded aggregates and the resulting depth profile of the averaged potassium concentration.

Further, the quantified data allows us to calculate a specific diffusion coefficient $D(RM)$ for potassium depending on the different repair mortar [24, 25]. The evaluation is based on Fick's second law of diffusion, for which a one-dimensional diffusion in a semi-infinite medium with a constant surface concentration (compare Equation (2)) is assumed:

$$C(x,t) = C_s * \operatorname{erfc} \left(\frac{x}{2\sqrt{D(RM)t}} \right) \quad (2)$$

The concentration $C(x,t)$ is the concentration of potassium at depth x and time t , which can both be derived from the LIBS measurements after a storage time of one day. It is assumed that within

the first day after application of the mortar, alkali transport is dominated by diffusion and the absorption phase only occurs in the first two hours [7]. The surface concentration C_s was derived from the LIBS measurements at the mortar–concrete interface. The erf is an error function to describe the potassium diffusion into the concrete including a decreasing potassium content with increasing depth.

The mortar–concrete interface was determined manually and was set as the surface of the semi-infinite medium to only take into account the diffusion within the substrate concrete (see Figure 6-7).

The final depth of the medium was set by cropping the depth profiles 20 mm in direction of the concrete starting at the mortar–concrete interface, resulting in only considering the carbonated concrete and to exclude any other transport processes coming from the non-carbonated concrete such as the rear-side re-alkalization [3].

The parameters C_s and $D(RM)$ were fitted based on the LIBS data between $x = 0$ and $x = 20$ mm with a non-linear least-squares optimization. For fitting, C_s was initially set to the maximum measured potassium concentration in the cropped area and $D(RM)$ was assumed to be in the range of 10^{-11} to 10^{-12} m²/s as this represents the range of diffusion coefficients of ions like Sodium (Na) or Chloride (Cl) in hardened cement paste [24]. The quality of the fit was evaluated based on the coefficient of determination R^2 .

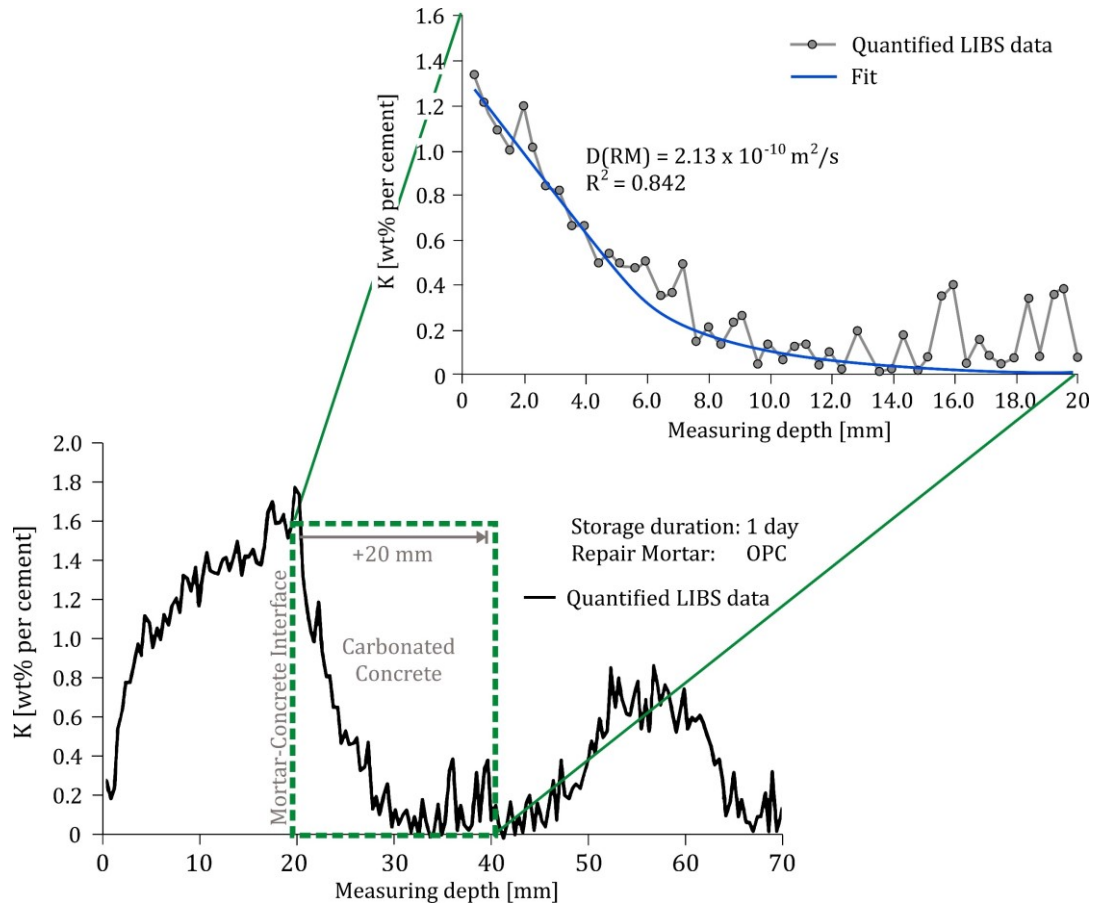


Figure 6-7: Example of the evaluation process to determine the potassium diffusion coefficient based on the LIBS depth profiles.

6.3.4 ADAPTION OF THE DIFFUSION MODEL TO PREDICT d_{CRA}

In order to calculate the possible maximum re-alkalization depth of each material, a simplified model was applied assuming the re-alkalization process to follow an adapted square-root-time law (Equation (3)) which is commonly applied to model unidirectional diffusion processes in semi-infinite media [24, 26]:

$$d_{CRA}(t) = \beta * \sqrt{D(RM) * t} \quad (3)$$

where $d_{CRA}(t)$ corresponds to the re-alkalization depth at time t , which depends on the diffusion coefficient $D(RM)$. To consider the deviation of the re-alkalization process from an ideal Fickian (diffusion-based) behavior, as it was already observed by Glawe et al. [6, 27], an empirical attenuation factor β is introduced. While β represents the difference between measured d_{CRA} and values which were calculated based on diffusion-based progression of the re-alkalization

exclusively, a value of 1 would indicate a purely diffusion-based CRA. Values above 1 indicate that the measured values of d_{CRA} at a given time are higher than the calculated values. This means that the CRA progresses faster compared to diffusion-based transport through, e.g., capillary suction. In comparison, values below 1 represent an attenuated diffusion-based CRA, where the measured values are below the calculated values for d_{CRA} . Therefore, the factor can be used to take into account binding of alkalis or alkali depletion of the repair mortar. The factor can be calculated based on the measured values for d_{CRA} (Equation (4)).

$$\beta = \frac{d_{CRA}(t)}{\sqrt{D(RM) * t}} \quad (4)$$

As the processes, which cause the deviation between the re-alkalization process and a diffusion-based process, may change over time, β represents a time-dependent factor. Therefore, the evolution of the attenuation factor was fitted using a power law (Equation (5)).

$$\beta(t) = a * t^b \quad (5)$$

The attenuation factor at each time can be calculated by fitting a which corresponds to the starting value at $t = 1$ and b describing how β decreases over time.

To determine $\beta(t)$, only values for d_{CRA} (measured and calculated) after 1, 7 and 28 days were used to test the transferability of the results to longer re-alkalization periods such as 90 and 180 days. Finally, the calculation of the re-alkalization depth based on the diffusion coefficient $D(RM)$ and the attenuation factor $\beta(t)$, which are both specific for each re-alkalization material and concrete, was carried out using Equation (6).

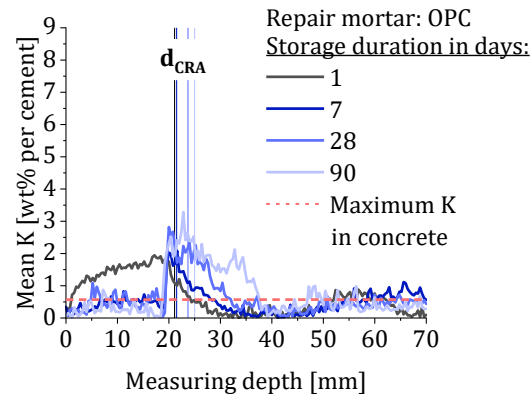
$$d_{CRA}(t) = a * \sqrt{D(RM)} * t^{b+0.5} \quad (6)$$

6.4 RESULTS

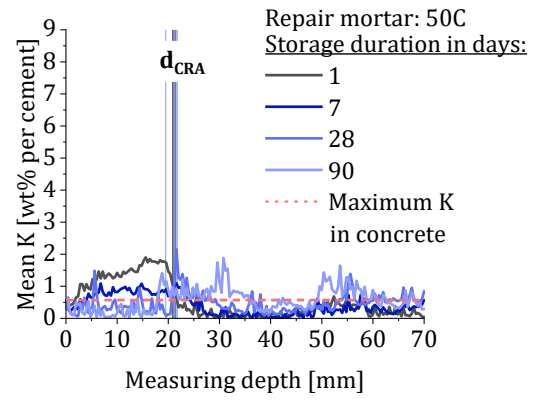
6.4.1 POTASSIUM PENETRATION OVER TIME

The quantification of the LIBS measurements enables the visualization of potassium transport over time during the CRA. The different depth profiles are given in Figure 6-8 and show the mean potassium concentration of each measuring depth at the different measuring times of all composite systems. The progression of the potassium penetration shows a dependency on the

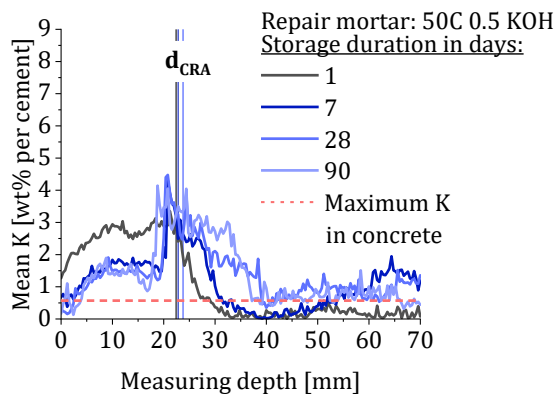
applied repair material and therefore on the present potassium concentration of the material. In accordance with the different compositions of the mortars, the mortars with high potassium content in Figure 6-8 (f) and (g) show the strongest increase in concentration within the concrete. It is striking that in some cases after just one day of storage in the irrigation system, the potassium concentration in the concrete is higher than in the mortar itself. This phenomenon becomes more pronounced up to day 28 and results in a sudden increase in the potassium concentration at the transition from mortar to concrete, which is on average about at 20 mm. The potassium-enriched area in the concrete adjacent to the mortar-concrete interface is characterized by a steep slope that decreases over time, indicating further penetration of potassium into the concrete. As the penetration depth progresses further over time, potassium continues to accumulate in the re-alkalized area while the repair layer gets depleted. In case of the repair material 50C 0.5 KOH KWG and 50C 2.3 KOH, the accumulation of potassium in the re-alkalized area results in exceeding the calibration range of the LIBS measurements.



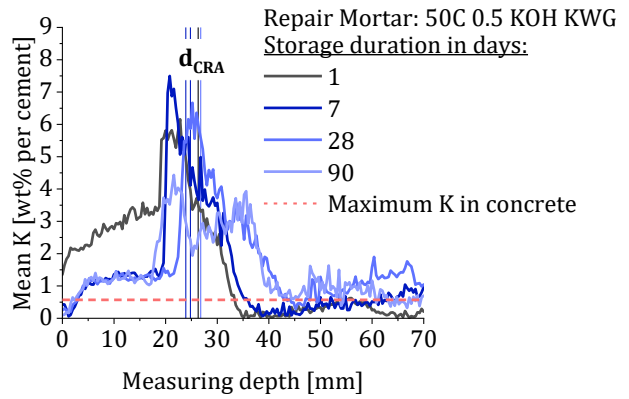
(a)



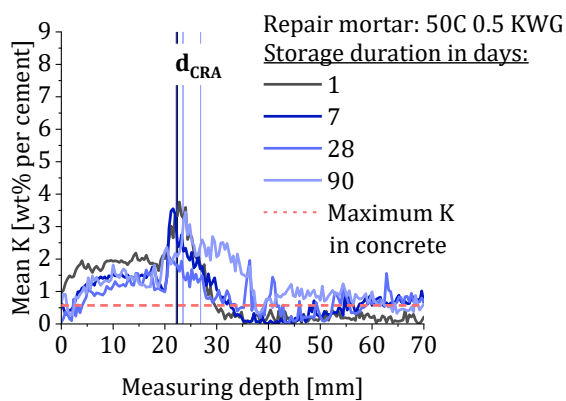
(b)



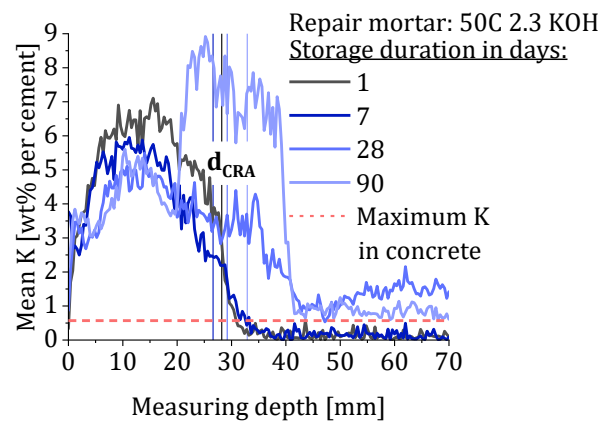
(c)



(d)



(e)



(f)

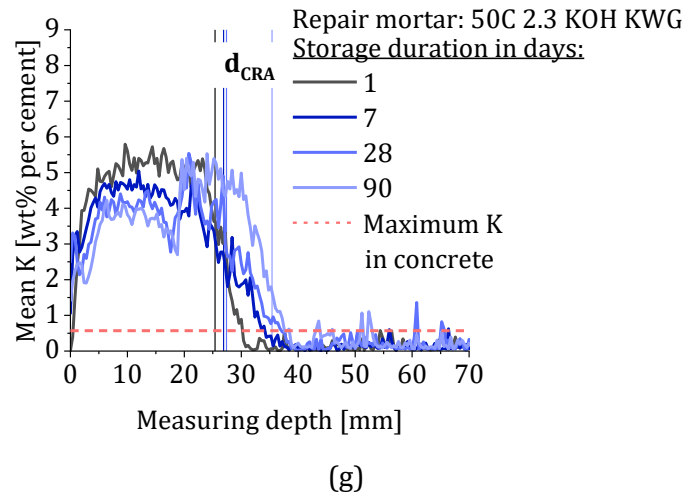


Figure 6-8: Quantitative depth profiles showing the mean potassium concentration of the different composite systems after different storage duration and the corresponding values for d_{CRA} and the maximum potassium concentration in the substrate concrete. (a) OPC. (b) 50C. (c) 50C 0.5 KOH. (d) 50C 0.5 KOH KWG. (e) 50C 0.5 KWG. (f) 50C 2.3 KOH and (g) 50C 2.3 KOH KWG.

The temporal development of the potassium concentration in the concrete suggests that the alkalis are bound in the concrete, causing the alkali concentration in the pore solution of the concrete to continually decrease [28, 29]. This results in a continuous release of dissolved potassium from the mortar into the concrete, even beyond concentration equilibrium. Further, after 28 days, no further accumulation in the bonding zone between mortar and concrete can be observed but a more even potassium distribution in the re-alkalized area. However, the concentration ratio measured using LIBS refers to the entire material and provides a mixed result of dissolved and bound potassium. A statement about the concentration ratio of dissolved potassium in the mortar and the concrete cannot be made based on these results.

Within the storage duration of 90 days, only the repair mortars with the highest potassium concentration enable full re-alkalization in case of a carbonation depth of 16 mm. However, the repair mortars with medium potassium concentration (0.5) show similar penetration depth, but with lower concentration at the re-alkalization front as well as the overall concentration within the re-alkalized area.

Based on the measured data during the 90-day study period, no uniform concentration distribution could be observed in the composite systems. It would be interesting to see to what

extent a uniform potassium concentration is established and to what extent the concentrations in mortar and concrete differ over time.

6.4.2 CORRELATION OF INDICATOR TESTS AND LIBS

The progression of the re-alkalization depth over time is given in Figure 6-9 and shows that only the materials with high potassium concentration are capable of a steady increase in the re-alkalization depth resulting in full re-alkalization. In case of fully re-alkalized concrete, the value for d_{CRA} was set to 16 mm as this represents the carbonation depth of the substrate concrete.

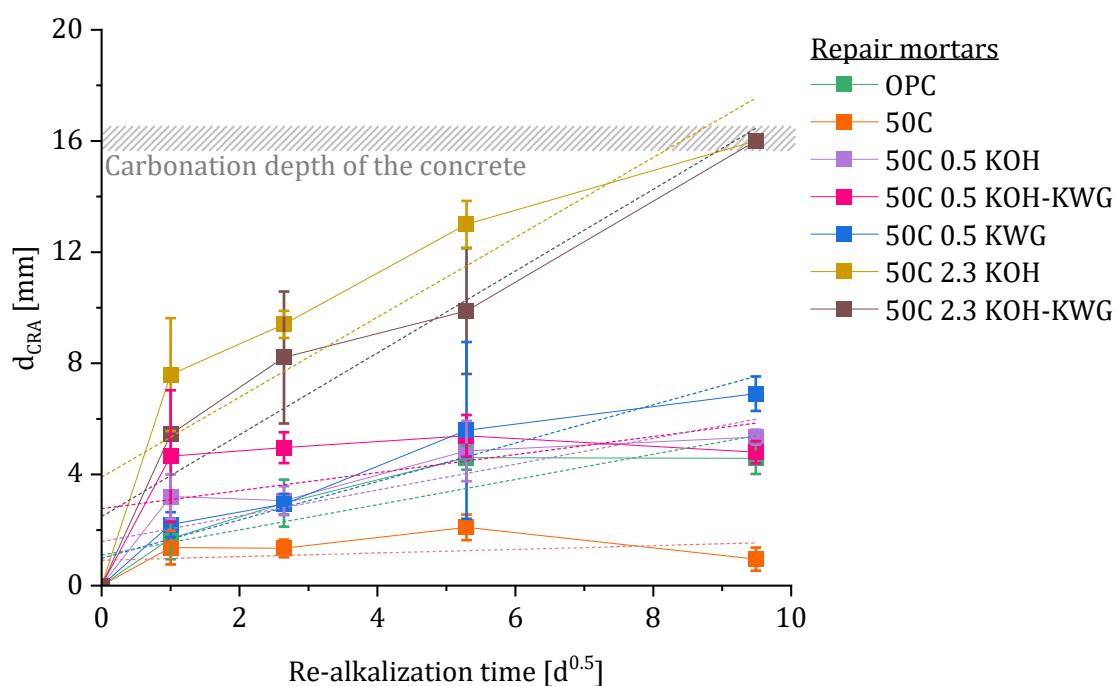


Figure 6-9: Evolution of the re-alkalization depth d_{CRA} over time with linear regression to calculate the re-alkalization coefficient k_{CRA} .

Based on the data, the re-alkalization coefficient k_{CRA} was calculated by applying a linear regression on the data. The results are given in Table 6-6. In case of the 50C and the 50C 0.5 KOH KWG mixture, the linear fit results in a weak measure of certainty accompanied by a low value for k_{CRA} .

Table 6-6: Results of the calculation of the re-alkalization coefficient k_{CRA} including the measure of certainty.

		OPC	50C	50C 0.5 KOH	50C 0.5 KOH KWG	50C 0.5 KWG	50C 2.3 KOH	50C 2.3 KOH KWG
k_{CRA}	mm/ $\sqrt{d}$	0.453	0.066	0.464	0.324	0.691	1.432	1.457
R^2	-	0.77	0.11	0.72	0.31	0.92	0.81	0.91

Referring to the different phases of the CRA, most of the repair materials show a maximum re-alkalization depth dominated by the suction phase. During the first 24 h after application of the mortar, approximately 50 % of the final re-alkalization depth is reached.

Even though the LIBS profiles show a steadily increasing penetration depth of the alkalis of all composite systems, the concentration is not sufficient to detect a successful CRA using the indicator. However, the composite systems with high potassium concentration show the highest potassium penetration depth while showing full re-alkalization. By looking at the different activator solutions, a generalized influence of the solution on the potassium penetration behavior cannot be formulated.

To directly compare the results of the indicator tests and the LIBS measurements, the penetration depth of potassium within the carbonated area was determined using the LIBS data. A limit of 0.57 wt% was assumed as the reference value for the concrete, so the depth at which the value in the concrete exceeded this limit was taken as the potassium penetration depth. The limit value represents the maximum potassium concentration of the concrete which was determined by measuring a carbonated concrete sample without an applied repair layer. In this observation, the area outside the carbonated area in the concrete was excluded because redistribution of alkalis may have already occurred at the carbonation front as a result of carbonation [30]. This means that penetration depths of potassium to depths outside the carbonated area were excluded from consideration.

The correlation of the data (compare Figure 6-10) shows that the penetration depth of potassium is in any case higher than the determined re-alkalization depth. However, there is no direct correlation of the parameters given by a weak measure of certainty ($R = 0.385$).

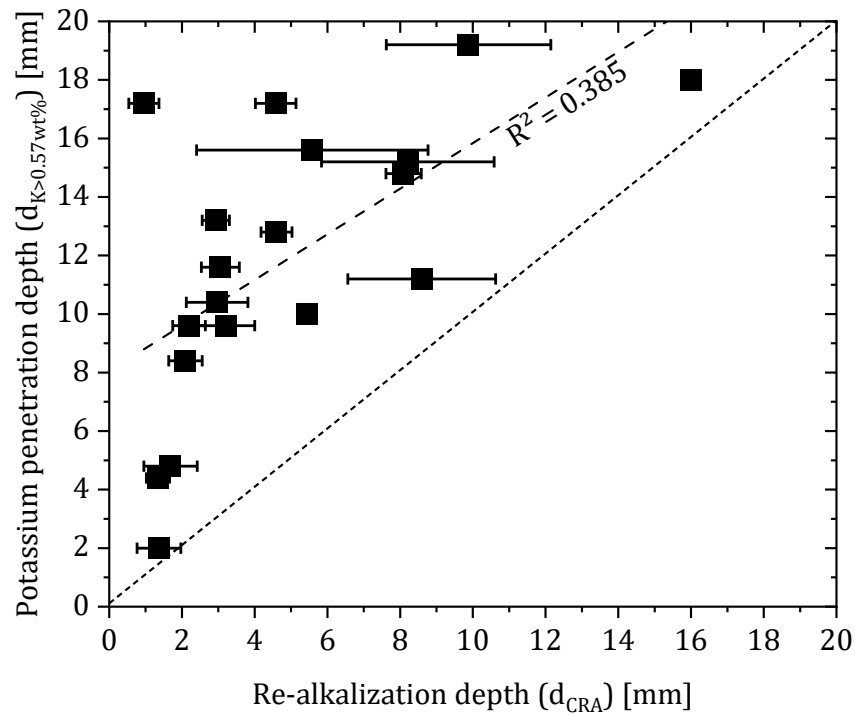


Figure 6-10: Correlation of d_{CRA} and the penetration depth of potassium where $K > 0.57 \text{ wt\%}$ (corresponds to the maximum potassium concentration of the substrate concrete).

While this correlation was applied to the totality of the measured values, Figure 6-11 shows the potassium concentrations at d_{CRA} related to the individual materials. Only at low potassium concentrations in materials without potassium water glass content, an approximately uniform value of the potassium concentration at d_{CRA} is given. The assumption of a concrete-specific critical potassium content for detecting CRA using Phenolphthalein cannot be confirmed based on the data.

On the one hand, the irrigation of the repair layer causes leaching in the near-surface area and, on the other hand, the mortar near the bonding zone is depleted of alkalis due to CRA. This occurs to an extent that the mortar loses its alkalinity to such an extent that it falls below the indicator limit of Mordant Orange 1 (compare Figure 6-12).

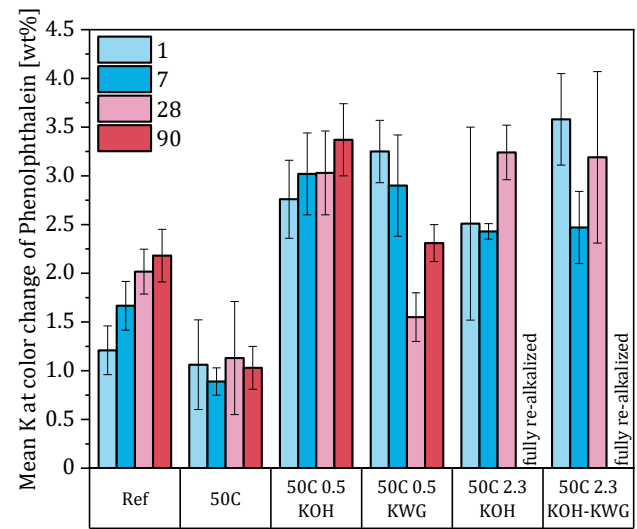


Figure 6-11: Potassium concentration at the color change in the indicator.

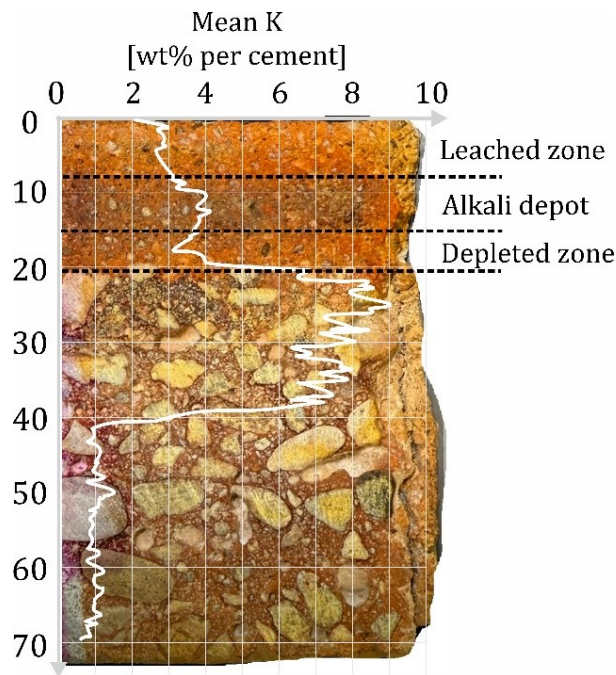


Figure 6-12: Visualization of the bi-directional alkaline loss of the repair layer as a result of leaching and CRA.

6.4.3 PARAMETRIZATION OF THE INVESTIGATION RESULTS

The results regarding the progression of the CRA and the correlation of the LIBS data with the indicator test results all point out that the connection of the potassium penetration and the CRA is non-linear. Especially the observation that the potassium concentration within the concrete increases over time leading to a depletion of the repair mortar as well as the formation of a potassium concentration plateau in the re-alkalized area indicate that the influence of alkali transport in the concrete on the re-alkalization process is decisive for the evolution of d_{CRA} .

To include this influence into the model to predict d_{CRA} at a specific time, the diffusion coefficient of potassium in the concrete was calculated based on the LIBS data which were obtained one day after the repair mortars were applied. The resulting diffusion coefficient of the different repair materials are given in Table 6-7.

Table 6-7: Fitted diffusion coefficients and surface concentrations of the different composite systems based on the LIBS data obtained after one day.

		OPC	50C	50C 0.5 KOH	50C 0.5 KOH KWG	50C 0.5 KWG	50C 2.3 KOH	50C 2.3 KOH KWG
D(RM)	$m^2/s \cdot 10^{-10}$	2.13	0.82	1.91	3.37	3.37	5.68	2.55
C_s	wt%	1.25	1.87	3.38	3.83	3.83	6.40	6.31
R^2	-	0.84	0.90	0.97	0.90	0.90	0.84	0.94

In most cases, the diffusion coefficient shows a good linear correlation with the re-alkalization coefficient which was calculated as described in [28] (see Figure 6-13). However, formulations with combined alkaline activation with potassium hydroxide and potassium silicate are outliers. At high potassium concentrations in the mortar (2.3), this leads to excessive re-alkalization compared to diffusion, while at lower potassium concentrations in the mortar (0.5), diffusion proceeds faster than re-alkalization. It is assumed that the interaction of the activators causes a reaction that influences the diffusion of potassium.

In contrast to that, the calculation of d_{CRA} based on $D(RM)$ using the root-time law of Equation (1) and replacing k_{CRA} with the correlation formula in Figure 6-13 results in an unrealistic overestimation of the achieved re-alkalization depth (see Appendix A Figure A6-1). As Glawe et al. mentioned, also the calculation including the re-alkalization coefficient to adapt Fick's second law results in an underestimation of the re-alkalization during the suction phase but an overestimation of the long-term performance of the repair material as k_{CRA} is obtained by a linear regression of the measured re-alkalization depth [6].

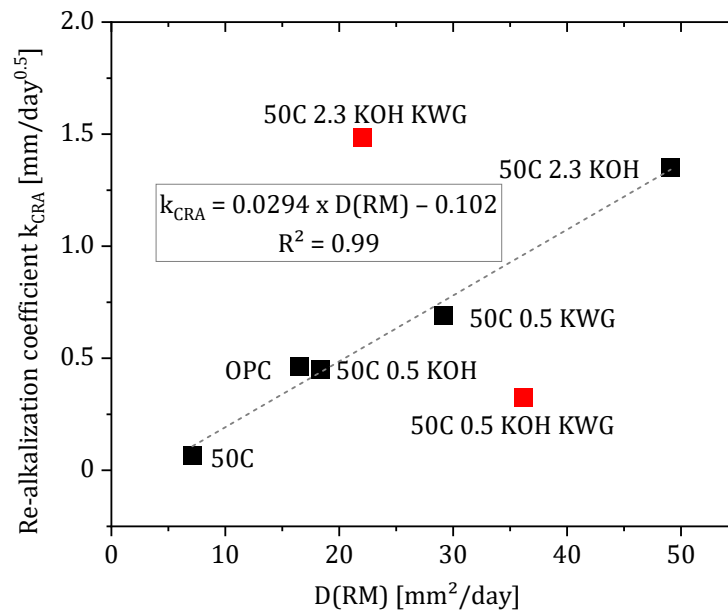


Figure 6-13: Correlation of the specific diffusion coefficient and the re-alkalization coefficient with linear regression excluding outliers (50C 2.3 KOH KWG, 50C 0.5 KOH KWG).

Furthermore, a good correlation between $D(RM)$ and k_{CRA} is only present if mixtures with potassium water glass are excluded. To counteract this overestimation, the attenuation factor β was introduced, which no longer assumes an exclusively diffusion-based re-alkalization, but takes into account other influences such as the following:

- Alkali binding in the concrete;
- Structural changes in the mortar;
- Alkali depletion of the repair material.

This allows the attenuation factor to be applied to different materials, as the calculation takes into account the influences of the respective material.

The results of the calculation of β are given in Figure 6-14 for 1, 7 and 28 days of re-alkalization. The consideration of the attenuation factor at each measuring time compared to the calculation of just one attenuation factor for each material, provides further information about the influences on the process of CRA.

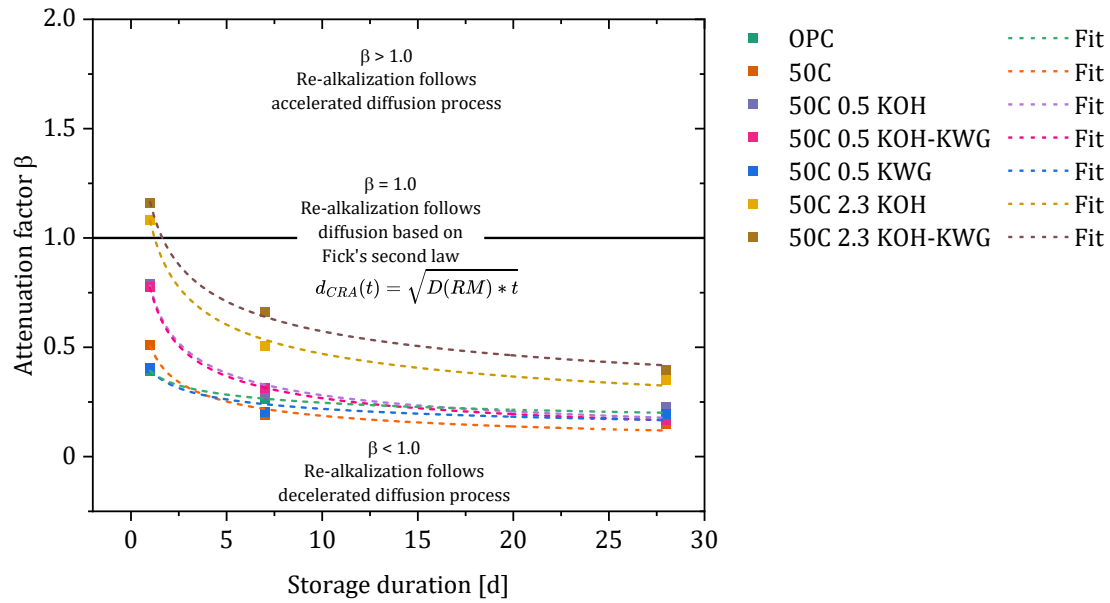


Figure 6-14: Evolution and fitting of the attenuation factors of the different materials over time.

The calculated values for β show that the investigated material can lead to a re-alkalization which progresses faster than a diffusion-based progress when the potassium concentration is 2.3 wt%, while a potassium concentration of 0.5 wt% or lower within the repair material results in a re-alkalization process which is slower compared to a diffusion-based process. However, regardless of the material, the re-alkalization process develops into a strongly decelerated diffusion process, which is defined by values of $\beta > 1$. At potassium concentrations of ≤ 0.5 , the attenuation factors are equalized after just 7 days. This means that the re-alkalization using these materials differs from an exclusively diffusion-based process to the same extend.

By fitting the attenuation factors of the different materials over time, the deviation of the CRA from the diffusion-based curve can be fully accounted for. The data could be best fitted using a power function given in Equation (5). The results of the fitted data can be found in Table 6-8.

Table 6-8: Results of fitting the power equation (Equation (5)) to the attenuation factors of the different materials.

	OPC	50C	50C 0.5 KOH	50C 0.5 KOH KWG	50C 0.5 KWG	50C 2.3 KOH	50C 2.3 KOH KWG
a	1.088	1.395	2.124	2.112	1.082	3.508	3.156
b	-0.234	-0.463	-0.423	-0.469	-0.251	-0.449	-0.289
R ²	0.97	0.98	0.98	0.99	0.95	0.98	0.99

6.4.4 PREDICTION OF d_{CRA}

Using the fitted data, the re-alkalization depth of the different materials was calculated. The results in comparison to the measured data for d_{CRA} using Phenolphthalein are given in Figure 6-15. Furthermore, the d_{CRA} was calculated for additional measuring times to test the extent to which forecasts for the further course of re-alkalization are possible using the measured values from 1, 7 and 28 days.

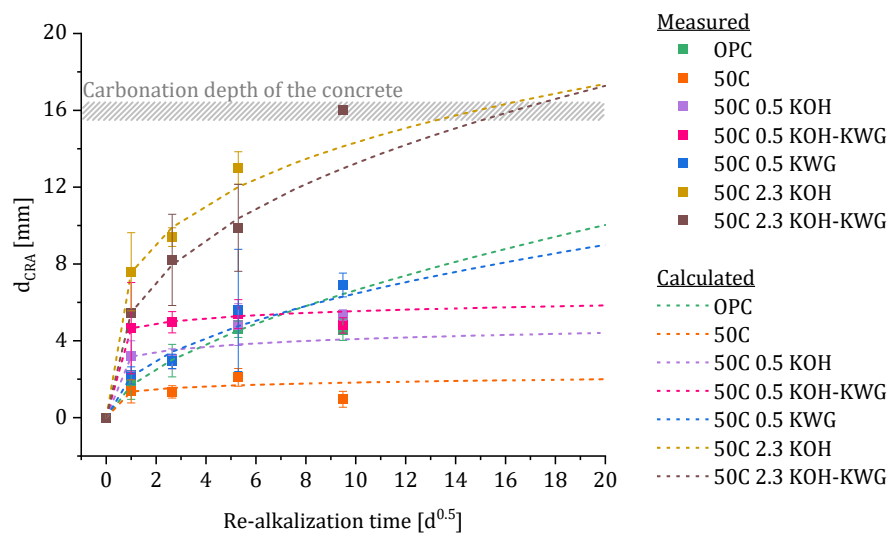


Figure 6-15: Comparison of the calculated and measured values for d_{CRA} .

Overall, the measured and calculated values show good agreement. Although the calculation of the attenuation function $\beta(t)$ was based on only three measured values of the re-alkalization depth, the prediction of re-alkalization depths for re-alkalization periods of 28 days and longer still shows a reliable agreement between the data (compare Figure 6-16).

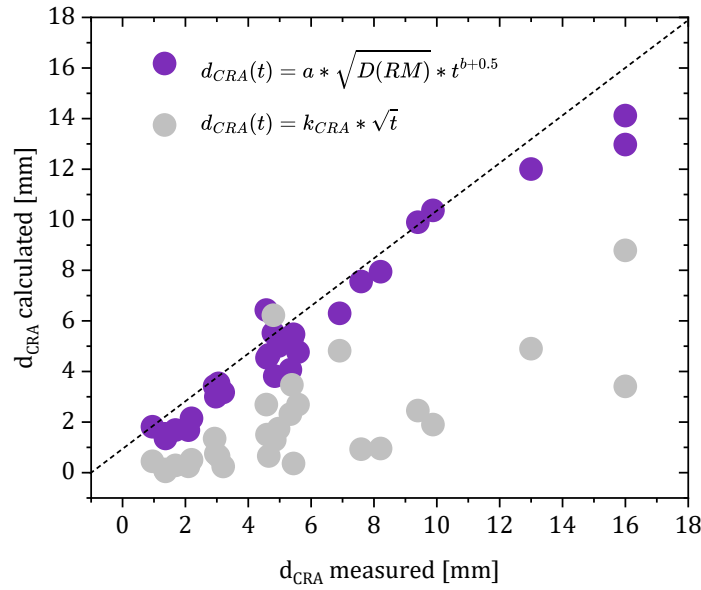


Figure 6-16: Correlation of the measured re-alkalization depths and the re-alkalization depth calculated using k_{CRA} compared to the calculation using the attenuation factor β .

In particular, the prediction of the expected maximum re-alkalization depth corresponds to the measured values. Repair mortars with a potassium content of 0.5 wt% and less show very little or even no re-alkalization progress after a period of 90 days. Compared to the prediction of the re-alkalization depth using the re-alkalization coefficient k_{CRA} the introduction of the attenuation factor results in a considerably more realistic prediction of the CRA and highlights the relevance of considering the two phases of re-alkalization and assuming a non-ideal Fickian process.

6.5 DISCUSSION

6.5.1 COMPARISON OF THE RESULTS WITH PREVIOUS STUDIES

The present investigations confirm the applicability of HAABs as a repair material for CRA as stated by Glawe et al. [6]. The present study also showed a clear influence of the potassium content in the repair material on the maximum achievable re-alkalization depth within 90 days. Interestingly, the materials in the studies by Glawe et al. achieved a higher re-alkalization depth in both the suction phase and the diffusion phase, despite significantly stronger pre-wetting of the samples prior to mortar application [6]. This is therefore not consistent with the preliminary studies on pre-wetting the concrete substrate in this study, in which a weaker pre-wetting by brushing the concrete surface with water in two layers should lead to a stronger suction phase.

Rather, the suction phase seems to be responsible for a CRA of 50 % regardless of the carbonation depth and moisture content of the concrete when a HAAB with at least 0.5 wt% potassium is used. Based on the observations and considering the results of all indicator tests at the various measurement times, it becomes clear that the mortars with medium and low potassium concentrations are almost completely depleted of potassium after just 28 days of re-alkalization, as evidenced by the light color of the Mordant Orange 1 indicator. Meanwhile, the phenolphthalein indicator continues to show a pH value above the transition point. Therefore, comparing the indicators is useful for evaluating repair materials, as the durability of the repair material can be assessed using Mordant Orange 1, while phenolphthalein can be used to determine the progress of the CRA and the carbonation resistance of the materials. Therefore, the results of Glawe et al. regarding the evaluation of Mordant Orange 1 as a better indicator for the assessment of CRA cannot be confirmed [6]. This may be due to the fact that the samples tested in this study were sawn samples, whereas previous studies examined broken samples using an indicator. Sawing the samples causes the samples to dry out in the near-surface area, as they were cleaned with compressed air after the sawing process. This suggests a stronger interaction between the indicator and the sample due to suction and leaching effects, which could result in weaker boundaries of the different areas [12]. However, a combination of both indicators is still recommended to investigate both the re-alkalization progress and the alteration of the re-alkalization material.

With regard to the model, the presented determination of the attenuation factor complements existing models such as Merkel's [7]. Merkel modeled re-alkalization primarily as a function of the substrate concrete, whose diffusion coefficient was corrected by taking tortuosity into account. The investigations also identified a dependence of the diffusion process on the re-alkalization material, which could not be further quantified due to a lack of values for the diffusion of the relevant alkalis in the concrete. In comparison, the present investigations using LIBS enable the determination of mortar-dependent diffusion coefficients of potassium. No adjustment was made for varying substrate concrete, but this should be the subject of future investigations.

6.5.2 LIBS FOR THE ANALYSIS OF CRA

The present study demonstrates the applicability of laser-induced-breakdown spectroscopy to analyze the CRA. Using LIBS, the alkali transport in composite systems can be quantitatively visualized in form of 2D mappings which can be transformed into depth profiles. Based on the depth profiles, the penetration depth of potassium can be determined and the potassium content in the range of the re-alkalization depth, which was determined using indicators. The depth

profiles further offer the possibility to determine the potassium diffusion coefficient for each composite system specifically.

The correlation of potassium penetration depth and potassium content with the re-alkalization depth performed in the first approach, showed only very weak systematic agreement. This can be explained primarily by the fact that potassium values obtained using LIBS are based on the measurement of the plasma, which includes both the solids and the pore solution contained therein. In contrast, the indicator results are based only on the reaction of the indicator with the pore solution of the material.

The correlation of the diffusion coefficient of the different materials with the re-alkalization coefficient which usually is used to adapt Fick's second law of diffusion to the re-alkalization process, a connection of both parameters was determined. However, the materials that were activated using the potassium solution in combination with potassium water glass were excluded to obtain a good correlation of the data. The transferability of the diffusion coefficient to the re-alkalization coefficient appears to be limited dependent on the applied re-alkalization material.

Although the reason for the deviation in the two mortar mixtures (50C 0.5 KOH KWG and 50C 2.3 KOH KWG) was not further analyzed, the interaction between the potassium solution and potassium water glass appears to be the cause of the deviations. This assumption is particularly supported by the fact that the formulations activated only with potassium solution or potassium water glass show a good correlation between the diffusion coefficient and k_{CRA} . It should also be noted that the calculation of the diffusion coefficient is based on the determined surface concentration, i.e., the potassium concentration at the interface between concrete and mortar. Since this value (C_s) is a fitted value, it depends primarily on a good calibration of the LIBS measurements. However, the measurements, especially at high potassium concentrations, yielded results that were at the limit of the calibration range, which can distort the depth profile by exaggerating the potassium concentration at the interface. A surface concentration that is too high leads to a steeper depth profile and results in a lower diffusion coefficient. In addition to the overestimation of the potassium content, temporary enrichments of potassium in the boundary zone can also lead to a steeper depth profile, which does not necessarily reflect the general diffusion pattern. Overall, the good correlation between $D(RM)$ and k_{CRA} can be explained by the fact that a higher potassium content of the material is associated with an increased CRA.

In some cases, a reduced potassium content can be measured in the LIBS results in the mortar area near the concrete boundary. While this was initially classified as a measurement inaccuracy, the alkali depletion could also be verified using the indicator measurements. Thus, in addition to the increased potassium release into the concrete, there also appears to be an overall decrease in

the pH value in this area. This contrasts with the alkaline core of the mortar, which, however, is subject to stress in two directions due to additional leaching. The extent to which this constant depletion affects the re-alkalization behavior could not be determined within the test period.

6.5.3 APPLICATION POTENTIAL AND LIMITATION OF THE PREDICTION MODEL

Since the CRA comprises the transport of alkalis through a porous material which is assumed to be a moisture-based process as water in the pores acts as a transport medium for the alkalis, the transport process usually is approximated using diffusion models. To model the CRA, Fick's second law of diffusion usually is adapted by including the re-alkalization coefficient k_{CRA} which is determined by a linear regression of the re-alkalization depth d_{CRA} over the root of time. The value for k_{CRA} corresponds to the slope of the regression line and is given in $\text{mm}/\sqrt{\text{time}}$ and assumes an ideal diffusion process. While previous research on CRA agrees that the process is non-linear, this is not taken into account in the root-time law.

As shown in the present study, this simplified assumption results in an overly simplified representation of the re-alkalization process and ultimately in an incorrect assessment of the re-alkalization potential of the different materials. In order to understand the re-alkalization process more precisely, LIBS measurements were carried out, which, in addition to the indicator tests, enable the investigation of the CRA over time.

Based on the LIBS measurements and the generated depth profiles, the diffusion coefficient $D(\text{RM})$ of potassium was determined after a re-alkalization period of one day as a function of the re-alkalization material. Using the diffusion coefficient, the deviation between the theoretical re-alkalization depths and the measured values could be determined, assuming an ideal diffusion process. The resulting systematic error can be incorporated into the modeling of the re-alkalization process as a time-dependent attenuation factor β .

This factor allows for the consideration of both the potassium concentration at the interface between mortar and concrete, as well as the penetration behavior of potassium into the concrete depending on the re-alkalization material. This allows for the increased alkali transport during the suction phase, which occurs within the first 24 h after mortar application, to be taken into account.

Subsequent processes such as the binding of alkalis in the carbonated concrete and the saturation of the concrete, as well as the depletion of the mortar, lead to a decrease in the re-alkalization rate. This decrease results in an increasing deviation of the re-alkalization process from an ideal diffusion process, which causes it to deviate further from the previously applied root-time law over time. If a continuous, infinite re-alkalization is assumed in the root-time law, the reducing

influence of these processes named above is taken into account when applying the attenuation factor.

Thus, based on the LIBS measurement after one day and the determination of re-alkalization depths at least three time points within 28 days, a material-specific attenuation factor can be calculated, which can be used to model the re-alkalization process. This not only improves the coefficient of determination of the prediction but also requires fewer values that could theoretically be determined within a quick test in the laboratory. Furthermore, by determining the reduction factor, a systematic deviation of the re-alkalization process from the ideal diffusion process could be parameterized for the first time.

The materials differ primarily in their initial attenuation factor during the suction phase, which is influenced not only by the moisture content difference but also by the concentration difference between mortar and concrete. Over time, the attenuation factor of the materials decreases in a similar manner, which presumably reflects less of an influence of the repair mortar than of the concrete, which was the same for all composite systems.

It should be noted that concrete with an extremely high w/b ratio and porosity was selected in order to accelerate the re-alkalization process. However, the determination of the attenuation factor can be applied to cement-based concretes with a lower w/b ratio leading to a lower porosity, as it can be assumed that lower porosity primarily only leads to a slowdown of the CRA. Other factors affecting the attenuation factor, such as the binding of alkalis in the concrete and the effects of the repair material, continue to apply. Finally, it should be noted that according to the present calculations, the re-alkalization process never follows an ideal diffusion process, which would be characterized by an attenuation factor of 1.

Nevertheless, the prediction described is only an approximation of the real data, since the re-alkalization process is underestimated, especially at high potassium concentrations. This discrepancy may be due to the fact that the present data are based on samples that were fully re-alkalized at high potassium concentrations within the 90-day measurement period.

Thus, correlation between the calculated and measured data is only possible to a limited extent, since a precise value for the actual re-alkalization depth cannot be determined with complete re-alkalization. In this case, the d_{CRA} value was assumed to be equal to the carbonation depth, which, however, was only determined using a reference sample. Due to the inhomogeneous structure of concrete, certain deviations in the carbonation depth within a sample are to be expected [20, 30].

6.6 CONCLUSIONS

The present study demonstrates the applicability of LIBS for the quantitative analysis of CRA to derive the material-specific diffusion coefficient, which can be used to calculate an attenuation factor that allows an improvement in the predictability of the re-alkalization process. By comparing the different investigation methods, in addition to the parameterization of the results, further insights into the re-alkalization process and the influence of the different re-alkalization materials could be gained. The main findings can be summarized as follows:

- During CRA, potassium accumulation in the concrete exceeds the concentration equilibrium between concrete and mortar, which indicates binding of potassium in the carbonated concrete. This enrichment occurs at the expense of the repair mortar, which becomes depleted of alkalis in the interface to the concrete.
- Using LIBS measurements, a diffusion coefficient $D(RM)$ can be determined, which can be used to determine the deviation of the re-alkalization process from a process based on Fick's second diffusion law. This deviation can be parameterized as a time-dependent attenuation factor $\beta(t)$.
- By adapting the diffusion law through the attenuation factor, the re-alkalization process in the suction and diffusion phase can be modeled, so that a comparison of the different materials with regard to the expected maximum re-alkalization depth is possible. This is crucial when the alkali concentration in the re-alkalization material is high compared to cement-based mortars, so as not to underestimate the re-alkalization potential of these materials.
- As a result of cyclical irrigation, the re-alkalization mortar is subjected to stress in two directions, which is characterized on the one hand by leaching and on the other hand by the excessive release of alkalis into the substrate.
- Although pre-wetting the concrete influences the absorption behavior of the concrete, this does not directly correlate with the re-alkalization progress during the suction phase of the CRA. A less pre-wetted substrate concrete does not automatically result in faster re-alkalization during the suction phase.

6.7 OUTLOOK

While the present study demonstrates the time-dependent deviation of the CRA from an ideal diffusion process, which can be taken into account by introducing the attenuation factor, the validation of this adaptation should be expanded to more material variations and longer re-alkalization periods. In this context, the alteration effects in the mortar should be investigated in

more detail with regard to their limiting influence on the CRA and, if necessary, quantified in order to further refine the prediction model. The influence of the substrate concrete should also be further investigated to determine the influence of a possible rear-side re-alkalization. For the practical development of CRA, systematic investigations should be carried out with regard to the pre-wetting of the substrate concrete.

Since the re-alkalization mortar is subjected to stress in two directions, the increased leaching of alkalis should be counteracted by optimizing the material. In addition, the influence of carbonation of the repair mortar and its effects on the CRA should also be investigated.

6.8 APPENDIX A

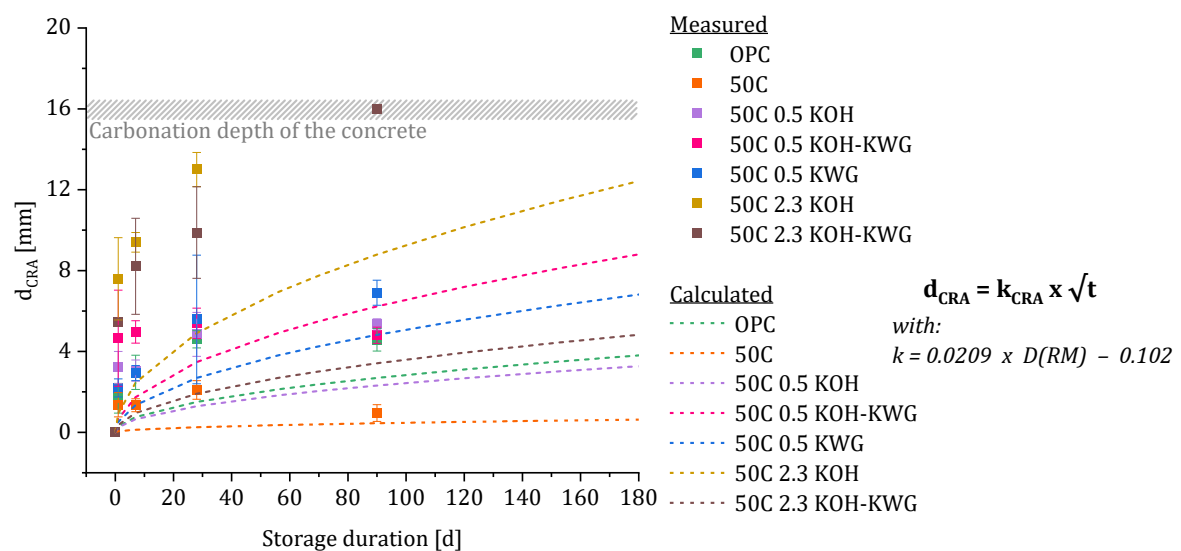


Figure A6-1: Comparison of the measured values and the values which were calculated based on the root-time law using the diffusion coefficient after 1 day to replace the re-alkalization coefficient (determined after 90 days).

Table A6-1: Composition of the LIBS calibration mixtures.

Mix.-No.	Name	CEM I 32.5	CEM I 52.5	Meta- kaolin	KOH _{sol} (50 %)	KWG (Silicate Mo- dulus 1.0)	Water by Solutions	Added Mixing Water	K
g									wt%
1	Ref-0	100	-	-	-	-	-	50	0.656
2	Ref-I	100	-	-	3.75	-	1.875	48.125	1.795
3	Ref-II	100	-	-	7.5	-	3.75	46.25	2.921
4	Ref-III	100	-	-	11.25	-	5.625	44.375	4.018
5	Ref-IV	100	-	-	15.0	-	7.5	42.5	5.070
6	37.5-C	-	62.5	85.0	-	-	-	50.0	0.595
7	25-C	-	75.9	84.0	-	-	-	50.0	0.633
8	12.5-C	-	87.5	83.0	-	-	-	50.0	0.667
9	50-C-0	-	50.0	50.0	-	-	-	50	0.560

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6.9 REFERENCES

- [1] DIN EN 1504-9:2008. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 9: General Principles for the Use of Products and Systems. *Beuth*, (2008) Berlin.
- [2] Deutsches Institut für Bautechnik (DIBt) Technische Regel - Instandhaltung von Betonbauwerken (TR Instandhaltung) - Teil 2: Merkmale von Produkten oder Systemen für die Instandsetzung und Regelungen für deren Verwendung. *Deutsches Institut für Bautechnik (DIBt)*, (2020) Berlin.
- [3] Réus, G. C.; Medeiros, M. H. F., Chemical realkalization for carbonated concrete treatment: Alkaline solutions and application methods. *Construction and Building Materials* (2020) 262, 120880. <https://doi.org/10.1016/j.conbuildmat.2020.120880>
- [4] Jung, A.; Weichold, O., Preparation and characterisation of highly alkaline hydrogels for the re-alkalisation of carbonated cementitious materials. *Soft Matter* (2018) 14, 8105-8111. <https://doi.org/10.1039/C8SM01158C>

- [5] Mukhin, P., (2024) Long-term durability of passive realkalization solution in concrete remediation: A 10-year old field study. Australasian Corrosion Association Conference. *The Australasian Corrosion Association Inc.* Cairns.
- [6] Glawe, C.; Raupach, M., Application of hybrid alkali-activated binders for chemical re-alkalization. *Materials and Structures* (2025) <https://doi.org/10.1617/s11527-025-02732-8>
- [7] Merkel, M., Realkalisierungspotenzial von zementgebundenen Werkstoffen im Trinkwasserbereich. Ph.D. Thesis, Technische Universität Kaiserslautern, (2021) Kaiserslautern, 15.07.2021.
- [8] Wang, Y.; Li, L.; An, M.; Sun, Y.; Yu, Z.; Huang, H., Factors influencing the capillary water absorption characteristics of concrete and their relationship to pore structure. *Applied Sciences* (2022) 12, 2211. <https://doi.org/10.3390/app12042211>
- [9] Bier, T. A., Carbonation and realkalization of cement paste and concrete. Ph.D. Thesis, Universität Fridericiana zu Karlsruhe, (1988) Karlsruhe, 23.12.1987.
- [10] Haardt, P.; Hilsdorf, H. K., (1993) Realkalisierung karbonatisierter Betonrandzonen durch großflächigen Auftrag zementgebundener Reparaturschichten. . *Internationales Kolloquium zum Thema Werkstoffwissenschaften und Bausanierung*. 666-684.
- [11] Wilsch, G.; Weritz, F.; Schaurich, D.; Wiggensauser, H., Determination of chloride content in concrete structures with laser-induced breakdown spectroscopy. *Construction and Building Materials* (2005) 19, 724-730. <https://doi.org/10.1016/j.conbuildmat.2005.06.001>
- [12] Bernal, S. A.; Dhandapani, Y.; Elakneswaran, Y.; Gluth, G. J. G.; Gruyaert, E.; Juenger, M. C. G.; Lothenbach, B.; Olonade, K. A.; Sakoparnig, M.; Shi, Z.; Thiel, C.; Van den Heede, P.; Vanoutrive, H.; von Greve-Dierfeld, S.; De Belie, N.; Provis, J. L., Report of RILEM TC 281-CCC: A critical review of the standardised testing methods to determine carbonation resistance of concrete. *Materials and Structures* (2024) 57, 173. <https://doi.org/10.1617/s11527-024-02424-9>
- [13] Sakoparnig, M.; Galan, I.; Müller, B.; Mittermayr, F.; Juhart, J.; Grengg, C., Optical pH imaging reveals what phenolphthalein conceals—A carbonation study on blended cements. *Cement and Concrete Research* (2024) 186, 107681.
- [14] Plusquellec, G.; Geiker, M. R.; Lindgård, J.; Duchesne, J.; Fournier, B.; De Weerd, K., Determination of the pH and the free alkali metal content in the pore solution of concrete: Review and experimental comparison. *Cement and Concrete Research* (2017) 96, 13-26.
- [15] Ranger, M.; Hasholt, M. T.; Barbosa, R. A., Pore solution alkalinity of cement paste as determined by Cold Water Extraction. *Cement* (2023) 11, 100055.

- [16] Deutsches Institut für Bautechnik (DIBt) Technische Regel - Instandhaltung von Betonbauwerken (TR Instandhaltung) - Teil 1: Anwendungsbereich und Planung der Instandhaltung. *Deutsches Institut für Bautechnik (DIBt)*, (2020) Berlin.
- [17] Thiel, C.; Kratzer, J.; Grimm, B.; Kränkel, T.; Gehlen, C., Effect of internal moisture and outer relative humidity on concrete carbonation. *CivilEng* (2022) 3, 1039-1052. <https://doi.org/10.3390/civileng3040058>
- [18] Loehmannsroebe, H.-G.; Roch, T.; Schaefer, R.; Schultze, R.; Vereecken, H., (1997) Laser-induced fluorescence (LIF) spectroscopy for in-situ analysis of fluorescence tracers in water and soils. *SPIE*. <https://doi.org/10.1117/12.274737>
- [19] Courard, L.; Lenaers, J.-F.; Michel, F.; Garbacz, A., Saturation level of the superficial zone of concrete and adhesion of repair systems. *Construction and Building Materials* (2011) 25, 2488-2494. <https://doi.org/10.1016/j.conbuildmat.2010.11.076>
- [20] Glawe, C.; Georget, F.; Raupach, M.; Matschei, T., Multi technique characterization of the carbonation affected zone including non-destructive single sided ^1H NMR *Cement and Concrete Research* (2024) 178, 107438. <https://doi.org/10.1016/j.cemconres.2024.107438>
- [21] Šavija, B.; Schlangen, E.; Pacheco, J.; Millar, S.; Eichler, T.; Wilsch, G., Chloride ingress in cracked concrete: a laser induced breakdown spectroscopy (LIBS) study. *Journal of Advanced Concrete Technology* (2014) 12, 425-442. <https://doi.org/10.3151/jact.12.425>
- [22] Molkenhuth, A., Laser-induzierte Breakdown Spektroskopie (LIBS) zur hochauflösenden Analyse der Ionenverteilung in zementgebundenen Feststoffen. Ph. D. Thesis, Universität Duisburg-Essen, (2009) Essen, 12.11.2008.
- [23] Pourbozorgi Langroudi, P.; Kapteina, G.; Illguth, M., Automated distinction between cement paste and aggregates of concrete using laser-induced breakdown spectroscopy. *Materials* (2021) 14, 4624. <https://doi.org/10.3390/ma14164624>
- [24] Ziehensack, E.; Keßler, S.; Angst, U.; Hilbig, H.; Gehlen, C., Diffusion potentials in saturated hardened cement paste upon chloride exposure. *Mater Struct* (2023) 56, 100. <http://doi.org/10.1617/s11527-023-02184-y>
- [25] Mateo, J.; García, M. C.; Roderio, A., Using laser-induced breakdown spectroscopy for the study of chloride diffusion in mortar and concrete. *Construction and Building Materials* (2023) 385, 131520. <https://doi.org/10.1016/j.conbuildmat.2023.131520>
- [26] Mangat, P. S.; Molloy, B. T., Prediction of free chloride concentration in concrete using routine inspection data. *Magazine of Concrete Research* (1994) 46, 279-287. <https://doi.org/10.1680/mac.1994.46.169.279>

- [27] Glawe, C.; Raupach, M., Basics and new opportunities for chemical re-alkalisation of carbonated concrete, including alkali-activated binders. *Magazine of Concrete Research* (2024) 76, 1185-1197. <https://dx.doi.org/10.1680/jmacr.24.00026>
- [28] Zajac, M.; Song, J.; Ullrich, P.; Skocek, J.; Ben Haha, M.; Skibsted, J., High early pozzolanic reactivity of alumina-silica gel: A study of the hydration of composite cements with carbonated recycled concrete paste. *Cement and Concrete Research* (2024) 175, 107345. <https://doi.org/10.1016/j.cemconres.2023.107345>
- [29] De Weerd, K.; Plusquellec, G.; Revert, A. B.; Geiker, M.; Lothenbach, B., Effect of carbonation on the pore solution of mortar. *Cement and Concrete Research* (2019) 118, 38-56. <https://doi.org/10.1016/j.cemconres.2019.02.004>
- [30] Georget, F.; Soja, W.; Louise Scrivener, K., Characteristic lengths of the carbonation front in naturally carbonated cement pastes: Implications for reactive transport models. *Cement and Concrete Research* (2020) 134, 106080. <https://doi.org/10.1016/j.cemconres.2020.106080>

7. MODELING THE CHEMICAL RE-ALKALIZATION OF CONCRETE BY APPLICATION OF ALKALINE MORTARS

7.1 ABSTRACT

Since the number of existing steel-reinforced concrete buildings affected by carbonation-induced corrosion is steadily increasing, there is a high demand for durable repair methods. Chemical re-alkalization (CRA) represents one such approach, relying on the transport of alkaline pore solution from a repair mortar into carbonated concrete. With the introduction of clinker-reduced binder systems such as hybrid alkali-activated binders (HAABs), their suitability for CRA and governing material parameters require further clarification. In this study, material-related chemical and structural influences on CRA were investigated using an adapted form of Fick's second law of diffusion, incorporating a time-dependent attenuation factor, $\beta(t)$. The CRA progression was evaluated over 28 days, distinguishing between an initial suction phase and a subsequent diffusion phase. The results show that a high initial alkalinity of the mortar pore solution ($\text{pH} > 14$) significantly enhances re-alkalization during the suction phase, reflected by suction factors $a > 1$. In contrast, progression during the diffusion phase is primarily governed by the potassium concentration gradient at the mortar-concrete interface, while structural parameters such as capillary porosity show no systematic correlation with the deceleration factor b ($-0.46 \leq b \leq -0.26$). The findings indicate that, within the investigated range, mortar pore solution chemistry has a stronger influence on CRA than structural properties, providing guidance for the targeted design of alkaline repair mortars.

7.2 INTRODUCTION

The repair of carbonation-induced corrosion in steel-reinforced concrete structures is one of the fundamental tasks that promote the maintenance and rehabilitation of existing buildings. In addition to chloride-induced corrosion, the carbonation of concrete is the most common durability-reducing process in the case of steel-reinforced concrete. There are different repair methods that can prevent carbonation from progressing further in the direction of steel reinforcements and also restore the passivity of reinforcements. Chemical re-alkalization (CRA) is one of these methods and consists of the application of an alkaline repair mortar on carbonated concrete to introduce an alkaline pore solution from the mortar into the concrete to increase the pH of the concrete's pore solution. CRA represents a repair method aimed at extending the service life of existing steel-reinforced concrete building structures without extensive concrete removal to contribute to resource-efficient and durable rehabilitation measures.

To be used as a repair material for CRA, a mortar must meet various requirements, which are defined in [1, 2]. Above all, the mortar must be able to mobilize alkalis for their transport into the concrete. If the carbonation depth is increased to up to 40 mm, which is the maximum carbonation depth to be re-alkalized by CRA according to German guidelines for repair [3], alkalis must be available over a specific period of time to ensure high penetration depths. In the case of cement-based mortars, the pore solution remains highly alkaline for a long period of time [4, 5]. The hydration of OPC forms a pore solution saturated with Ca(OH)_2 , which can typically have a pH of up to 13 [6]. Even if carbonation leads to the binding of Ca(OH)_2 during the formation of carbonates (CaCO_3), this can be buffered by its solid form, portlandite, and later by the decalcification of the C-S-H phases [7, 8].

The use of clinker-reduced to clinker-free binders leads to a different composition of the pore solution, which means that the suitability of these binders for use in repair mortars cannot always be assumed. However, alkaline activation of these binders can create a high pH value that can be maintained over a longer period of time [9]. Nevertheless, it remains to be clarified whether a high pH value indicates a mortar's suitability for chemical re-alkalization. Initial studies on the use of cement-reduced and alkali-activated binders are available that confirm their suitability for chemical re-alkalization [10, 11]. In these hybrid alkali-activated binders (HAAB), the cement is substituted by metakaolin to 50%, while sufficient strength is ensured by alkaline activation using potassium hydroxide and water glass. Within the scope of this work, CEM I was used as a reference binder with a well-established pore solution chemistry, while partial substitution by metakaolin in the investigated hybrid alkali-activated binders was intentionally applied to systematically modify the binder's chemistry in order to investigate its influence on the chemical re-alkalization process [4, 12-14].

To date, investigations on the use of hybrid alkali-activated binders as repair mortars for CRA are limited. Existing studies have primarily focused on the achievable re-alkalization depths under defined laboratory conditions, including variations in carbonation depth, while the influence of environmental conditions and different concrete substrate properties has not yet been systematically addressed. In contrast, when using cement-based mortars, the influence of ambient humidity on CRA has been predominantly investigated [15, 16]. Using HAABs for re-alkalization mortars, re-alkalization depths of up to 33 mm can be achieved under specific conditions, such as cyclic watering for concretes with extremely high porosity [11]. Compared to OPC-based mortars, for which a maximum re-alkalization depth of only 14 mm has been demonstrated so far, the use of HAABs allows for a significant increase in the maximum re-alkalization depth [17]. However, since it is currently assumed in a German guideline that non-carbonated concrete can re-alkalize

in so-called rear-sided re-alkalization at up to 20 mm, a re-alkalization depth of 15 mm through the mortar would be sufficient, e.g., with a typical concrete cover of 35 mm [1, 18]. Rear-sided re-alkalization, however, has not yet been reported. During the re-alkalization process, the re-alkalization rate changes as a function of time, resulting in a non-linear progression of the process. The progression of CRA when using HAABs is primarily characterized by a strong progression during the first 24 h after mortar application, also referred to as the suction phase [10, 19]. The suction phase involves a combination of moisture and concentration gradients between mortar and concrete, leading to pronounced transport after mortar application. The transport mechanism during this phase is often referred to piggyback transport, which describes the convective penetration of alkalis dissolved in water in the form of the mortar pore solution [20, 21]. Different re-alkalization depths have been observed depending on the applied mortar, suggesting a strong dependence on the mortar used during the suction phase of CRA. Accordingly, a high initial alkalinity in the form of a high pH value is crucial for the course of CRA, but no pH values are yet available for the HAABs used.

Comparing CRA progression when using HAABs with that when using cement-based binders, the latter exhibits a less pronounced suction phase [19]. This can be explained by a slower pH adjustment, which, in the case of HAABs, is immediately present due to the addition of strongly alkaline solutions to the freshly prepared mortar and results in steep concentration gradients between the mortar and concrete shortly after mortar application [22, 23]. While such a pronounced suction phase may suggest strong alkali depletion in the mortar, available observations indicate that it does not necessarily result in a stronger deceleration during the subsequent diffusion phase. Instead, the progression of CRA in the later state appears to remain governed by the prevailing concentration gradient at the mortar–concrete interface. In comparison, CRA progression when using cement-based mortars shows a more steady re-alkalization process, which, although slower, also shows increasing re-alkalization depths over longer time periods, which is defined as the diffusion phase [19]. Although Merkel already distinguished between the suction phase and the diffusion phase based on the temporal evolution of the re-alkalization depth, no standardized methodology exists for the distinction of these two phases [19]. Furthermore, no established model or formula is currently available that enables the selection or optimization of repair mortars for CRA based on quantitative differentiation of these phases.

As the mortar hardens, not only the pH value but also the structure of the binder is assumed to influence the transport of alkalis from the mortar into the concrete, as well as the structure of the concrete [10, 24]. As the re-alkalization period progresses, not only does the availability of alkalis

decrease, but the developing microstructure of the mortar also influences the re-alkalization progress. Glawe et al. summarized this as an attenuation factor $\beta(t)$, which describes the time-dependent systematic deviation of the transport processes during CRA from ideal diffusion [10]. The temporal evolution of the attenuation factor follows the power law $\beta(t) = a * t^b$, which is used to adapt Fick's second law of diffusion to the CRA. Through the variations in a and b , Figure 7-1 clearly shows which part of CRA is primarily influenced by each respective factor.

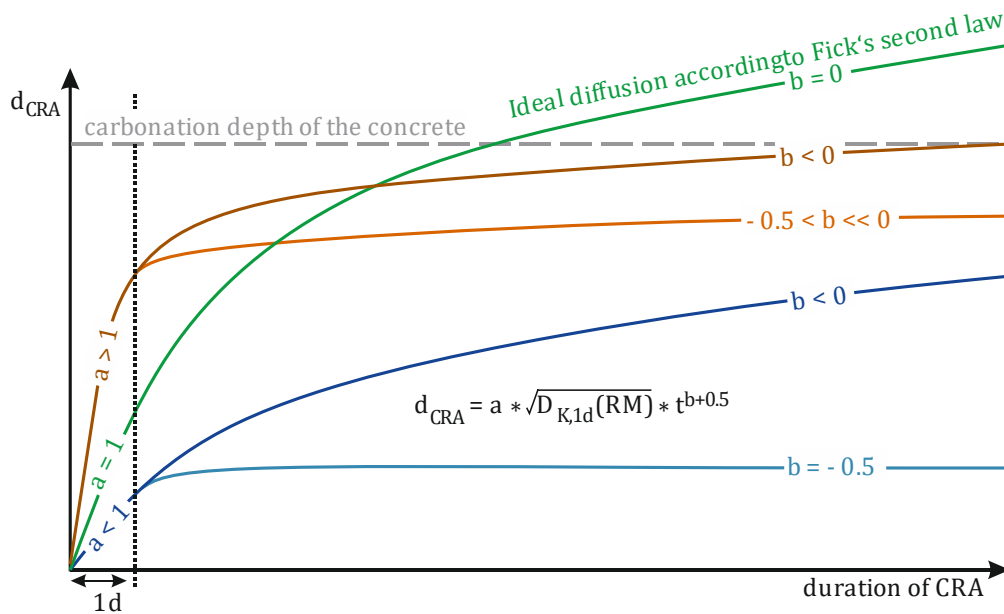


Figure 7-1: Schematic representation of the adapted diffusion law by Glawe et al. and the impacts of the material-specific factors a and b on the time-dependent evolution of d_{CRA} [10].

Factor a determines the initial course of CRA within the suction phase. This assumes that the CRA is only considered after one day. Since data on the CRA at a time before one day is generally unavailable, it is not represented in detail by the adapted equation. However, the results of Glawe et al. clearly demonstrate that this simplified assumption does not lead to excessive loss of plausibility regarding the calculated re-alkalization depths at a later time. Since a can also be understood as a suction factor for the diffusion coefficient $D_{K,1d}(RM)$ of potassium in the substrate concrete after 1 day of CRA, depending on the applied repair mortar, a value of 1 equals ideal diffusion, while $a < 1$ results in a comparably lower d_{CRA} and $a > 1$ in a higher d_{CRA} at the end of the suction phase. In a first assumption based on the investigations of Glawe et al., a is influenced by the applied mortar, as it is proportional to its potassium content [10].

Therefore, factor b defines the extent to which the progression of the CRA after the suction phase is retarded compared to ideal diffusion and can be understood as a deceleration factor. In case $b = -0.5$, this would mean that the final d_{CRA} equals the d_{CRA} that was achieved at the end of the suction phase. A value between 0 and -0.5 results in ongoing CRA after the suction phase and during the diffusion phase, where the final re-alkalization depth is limited by the carbonation depth of the concrete but is reached after different amounts of time. In the investigation of Glawe et al., the value for b was relatively lower in the case of $a > 1$, leading to a stronger retardation of the CRA after the suction phase, during which a high d_{CRA} was already achieved [10]. However, the results of Glawe et al. did not reveal a clear correlation between the applied mortar and b and also assumed that variation in the progression of the CRA after the suction phase corresponded to the completed formation of the microstructure in the mortar. However, a quantification of the structural influence has not yet been undertaken.

In general, Glawe et al. mentioned further influences on the attenuation factor, namely alkali depletion in the mortar and alkali binding in the concrete [25]. The latter was primarily investigated by Réus et al., who showed clear binding of penetrating alkalis in the carbonated concrete, dependent on the concrete composition [24]. However, for these investigations, an alkaline solution was used instead of mortar as the re-alkalization material. In the present study, the concrete substrate was intentionally kept constant in order to isolate the influence of repair mortar properties on the re-alkalization process. While the role of concrete composition on alkali binding has been addressed in previous studies, the present work focuses on mortar-related contributions to the attenuation of alkali transport [24].

This study is not intended to evaluate the overall performance of a specific repair system, but instead to identify material-related, re-alkalization-relevant properties. For this, the adapted diffusion model is not further developed in this study but instead used as a fixed analytical framework to relate material properties of the mortar and the mortar–concrete composite system to the suction factor a and the deceleration factor b . In addition to measuring the changes in the pH and electrical conductivity of the pore solution, the structural influences of the binders in the form of the formation factor and the porosity of the repair mortar on the re-alkalization process are investigated to determine their influences on the suction and deceleration factors. Furthermore, data from previously published studies on alkali concentration in HAAB-based mortars and substrate concrete during CRA are re-evaluated and discussed to complement the experimental findings of this work. By quantitatively linking mortar characteristics with the process-defining parameters a and b , the present study provides a basis for the targeted design of repair mortars for CRA.

7.3 MATERIALS AND METHODS

The investigated materials are based on previous investigations by Glawe et al. in order to enable correlation of the present study and existing data [10, 11]. Therefore, the used materials consisted of five mixtures of HAABs and one reference mixture without additional alkali activation. For alkali activation, a 50 % potassium hydroxide solution (KOH) and a potassium water glass (KWG) (silicate modulus = 1.0) were used. All mixtures contained 50 wt% CEM I 52.5 R and 50 wt% metakaolin, for which oxide compositions are given in Table 7-1.

Table 7-1: Oxide composition of the used materials.

Component	Unit	CEM I 52.5 R	Metakaolin
SiO ₂		20.21	60.97
Al ₂ O ₃		5.61	35.01
Fe ₂ O ₃		2.15	1.26
MnO		0.06	0.00
TiO ₂		0.33	1.63
P ₂ O ₅		0.28	0.04
CaO	wt%	64.46	0.24
MgO		1.57	0.13
K ₂ O		1.00	0.51
Na ₂ O		0.11	0.06
SO ₃		3.85	0.04
Sum		99.63	99.92
LOI		2.60	1.03

Both paste and mortar samples were prepared for the investigations. The paste samples were used to obtain the pore solution of the mixtures by extraction for the determination of the pH value and the electrical conductivity while the mortar samples were investigated regarding the pore structure as well as the electrical resistivity. The testing procedure is shown in Figure 7-2.

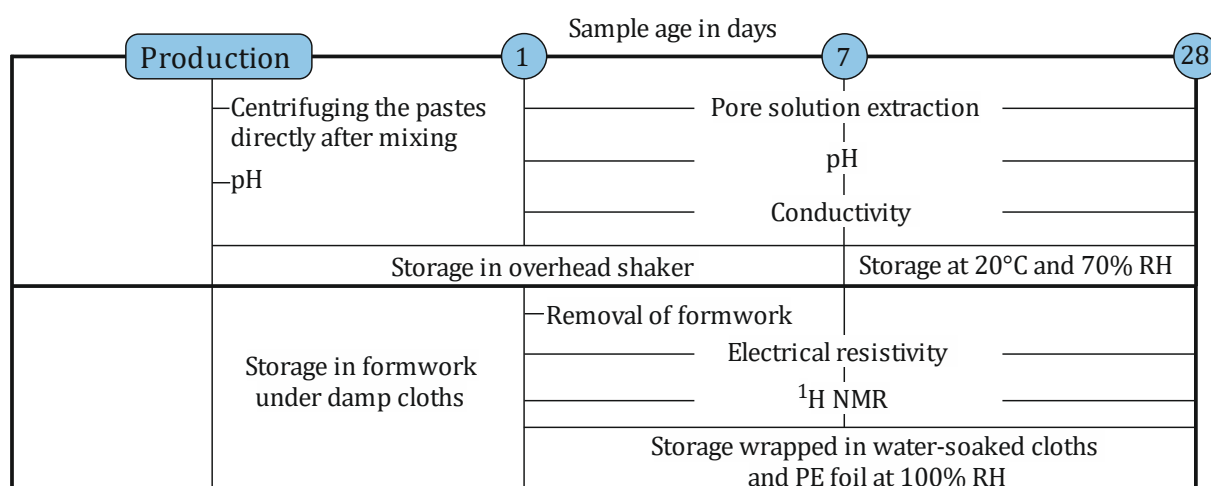


Figure 7-2: Overview of the experimental procedure applied on the mortar samples and the pore solution obtained by pore solution expression (PSE).

The compositions of the paste and mortar samples are given in Table 7-2 and Table 7-3. To ensure comparability, the w/b of 0.58 was the same for all mixtures. The activator solutions were considered in the w/b ratio in such a way that the dissolved solids, such as KOH and SiO₂, were included in the binder component, while the water for preparing the solution was included in the liquid components.

Table 7-2: Mixtures of the investigated pastes based on [10].

		50C	50C 0.5 KOH	50C 0.5 KOH KWG	50C 0.5 KWG	50C 2.3 KOH	50C 2.3 KOH-KWG
Cement Type	-	CEM I 52.5 R					
Cement		534.7	522.3	520.6	518.9	467.9	459.5
Metakaolin		534.7	522.3	520.6	518.9	467.9	459.5
Water	kg/m ³	624.6	599.2	596.5	593.8	488.1	475.9
KOH _{sol} (50%)		-	52.2	26.0	-	280.7	137.9
Potassium Waterglass (silicate modulus = 1.0)		-	-	34.7	69.1	-	183.7
w/b		0.58					
Potassium in fresh paste (calculated)	wt%	0.40	1.46	1.45	1.44	6.08	5.93

Table 7-3: Mixtures of the investigated mortars based on [10].

		50C	50C 0.5 KOH	50C 0.5 KOH KWG	50C 0.5 KWG	50C 2.3 KOH	50C 2.3 KOH KWG
Cement Type	-	CEM I 52.5 R					
Cement		225.3	223.0	222.7	222.4	212.4	210.7
Metakaolin		225.3	223.0	222.7	222.4	212.4	210.7
Aggregates							
0.0–0.25 (quartz powder)	kg/m ³	355.5	341.2	340.7	340.3	324.9	322.3
0.1–2.0		996.1	996.8	995.5	994.1	949.2	941.7
Water		263.1	255.8	255.2	254.5	221.5	218.2
KOH _{sol} (50%)		-	22.3	11.1	-	127.4	63.2
Potassium Waterglass (silicate modulus = 1.0)		-	-	14.8	29.6	-	84.2
w/b		0.58					
Potassium in fresh mortar (calculated)	wt%	0.14	0.50	0.50	0.50	2.3	2.3

For simplicity, the names of the mixtures were adopted from Glawe et al., where 0.5 and 2.3 represent the potassium concentration in the fresh mortar. Although this is not the case for the paste samples, the consistent names allow for better comparability of the results.

The paste samples were produced by first homogenizing the dry components and the wet components separately and then mixing all components together by stirring for 2 min. To determine the pH value of the mixture directly after the mixing process, the fresh mixture was filled into plastic centrifuge tubes and centrifuged for 5 min at 2000 rpm. After the centrifugation, the settled solution was transferred into a 50 mL plastic bottle flooded with argon to prevent any carbonation of the solution until the time of measurement, which was a few minutes after sample production.

For the analyses of the pore solutions at further time points, the pastes were transferred into 250 mL plastic bottles flooded with argon. For each mixture, 3 bottles were filled with the paste for investigations 1, 7 and 28 days after production. The bottles were sealed by placing PE foil over the bottle opening before screwing the lid. To prevent any sedimentation during the hardening of the pastes, the bottles were placed in an overhead shaker and were shaken at 5.5 rpm. The bottles containing the samples for the investigations after 1 day were shaken for 24 h, while the samples for the 7- and 28-day measurements were shaken for 7 days. For the samples measured after 28 days, the bottles were stored at 20 °C and 70 % RH.

The structural investigation was conducted using mortar samples. The components were mixed in the same way as during the production of the pastes. After mixing, the fresh mortar was transferred into a disk-shaped formwork with a diameter of 100 mm and a height of 20 mm. As the investigation of the pore structure as well as the resistivity measurements were non-destructive procedures, for the three measuring times of 1, 7 and 28 days of sample age, only one sample set consisting of three samples was produced for each mixture.

After transferring the fresh mortar into the formwork, the samples were sealed with damp cloths and PE foil to prevent the samples from drying out. The mortar disks were taken out of the formwork after 24 h, wrapped in damp cloths and PE foil and were additionally stored at 100 % RH until the measurements to ensure water saturation.

7.3.1 EXTRACTION OF THE PORE SOLUTION

The extraction of the pore solution was conducted on the prepared paste samples after 1, 7 and 28 days. For the extraction process, the samples were cut out of the plastic bottles and were placed in an adapted compression testing machine, which enabled the collection of the squeezed pore solution. The compression device is schematically shown in Figure 7-3. Before each extraction process, all surfaces of the compression machine were cleaned using isopropanol and distilled water.

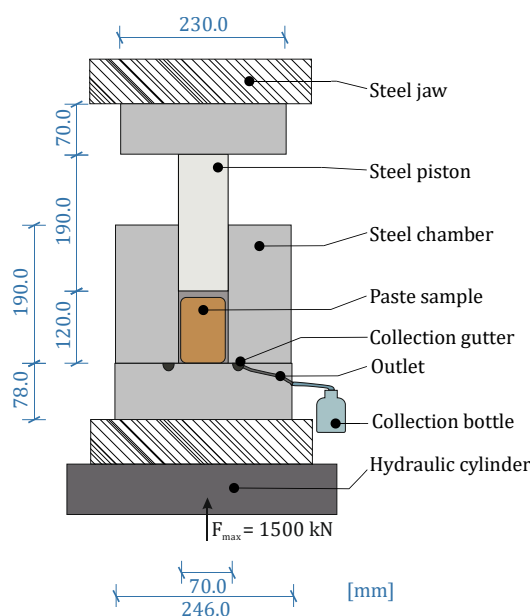


Figure 7-3: Schematic representation of the pore solution extraction device.

After placing the paste sample in the sample chamber, the pressure piston was introduced into the sample chamber from the top. The piston was moved at a loading speed of approximately 5 kN/s up to the maximum load of 1500 kN. During the compression process, the extracted pore solution was collected in an argon-filled plastic bottle, which was connected to the sample chamber. After each extraction process, the sample was measured immediately.

7.3.2 MEASUREMENTS ON THE EXTRACTED PORE SOLUTIONS

The centrifuged and extracted pore solutions were measured for their pH and electrical conductivity. The pH was measured using a pH meter 1140 (METTLER TOLEDO, Columbus, OH, USA). The results of the conductivity measurements were used to calculate the formation factor according to [26]. As the calculation of the formation factor was based on the ratio of the electrical resistivity of the pore solution and of the mortar disks, it presupposes a hardened mortar disk. Therefore, no measurements of resistivity in the centrifuged pore solutions were conducted, as no corresponding hardened mortar disks were available directly after mixing the mortar components.

In the case of the pore solutions extracted after 1 day, electrical conductivity could not be measured using a conventional conductivity electrode. The electrode which was used in these measurements was a microprocessor conductivity meter LF 2000 (WTW). In order to still be able to determine the conductivity values, a newly developed measuring cell was used which was based on a 4-electrode method (compare Figure 7-4).

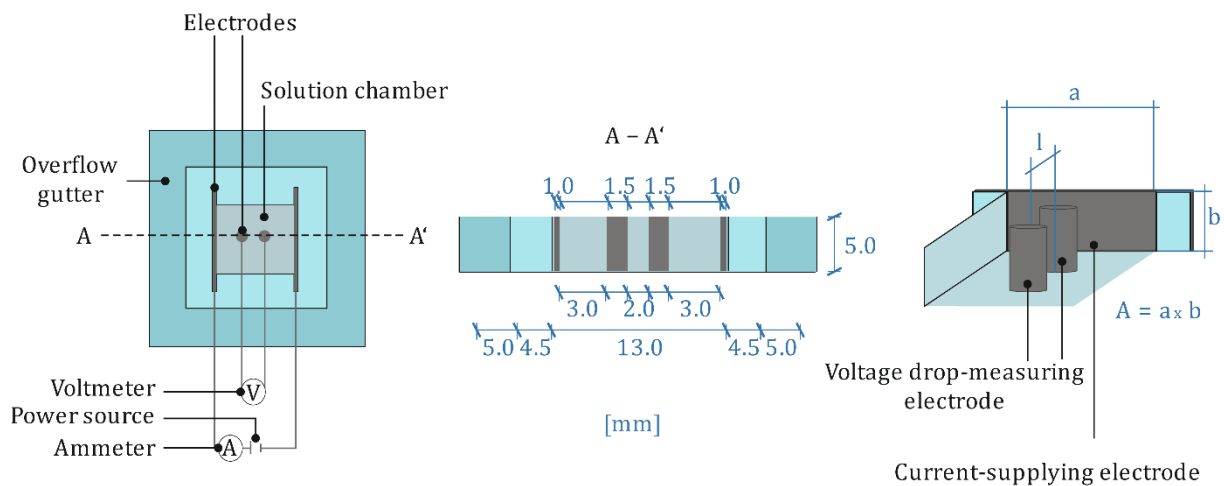


Figure 7-4: Measuring cell for the resistivity measurements of the pore solutions.

The measuring cell consists of two sample chambers, which are filled with the pore solution to be measured. An alternating current is introduced via the two outer electrodes, which allows the measurement of the electrical resistance between the two inner electrodes resulting from the pore solution. Following the relationship in Equation (1) to calculate the electrical resistivity,

$$\rho = R * \frac{A}{l} \quad (1)$$

the electrical conductivity (σ) can be calculated using Equation (2) based on the measured electrical resistance (R), taking into account the geometry factor of the measuring cell (A/l).

$$\sigma = \frac{1}{\rho} \quad (2)$$

The geometry factors for the two measuring cells are 0.0128 and 0.0131 m, respectively. For the pore solutions that could not be measured using the conductivity electrode, extracted pore solutions were measured in both cells, and the resulting conductivity was calculated by averaging the two measurements.

7.3.3 MEASUREMENTS ON THE MORTAR DISKS

Mortar disks with a diameter of 100 mm and a thickness of 20 mm were measured regarding their electrical resistivity as well as their porosity in a water-saturated state. Three samples were measured for each mixture. For the resistivity measurements, a two-electrode method was used at 10.000 Hz. The coupling of the electrodes was ensured by wet cloths, which were placed between the electrodes and the sample surface.

To determine the formation factor, the measured resistivity was converted into the electrical conductivity according to Equation (2). The geometry factor was calculated by dividing the contact area, which corresponds to the cross-sectional area of the electrodes, by the height of the disk, which defines the distance between the two electrodes during the measurement.

Finally, the formation factors (FF) of the mortars were calculated using Equation (3) by dividing the electrical conductivity of the pore solution, $\sigma_{\text{Pore Solution}}$, by the electrical conductivity of the pore mortar, σ_{Mortar} .

$$FF = \frac{\sigma_{\text{Pore Solution}}}{\sigma_{\text{Mortar}}} = \frac{\rho_{\text{Mortar}}}{\rho_{\text{Pore Solution}}} \quad (3)$$

The mortar disks were further analyzed using single-sided ^1H NMR to obtain the porosity of the different materials at sample ages of 1, 7 and 28 days. As these measurements were conducted in the water-saturated state, we could use the same samples that we used for the measurement of the mortar resistivity.

For the NMR measurements, the NMR MOUSE PM25 (Magritek, Aachen, Germany) was used, which allows a maximum measuring depth of 25 mm at a radio frequency of 13.12 MHz.

A CPMG measurement sequence was selected, which enables data acquisition in different measuring depths. For the present study, only one measuring depth in the center of the sample at 10 mm was used to exclude any cross-sectional anomalies caused by the low thickness of the mortar disks.

At a 10 mm depth, a CPMG sequence with 1024 scans and 200 echoes, with an echo time of 0.158 ms and a recycle delay of 500 ms, was used. The pulse lengths of the 90° and 180° pulses during the measurement were 10 μs . The 180° pulse was amplified by 6 dB to maintain the size of the sensitive volume during the measurement. Using these settings, a signal-to-noise ratio (S/N) of 93.9 was achieved, which was calculated by dividing the amplitude of the first echo by the standard deviation of the last 20 echoes [27].

The resulting data are represented in the form of an exponential decay curve, which was evaluated regarding the total porosity as well as the pore types by differentiating capillary pores and gel pores within the sensitive volume. To calculate the proportion of the different pore types, the decay curve was described by the sum of two decaying exponentials using Equation (4), which were transformed into a distribution of the amplitudes (A_i) of the different relaxation times ($T_{2,i}$) using the inverse Laplace transformation (ILT).

$$S(t) = \sum A_i e^{-t/T_{2,i}} \quad (4)$$

The resulting T_2 distribution spectrum is related to the pore-size distribution, as the T_2 is governed by the surface-to-volume ratio of the pores and the surface relaxivity.

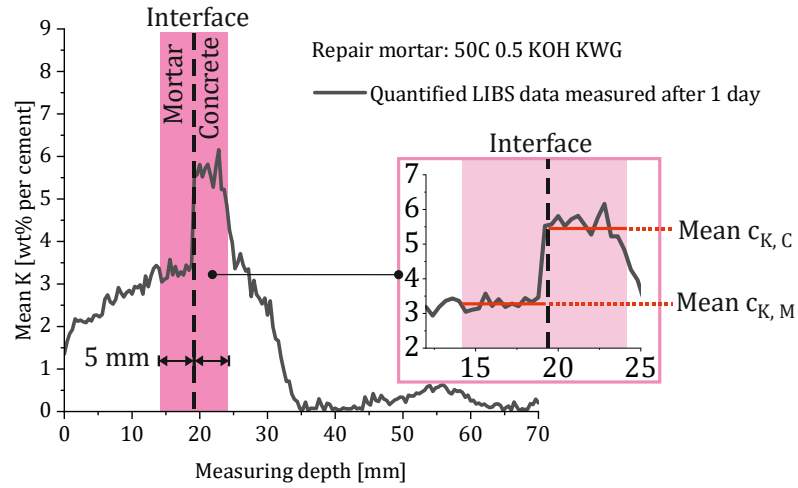
The relaxation time distribution was divided into two pore domains, with a cut-off at 1 ms to distinguish between gel and capillary pores, corresponding to an often-assumed boundary between these two pore types in cementitious materials, which were used as a reference in the

first approach due to the 50% cement content in the mixtures used, since no explicit values for differentiating different pore types are available for the materials at hand [27, 28]. To quantify the relative pore water content as a measure of total porosity, the integrated amplitudes were normalized by the maximum amplitude of pure water, which was 3493 using the settings mentioned above [29].

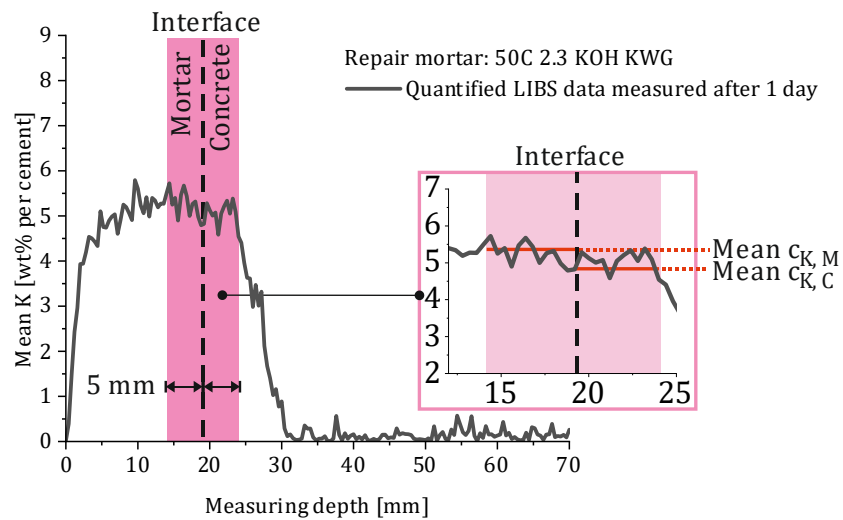
7.3.4 RE-EVALUATION OF PREVIOUSLY PUBLISHED LIBS PROFILES OF THE MORTAR AND CONCRETE POTASSIUM CONCENTRATION

To investigate the relationship between the potassium concentration of both the mortar and the concrete in the progression of CRA, the concentration gradients between the mortar and concrete were evaluated. The mean potassium concentration at the different measuring times after 1, 7 and 28 days of CRA was calculated based on the profiles measured by Glawe et al. using laser-induced breakdown spectroscopy (LIBS) [10].

Since the potassium concentration shows a strong variation in the full cross-sectional area of the concrete and the mortar, the values were calculated based on the potassium concentration in a limited interfacial area of the composite systems to exclude external influencing factors such as leaching of the mortar. Figure 7-5 shows an example representation of the calculation of the mean potassium concentration of the mortar and the concrete in the interfacial area, for which a distance of 5 mm from the mortar–concrete boundary was defined as the limit.



(a)



(b)

Figure 7-5: Schematic representation of the calculation of the potassium concentration at the interface area of concrete and mortar with different states of the concentration gradient, e.g., (a) concrete has a higher potassium concentration than mortar, (b) mortar has a higher potassium concentration than the concrete.

In the investigated composite systems, two main cases regarding the concentration gradients between mortar and concrete were observed. Both cases are illustrated in Figure 7-5 (a) and (b). The case shown in Figure 7-5 (a) involves the mortar having a higher potassium concentration than the concrete, and the other (see Figure 7-5 (b)) shows a lower potassium concentration in the concrete compared to the mortar. It can already be stated at this point that the unusual phenomenon of the potassium concentration in the concrete being higher than that in the mortar is consistent with the subsequent development of re-alkalization over time, as discussed later. However, it is important to consider that the LIBS analysis method used for the determination of the potassium concentration measures a combination of potassium in the solid state and potassium dissolved in the pore solution of the material.

Using the calculated values for $c_{K,M}$ and $c_{K,C}$, the concentration gradient of potassium, $\Delta c_K(t)$, was calculated according to Equation (5) for the values of 1, 7 and 28 days.

$$\Delta c_K(t) = c_{K,M}(t) - c_{K,C}(t) \quad (5)$$

Based on the values for Δc_K of each mortar–concrete combination, the potassium concentration gradient decay rate (CGDR_K) was calculated using Equation (6).

$$CGDR_K = \frac{\Delta c_K(28 \text{ d}) - \Delta c_K(1 \text{ d})}{28 - 1} \quad (6)$$

The CGDR_K of the time periods of 1 to 7 and 7 to 28 days was calculated equally. The resulting values for CGDR_K quantify the rate at which the potassium concentrations in the mortar and the concrete equalize over the different durations of CRA of 6, 21 and 27 days.

7.4 RESULTS

The adaption of Fick's second law of diffusion to the progression of the CRA is based on the attenuation factor $\beta(t)$, which is defined by the two factors a and b . Previous studies by Glawe et al. have shown that both factors depend on the mortar used, which is applied to the substrate concrete [10]. However, no direct correlation has yet been established between specific material properties and factors a and b .

In the following results, the material properties of mortar and concrete are systematically correlated with these two factors in order to determine their influences on CRA. The values for the factors which were determined by Glawe et al. are given in Table 7-4.

Table 7-4: Values for the factors a and b taken from [10].

	50C	50C 0.5 KOH	50C 0.5 KOH KWG	50C 0.5 KWG	50C 2.3 KOH	50C 2.3 KOH KWG
a	0.507	0.781	0.773	0.398	1.078	1.165
b	-0.435	-0.445	-0.462	-0.261	-0.361	-0.308

should be noted in all considerations that the values were determined using laboratory samples that were not applied as a repair layer to concrete. The exception to this is the determination of the mean potassium concentration in the mortar and concrete layer, which was measured by LIBS on mortar applied to concrete.

Due to transport processes during CRA, changes in other mortar properties or pore solution properties, in addition to changes in potassium concentration, must also be assumed, which are not considered in this study.

The number of analyzed specimens (n) is given in the caption of each figure. For the correlation, error bars are not shown, as correlated parameters were derived from single-specimen measurements or mean values to indicate trends rather than provide statistically robust relationships. Unless stated otherwise, measurements of the pore solution properties (pH value and conductivity), mortar porosity and LIBS-based potassium concentration profiles were performed on a single specimen for each mortar composition. Electrical resistivity measurements of the hardened mortars were conducted on three replicate specimens, and the corresponding formation factors were calculated accordingly.

7.4.1 CHEMICAL CHARACTERIZATION OF THE REPAIR MORTARS

The investigation of the influence of the chemical properties of mortar on CRA was carried out using the pH value and the electrical conductivity of the pore solution.

The temporal changes in the pH and the electrical conductivity of the pore solution of the materials are shown in Figure 7-6 and Figure 7-7. The measurements were conducted on one sample for each mixture. Regarding the changes in the pH over time, the mixtures can be divided into two groups. The non-activated 50C mixtures and the mixtures with a mortar potassium content of 0.5 wt% showed similar behaviors, as the pH increased between the fresh-state sample and the sample aged by 1 day. The second group consists of the mixtures which were alkali-activated, resulting in a potassium content of 2.3 wt%, showing the highest pH in the fresh state, which then decreased with increasing sample age. However, a higher potassium concentration resulted in a higher pH for the pore solution, giving the mixtures with 2.3 wt% the highest pH in

the fresh state, with values over 14, as well as after 28 days, while the non-activated mixture showed the lowest pH values, which dropped below 12.5 after 28 days. The mixtures with the lower potassium concentration of 0.5 showed a similar behavior, although different activator solutions were used.

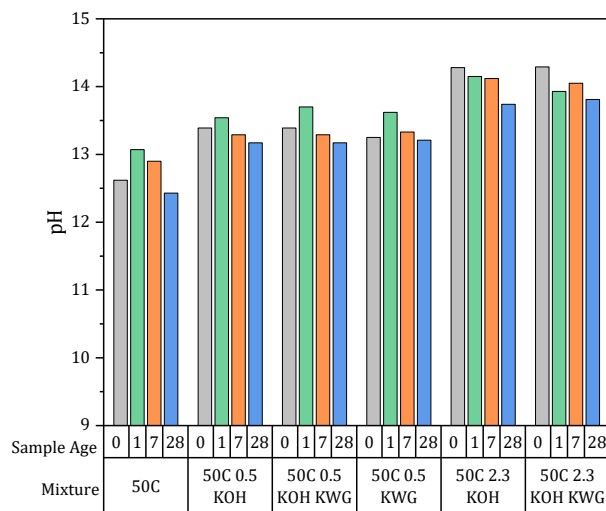


Figure 7-6: pH values of the different mixtures in the fresh state and after 1, 7 and 28 days ($n = 3$).

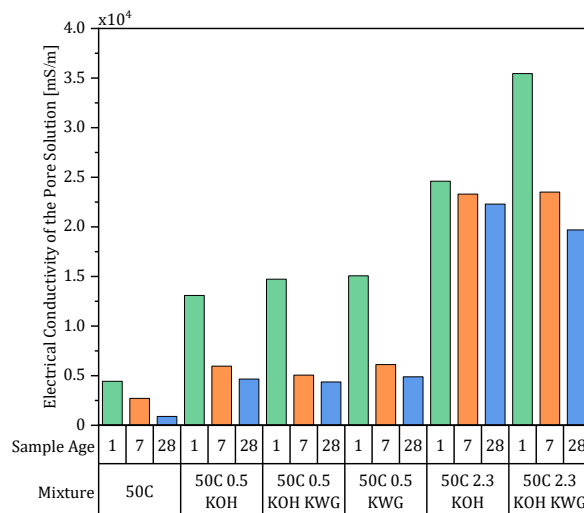


Figure 7-7: Electrical conductivity of the different mixtures after 1, 7 and 28 days ($n = 1$).

Since the electrical conductivity was primarily measured to calculate the formation factor, no values for the conductivity in the fresh state are available.

However, the mixtures exhibit similar behavior to the pH values, showing decreasing conductivity with increasing sample age. The grouping of the mixtures is also present here, with the mixture with high potassium concentration and alkali activation using KOH and KWG showing a very high conductivity after one day. Overall, the pH and the electrical conductivity show systematic, time-dependent changes, with decreasing values at increasing sample ages.

7.4.2 STRUCTURAL CHARACTERIZATION OF THE REPAIR MORTARS

To see how CRA is influenced by the structure of the mortars, two different approaches were pursued. First, the formation factor was calculated at sample ages of 1, 7 and 28 days. Second, and at the same sample ages, the porosity was measured using single-sided ^1H NMR.

The electrical resistivity of the mortars, which results from the average of three individually measured samples, and the pore solutions are given in Figure 7-8 (a) and (b), and the resulting formation factors, which were calculated according to Equation (3), are shown in Figure 7-9 for each mixture at the different sample ages. Again, the mixtures can be divided into two groups based on the deviating temporal changes in the formation factor with increasing sample age. The non-alkali-activated mixture and the alkali-activated mixtures with low potassium content both demonstrated, regarding their pore solution and mortar state, an increasing electrical resistivity and a resulting increasing formation factor with increasing sample age. However, an exception is the mixture that was activated exclusively with KWG, which showed a decreasing formation factor between 7 and 28 days. Looking at the resistivity of the pore solution and of the mortar of this mixture separately, the mortar resistance increased by less between 7 and 28 days compared to the other two mixtures with low potassium concentrations. This resulted in a nearly constant resistance at both 7 and 28 days for this mixture. In contrast, the development of the pore solution resistance in the KWG-activated mixture corresponded to those of the other mixtures with low potassium concentrations over time.

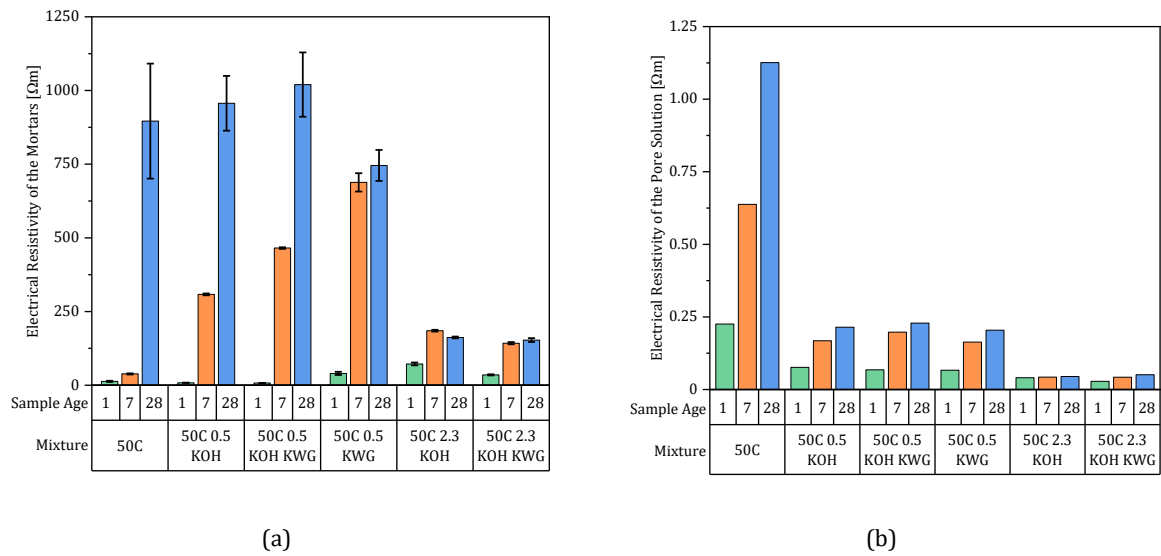


Figure 7-8: Electrical resistivities ($n = 3$) of the mortars (a) and the corresponding pore solutions (b) ($n = 1$).

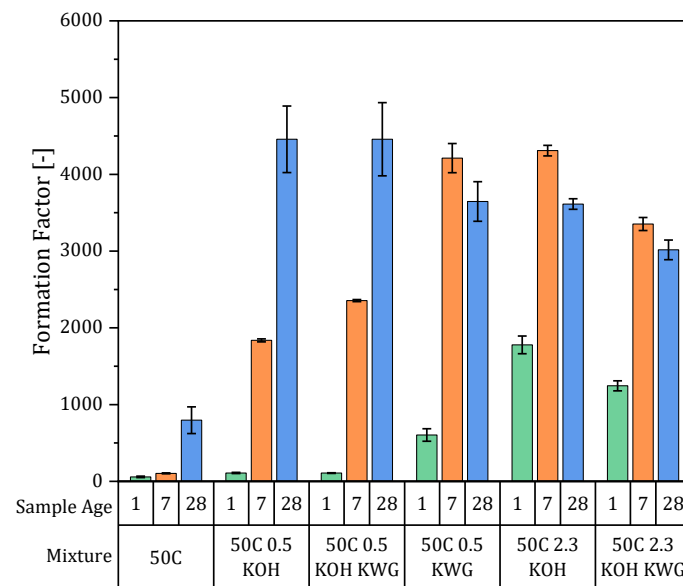


Figure 7-9: Formation factors of the different mortars at sample ages of 1, 7 and 28 days.

The second group based on the formation factor consists of mixtures with high potassium content that first show an increasing trend up to a sample age of 7 days and then a decreasing trend between 7 and 28 days. This is the result of very low mortar resistances at high potassium concentrations, which, unlike the other mixtures, cause them to show a constant or decreasing resistivity. Since the samples were wrapped in water-soaked cloths for storage prior to measurement, leaching in the samples was to be expected, which was assumed to hinder the formation of the material's structure. This was confirmed by the constant electrical resistance of the mortar disks after 7 and 28 days.

Since the formation factor indicates the structural influence on the conductivity of the mortar and results from the porosity and connectivity of the pores, the porosity of the mixtures was also determined (compare Figure 7-10).

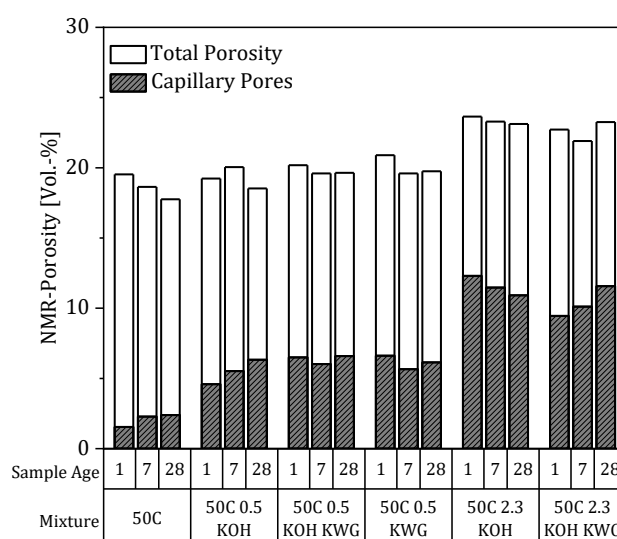


Figure 7-10: Total porosity and proportion of capillary pores of the mortar mixtures ($n = 1$).

Within the NMR porosity analysis, only slight differences in total porosity are discernible between the various mixtures. In contrast, the evaluation of the capillary pore fraction shows strong differences, and three fractions can be distinguished.

The first fraction consists of the non-activated mixture, 50C, showing a decreasing total porosity over time from 19.5 to 17.8 Vol.-%, while the capillary pores increase but are almost constant between 7 and 28 days. This already shows the weak correlation between the NMR porosity and the formation factor, which shows stronger temporal changes than the results of the NMR measurements regarding all mixtures. Particularly interesting is the fact that this mixture already

exhibits a well-developed porosity with a low proportion of capillary pores after just one day, indicating a dense structure. In contrast, the formation factor is low at sample ages of 1 and 7 days, meaning the developed structure had only a minor influence on the electrical resistance of the mortar, leaving pore connectivity as the main defining parameter.

The second fraction consists of the alkali-activated mixtures with low potassium concentrations that showed an overall similar total porosity as well as a capillary porosity between 4.6 and 6.6 Vol.-%. The third fraction is defined by a higher total porosity of between 21.9 and 23.6 Vol.-% in the case of mixtures with potassium concentrations comparable to the other fraction. These mixtures also show the highest proportion of capillary pores, which decreases over time for the KOH-activated mixture and increases over time in the case of the KOH-KWG-activated mixture.

Although temporal trends in porosity within a mortar mix were evaluated in some cases, these were very small and showed no systematic correlation with the course of the CRA. Due to the small magnitudes of the observed changes and the associated uncertainty of the porosity measurements, no further interpretation of the results was undertaken. The results suggest that potential microstructural changes remain secondary compared to chemical effects under the investigated conditions.

However, alkali activation and potassium concentration in the mixtures had an influence on the total porosity, as well as the pore-size distribution represented by the capillary pores.

7.4.3 CONCENTRATION GRADIENT DECAY RATE

The calculated potassium concentration gradient decay rates ($CGDR_K$), which are based on the concentration gradients given in Table 7-5, are presented in Figure 7-11 (a) and (b). The LIBS-based concentration profiles were based on a single specimen per mortar composition ($n = 1$). Mean concentration profiles were used for further evaluation in order to reduce the influence of local measurement noise. Due to the pronounced signal scatter inherent to the LIBS technique, no standard deviations are displayed for the derived concentration gradients. Since the values will later be correlated with the deceleration factor b , which was calculated based on a re-alkalization period of 28 days, the following section focuses on the calculated decay rate values for the period between 1 and 28 days (compare Figure 7-11 (a)). However, the decay rates for the periods between 1 and 7 days and 7 and 28 days were also calculated (compare Figure 7-11 (b)).

Table 7-5: Results of the calculation of the potassium gradient between mortar and concrete after 1, 7 and 28 days according to Equation (5) ($n = 1$).

	50C	50C 0.5 KOH	50C 0.5 KOH KWG	50C 0.5 KWG	50C 2.3 KOH	50C 2.3 KOH KWG
$\Delta c_K(1)$	0.081	-0.409	-1.019	-1.291	-0.935	-1.319
$\Delta c_K(7)$	0.070	1.393	3.663	1.048	0.353	0.912
$\Delta c_K(28)$	-0.609	-1.679	-2.968	-0.353	-0.648	-1.337

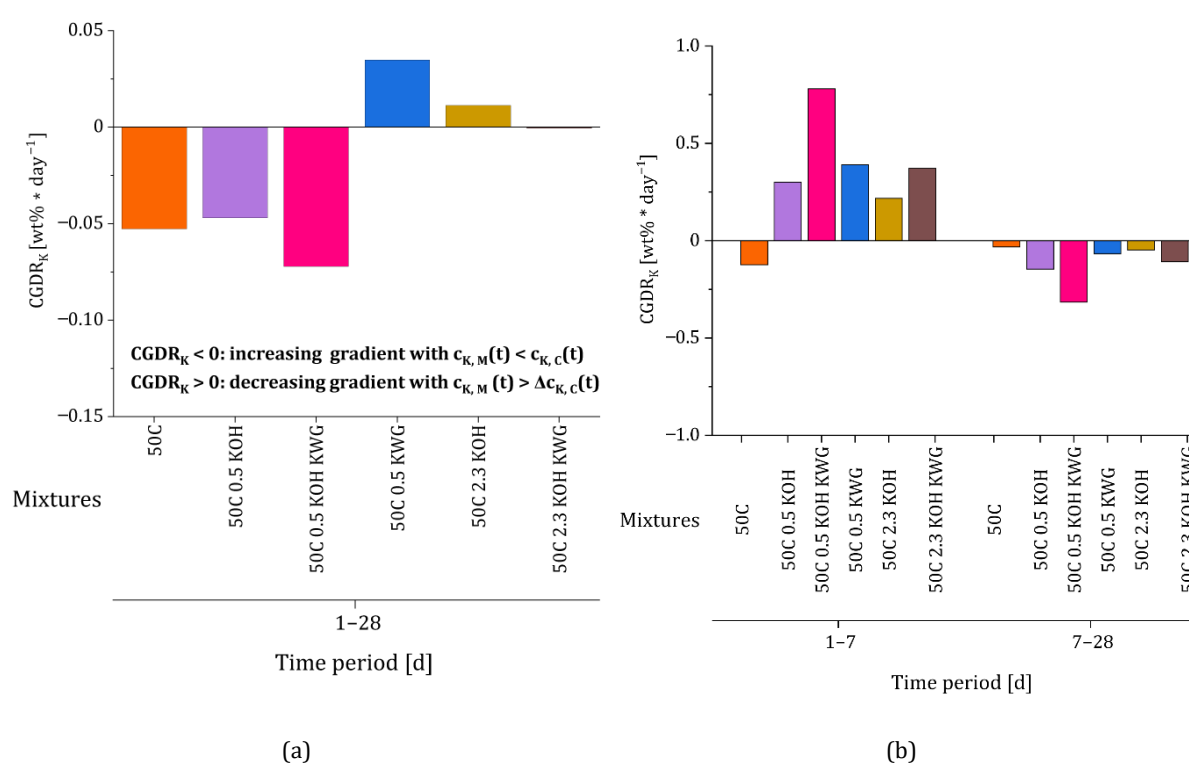


Figure 7-11: Results of the potassium concentration gradient decay rate ($CGDR_K$) calculated based on the LIBS measurements of Glawe et al. [10] for the different time periods: (a) 1 to 28 days, (b) 1 to 7 and 7 to 28 days ($n = 1$).

Based on the results for the period of 1 to 28 days, the investigated composite systems can be divided into two groups. The systems with $CGDR_K < 0$ are characterized by increasing potassium concentration gradient over time between the mortar and the substrate concrete, with a potassium concentration in the concrete which exceeds the potassium concentration in the mortar. This is present when applying mortars which are alkali-activated using KOH or a mixture

of KOH and KWG with a potassium concentration of 0.5 wt% or when applying a non-activated mortar with a substitution rate of 50%. Such a gradient results in a decelerating potassium transport from the mortar into the substrate concrete.

The second group with $CGDR_K > 0$ or nearly $CGDR_K = 0$ includes mortars with high potassium concentrations, as well as the mortar with a low potassium concentration which was alkali-activated using only KWG. These composite systems are characterized by a constant or decreasing potassium concentration gradient between the mortar and concrete, with a permanently higher potassium concentration in the mortar than in the concrete, resulting in ongoing potassium transport from the mortar into the substrate concrete.

7.4.4 INFLUENCES ON EARLY STATE CRA

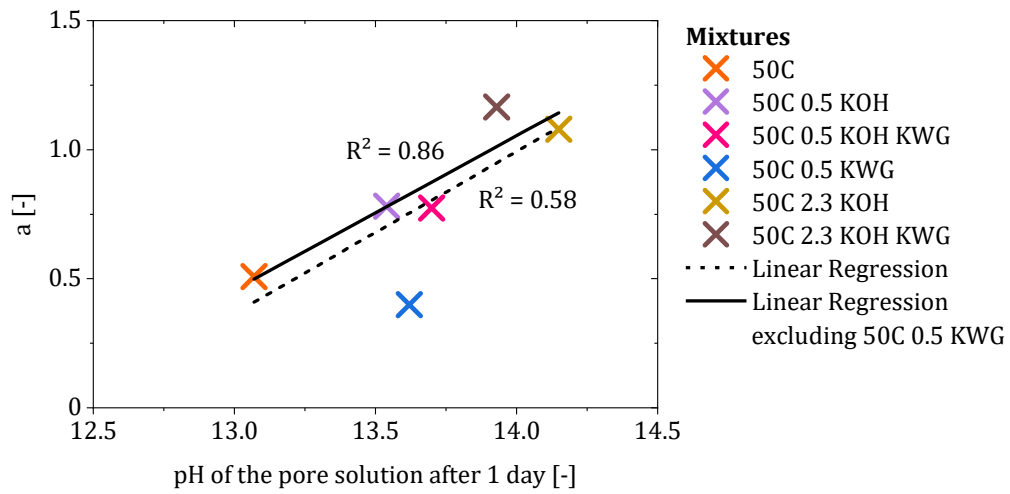
In general, CRA is divided into two phases, the suction phase, which takes place during the first 24 h after the repair mortar is applied, and the diffusion phase, which encompasses all points in time after the suction phase.

The early state of CRA during the suction phase is characterized by a high re-alkalization rate, which has been assumed to be mainly driven by the moisture gradient between the mortar and the substrate concrete until now [19]. Additionally, Glawe et al. observed a clear positive correlation between the re-alkalization rate during the suction phase and the alkali concentration in the mortar [10]. It was further stated that the transport processes during the suction phase and the diffusion phase can be mathematically described by an adaption of Fick's second law of diffusion using the attenuation factor $\beta(t)$. Including the attenuation factor, which is defined by the two factors a and b , the early state of CRA is adapted by the factor a .

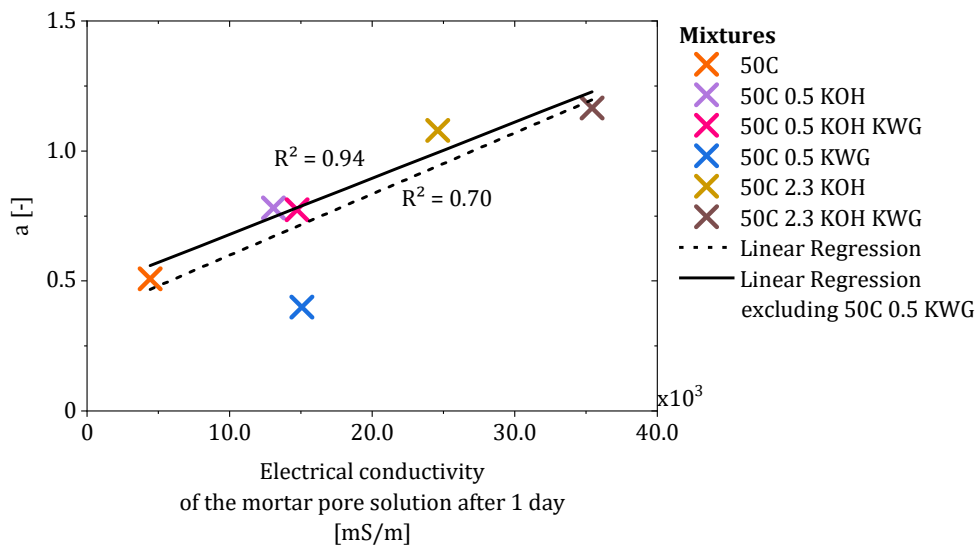
Since a correlation between the potassium concentration of the applied mortar and the re-alkalization rate during the suction phase was already observed by Glawe et al., the alkali concentration in the mortar was analyzed based on the pH and the electrical conductivity of the pore solution of the mortar in the present work. The correlation of the pH and the electrical conductivity of the pore solution of the mortar after one day with the factor a is shown in Figure 7-12 (a) and (b).

The data were correlated using a linear regression to calculate the coefficient of determination to compare the correlations of the different properties with the factor a . The parameter a represents the early-stage progression of chemical re-alkalization during the suction phase and is commonly interpreted as a measure of the initial transport behavior, which is based on varying moisture and concentration gradients between mortar and concrete based on the applied mortar. For the chemical properties of the pore solution of the mortar, a correlation between the pH and the

electrical conductivity of the pore solution can be observed. The coefficient of determination increases after the exclusion of the mortar 50C 0.5 KWG, which showed a high pH and electrical conductivity and a comparably low value for factor a , which led to a low re-alkalization rate during the suction phase compared to other mixtures with similar pore solution properties. However, the pore solution was shown to have a strong influence on factor a and therefore the re-alkalization depth that can be achieved during the suction phase. This interpretation is consistent with the adapted description of the CRA process by Glawe et al., where factor a primarily reflects mortar-related influences during the initial suction phase. A high initial pH for the pore solution results in a high concentration gradient between the mortar and concrete, which leads to increased transport from a high to low concentration by piggyback convection in order to achieve concentration equilibrium. Such an influence can also be assumed with regard to the moisture gradient, which is probably highest at the beginning of the suction phase, but this could not be proven based on the available data.



(a)



(b)

Figure 7-12: Correlation of the pH (a) and the electrical conductivity (b) of the pore solution of the mortar after 1 day with the suction factor a .

Since the investigated mortars showed variation regarding structural properties such as the formation factor, an influence of these properties in the early state of CRA could be assumed. Therefore, the formation factor and the capillary porosity of the mortars were correlated with factor a (compare Figure 7-13 (a) and (b)).

The correlation of the capillary pores and factor a showed a coefficient of determination of 0.54, which increased to 0.84 when the mortar 50CKWG was excluded. Since the chemical properties also showed a deviation, excluding this mixture seemed sensible in order to check the relationships between the properties of the other mortars and factor a . As a result, the proportion of capillary pores in the mortar appeared to influence the progression of CRA during the suction phase. Based on the literature, the water present in capillary pores is often characterized as mobile water which can move through the pore structure of the material [28]. This leads to the assumption that the achieved re-alkalization depth during the suction phase depends on the mobile water present in the mortar, which acts as a transport medium for the alkalis in the form of piggyback transport [30].

In the case of the correlation of the formation factor after 1 day, only a weak correlation ($R^2 = 0.48$) could be observed, which made the exclusion of the 50C KWG mixture seem unnecessary. However, the results would mean that a higher formation factor would lead to a higher re-alkalization rate during the suction phase. As the formation factor characterizes the structural influence on the conductivity of the mortar in terms of ion transport through the pore system of the material, the present weak correlation is contradictory [26]. Therefore, the chemical composition of the pore solution of the mortar is the driving force during early-state CRA, while the investigated structural properties of the mortar seem to play only a subordinate role.

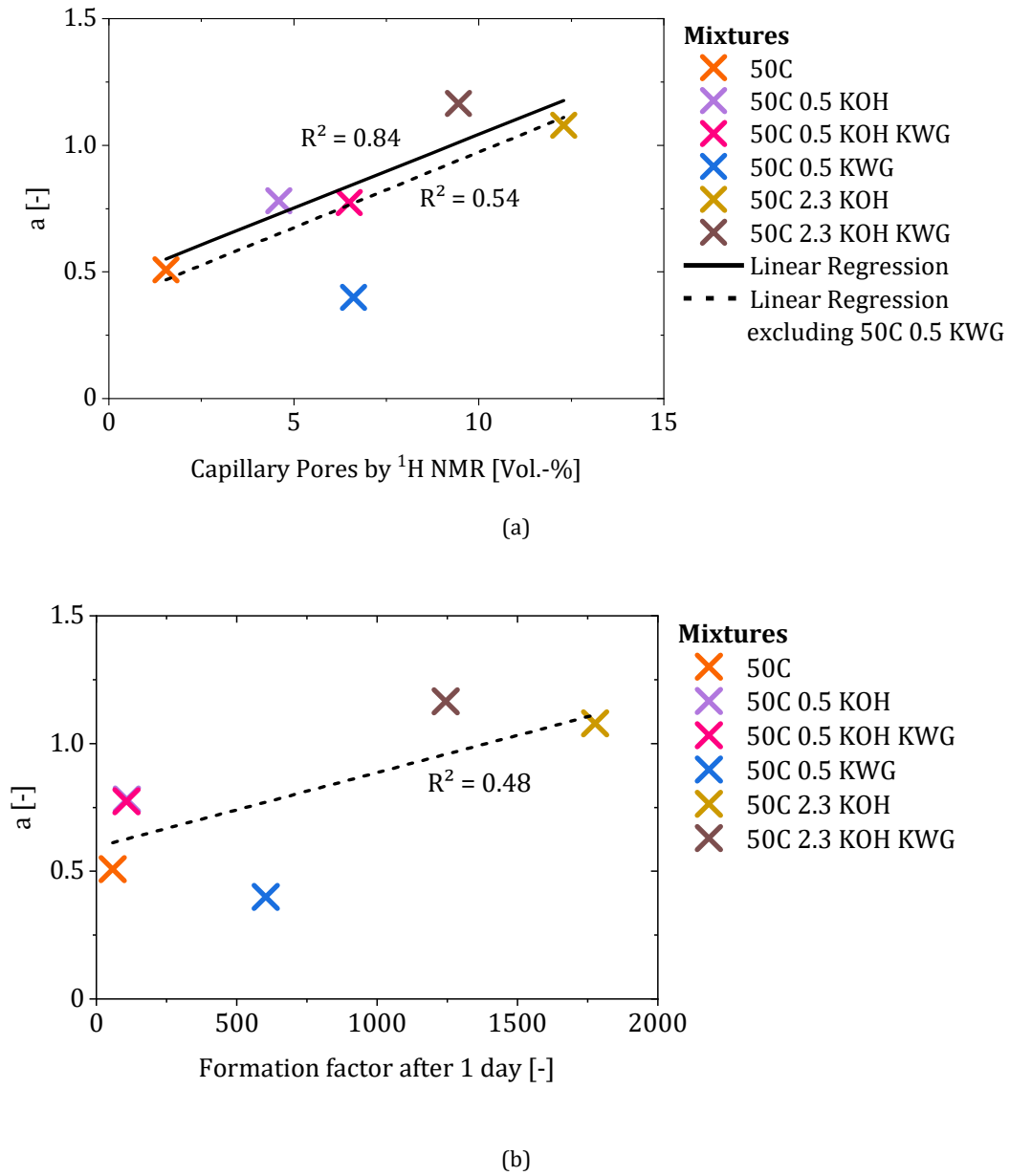


Figure 7-13: Correlation of the capillary pores (a) and the formation factor (b) of the mortars with the suction factor a .

7.4.5 INFLUENCES ON LATER STATE CRA

The progression of CRA after the suction phase is defined by the deceleration of the process which is given by the factor b . Based on previous research by Glawe et al., factor b cannot be explained simply by the initial characteristics of the applied mortar, e.g., the potassium concentration [10]. Rather, it seems likely that changes in the mortar or concrete over time have a direct influence on the deceleration of the CRA during the diffusion phase. In an initial approach, Glawe et al. summarized this through the structural development and decreasing alkali buffer of the mortar, as well as the alkali binding in the concrete [10].

Therefore, structural changes in the mortar in the form of the difference between the formation factors at 1 and 28 days were correlated with factor b . The results of the correlation are given in Figure 7-14 and show that there is no connection between the structural changes in the mortar and the decelerating behavior of CRA.

A correlation between structural changes in the form of porosity, determined using ^1H NMR, is omitted here, as the mortars do not show any significant changes over time based on the available results.

To include the interaction of the alkali concentration in the mortar and the concrete, the CGDR_K values of different time periods were calculated and also correlated with b , as it describes changes in potassium concentration differences in the concrete and the mortar in the interfacial area of the composite system. Since the deceleration factor b defines the progression of CRA in the later state, only a correlation was conducted with the values for CGDR_K of the periods between 1 and 28 and 7 to 28 days (compare Figure 7-15 (a) and (b)). The results showed a high apparent correlation between the changes in the potassium concentration gradient during the re-alkalization period from 1 to 28 days and the deceleration factor b ($r = 0.95$ with $p = 0.004$; $\rho = 0.89$ with $p = 0.002$). Despite the limited number of mortar mixes ($n = 6$), the low p -values indicate that the observed correlation was unlikely to be purely random; however, the wide confidence interval (95 %-CI: 0.58; 0.99) reflects considerable uncertainty, and the correlation should therefore be interpreted as indicative rather than statistically robust.

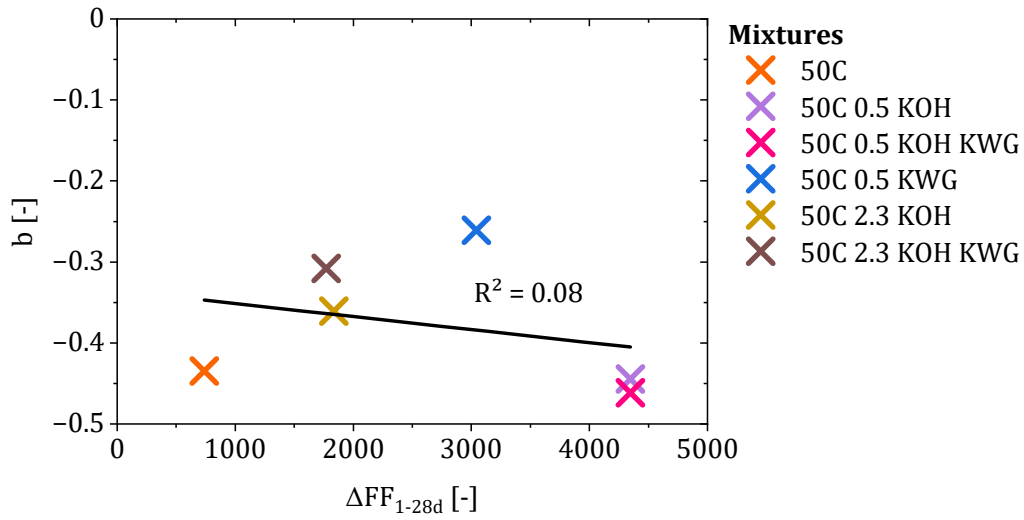


Figure 7-14: Correlation between the deceleration factor b and the changes in the formation factor of the mortars at sample ages of 1 and 28 days.

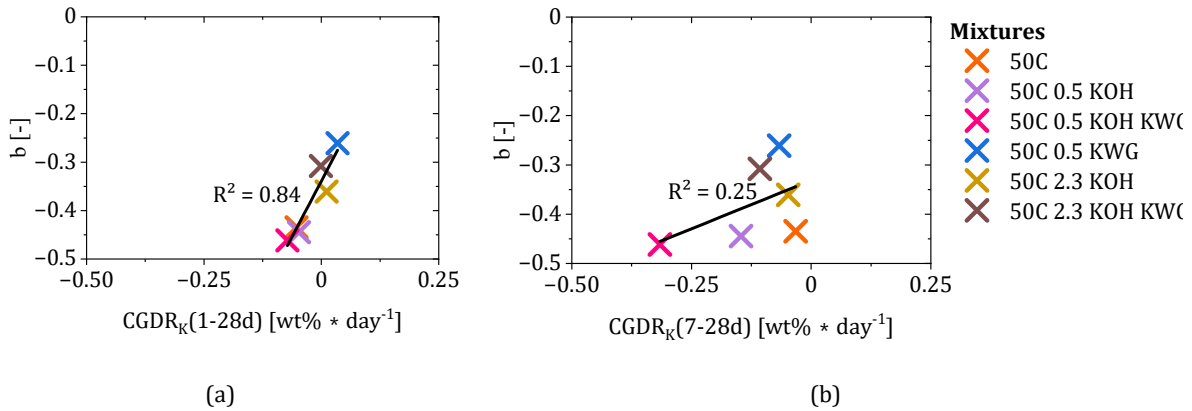


Figure 7-15: Correlation of the deceleration factor b and the potassium concentration gradient decay rate between 1 and 28 (a) and 7 and 28 (b) days of CRA.

In the case of values for $CGDR_K < 0$, which indicates a decreasing gradient between the mortar and concrete, leading to a potassium concentration in the concrete that equals or exceeds the potassium concentration of the mortar, the value of b becomes more negative. As b approaches the value -0.5 , the maximum achievable re-alkalization depth is increasingly dominated by the suction phase. Due to the relationship between b and $CGDR_K$, a rapidly decreasing concentration gradient between the mortar and concrete in the interfacial area leads to a significant deceleration of the CRA during the diffusion phase.

Regarding the investigated mortars, the concentration gradient shows the highest decay rate for mortars with low potassium concentrations. The exception is the mortar 50C 0.5 KWG, which shows a $CGDR_K > 0$ and the highest value for b , which means that the CRA shows a strong progression during the diffusion phase. However, this mortar only shows a final re-alkalization depth that is lower compared to the mortars with high potassium concentrations, which is based on the different behaviors of the mortars during the suction phase. It has to be noted that, despite the deviating behavior of the mixture 50C 0.5 KWG, exclusion of this mixture did not need to occur to obtain a high coefficient of determination.

The mortars with a high potassium concentration were characterized by a $CGDR_K$ of approximately 0, meaning that the concentration gradient between the mortar and concrete remained nearly constant over the investigated re-alkalization period of 28 days.

In combination with a high re-alkalization rate during the suction rate, these mortars showed the highest final re-alkalization depths [10].

In comparison, only a weak correlation of the deceleration factor b and the values for $CGDR_K$ between 7 and 28 days could be observed. This confirms that the deceleration factor is sensitive to changes in the concentration gradient between the mortar and concrete throughout the entire diffusion phase. Therefore, a comparison with $CGDR_K$ values at 1 to 7 days would be misleading, as these values also reflect processes from the initial suction phase.

7.5 DISCUSSION

The present study focuses on the determination of the influences of HAAB-based mortars and concrete on the progression of CRA during different phases of the re-alkalization process. For this purpose, various properties of mortar and concrete were correlated with the factors a and b , which were taken from a previous study by Glawe et al., as these characterize the course of CRA during the initial suction phase and the subsequent diffusion phase, respectively [10].

A direct quantitative comparison with previous, independent studies is limited, as HAABs have so far not been systematically investigated as repair mortars for CRA by other researchers. Existing studies primarily focus on OPC-based repair mortars or alkaline solutions, which strongly differ in terms of pore solution chemistry, hardening processes and transport mechanisms. This is mainly due to the fact that OPC-based mortars have so far only been investigated at low carbonation depths of up to 14 mm, and alkaline solutions differ significantly from the properties of HAAB-based mortars due to a permanently, significantly increased moisture supply [17, 19]. However, across all studies, a correlation is evident with regard to the differentiation of the individual phases of CRA for all the repair materials used.

In the beginning of CRA, the suction phase starts directly after the repair mortar is applied. During this phase, it becomes apparent that the alkalinity of the mortar, in the form of the pH of the pore solution and the electrical conductivity, and the available mobile water, in the form of the capillary pores, have a significant influence on the course of the CRA. Especially at very high pH values ($\text{pH} > 14$), small changes in pH correspond to large changes in hydroxide ion concentration due to the logarithmic nature of the pH scale. Consequently, mortars exhibiting pH values above 14 possess a substantially larger alkali depot, which can sustain strong alkali emission in the early state without rapid depletion.

In comparison to existing studies by Reus et al., the use of a pure KOH solution results in an even more pronounced suction phase. Although the studies do not provide re-alkalization values after 1 day, almost complete re-alkalization was achieved after just 7 days, whereas with the use of HAABs, approximately 50% of the maximum re-alkalization depth was reached within this time period [31]. Accordingly, it can be assumed that, under otherwise identical conditions, the value for the absorption factor a would exceed those of HAAB-based mortars when using alkaline solutions. The investigations by Merkel would accordingly show a significantly reduced absorption factor ($a < 1$), since cement-based mortars exhibit a less pronounced suction phase, which can still be differentiated from the subsequent diffusion phase [19]. The results of Bier et al. also confirm the presence of a less pronounced suction phase when using cement-based repair mortars, even though such a distinction was not explicitly made in these studies [17, 32].

Although the proportion of capillary pores represents a structural parameter of the mortars and provides pathways for ionic transport, the proportion alone does not determine the re-alkalization rate during the suction phase. The formation factor, as an additional structural parameter derived from the electrical resistivity of the pore solution and the mortar, shows a non-systematic relationship with the re-alkalization rate during the suction phase. This illustrates that, while the capillary pores are a prerequisite for moisture-based transport, their proportion primarily reflects the amount of mobile pore water instead of the transport kinetics. A similar proportion of mobile water does not necessarily lead to a similar value for the suction factor a , as is the case for the mixtures of 50C 0.5 KOH KWG and 50C 0.5 KWG. Here, 50C 0.5 KWG shows a much lower value for factor a that results in relatively lower CRA during the suction phase compared to 50C 0.5 KOH KWG, while both mixtures show similar capillary pores. This underlines that, overall, the early-stage progression of CRA is governed predominantly by the chemical composition of the pore solution, which can outweigh purely structural effects under highly alkaline conditions and under the investigated conditions [31].

The diffusion phase starts after the suction phase, which is assumed to take a maximum of 24 h. In previous research, the transition from the suction phase to the diffusion phase has been characterized by a deceleration of the process [11, 33]. This deceleration was introduced as the factor b by Glawe et al. and enabled adaptation of Fick's second law of diffusion to the re-alkalization process [10].

To determine the influences on the deceleration behavior of CRA during the diffusion phase, the changes in mortar and concrete properties over time were correlated with factor b . This again showed that the developing structural influence of the mortar, in the form of the formation factor, has no correlation with b . Since the proportion of the capillary pores in the mortars shows only minor changes over time, no systematic relationship between the investigated structural parameters and the re-alkalization behavior during the diffusion phase could be identified within the present dataset.

In contrast to this, the potassium concentration gradient decay rate $CGDR_K$ shows a very strong correlation with the deceleration factor b , leading to the conclusion that the concentration gradient at the mortar concrete interface dominates the progression of the CRA during the diffusion phase. According to this, the strongest deceleration in the form of relatively more negative values for b can be observed for the mortars with the highest $CGDR_K$ between mortar and concrete. In the case of the mixtures 50C 0.5 KOH and 50 C 0.5 KOH KWG, the potassium concentration of the concrete exceeds the concentration equilibrium between mortar and concrete, which indicates binding of potassium in the near interfacial area of the concrete [24]. Therefore, factor b is defined by a combination of mortar and concrete properties. More precisely, factor b indicates how many alkalis the mortar can provide and how quickly, in relation to the absorption rate and absorption capacity of the concrete. In the case of the mixture 50C 0.5 KWG, which is characterized by a low factor a and a less negative value for factor b , the mortar releases the alkalis more slowly but over a longer period of time compared to the other mixtures with similar potassium concentrations, resulting in a lower $CGDR_K$.

A comparison with existing studies by Merkel and Reus, which used cement-based mortars or alkaline solutions for re-alkalization, respectively, confirms the interpretation of the decelerating factor b [19, 31]. In the case of cement-based mortars, which typically have an initial pH of 12.5 - 13.5, only a weakly pronounced suction phase is observed, followed by a diffusion phase with minimal deceleration. Due to the low release during the absorption phase, the CRA is only weakly decelerated during the diffusion phase. In the case of the alkaline KOH solution, which is characterized by a very high, easily available alkali depot, the diffusion phase is only weakly decelerated even after a strong suction phase. Although no explicit pH values for the solution are

given, a pH of approximately 14.4 can be assumed for the described solution with 150 g/L KOH [31].

It is important, however, not to evaluate the potassium concentration of the entire mortar layer or the bulk concrete, as leaching can occur in the near-surface area of the mortar as a result of cyclic irrigation, which would distort the average values for the potassium concentration. However, in the present study, cyclic irrigation results in continuous but controlled leaching under identical exposure conditions for all composite systems. Such leaching effects were already observed by Glawe et al. and occurred primarily in mortars with high potassium concentrations, which nevertheless exhibited only a weak slowdown during the suction phase [10]. This indicates that, under the investigated conditions, leaching affects local concentration levels but does not dominate the overall progression of CRA. However, under scenarios involving permanent water contact, such as applications in drinking-water environments, more pronounced leaching may occur and should be considered separately.

7.6 CONCLUSIONS

The investigations presented here provide the first quantitative, parameter-based evaluation of the material-related influences of HAAB-based repair mortars on CRA. Based on the systematic correlation of the obtained results for the investigated materials with the existing adapted diffusion model, the following conclusions can be drawn.

- Using the adapted diffusion framework, this study provides the first quantitative correlation of mortar- and concrete-related properties and the re-alkalization-defining parameters, the suction factor a and the deceleration factor b .

The suction factor a defines CRA during the initial suction phase and is mainly influenced by the alkalinity of the mortar pore solution, with pH values exceeding 14 leading to pronounced early-stage CRA with $a > 1$.

- Strong re-alkalization ($a > 1$) during the suction phase does not inevitably lead to a strong deceleration of CRA, as the potassium concentration gradient between the mortar and concrete is maintained in the case of initial mortar pore solution pH values above 14, as such high pH values correspond to substantially higher alkali concentration.
- The influences on the diffusion phase, which are defined by the deceleration factor b are dominated by the concentration gradient decay rate $CGDR_K$, which describes the temporal development of the potassium concentration gradient between the mortar and concrete in the interfacial area during the diffusion phase.

- The structural properties of the applied repair mortar seem to have a less pronounced influence on both the suction factor a and the decelerating factor b , suggesting that future optimization of repair mortars should primarily address pore solution chemistry rather than pore structure alone.

7.7 OUTLOOK

The present investigations focused primarily on the mechanisms of chemical re-alkalization and the influence of mortars and the substrate concrete on this process. While the presented influences of the investigated materials show good correlation results with the introduced factors a and b , further material variations should be analyzed to verify the results of this study. Furthermore, additional substrate concretes with varying structural properties and binders should be investigated, as there has been only one type of concrete used so far. Since one of the mortar mixtures shows deviating behavior, the mortar composition should also be varied in regard to binder and activator solutions in future research. In addition, previously used clinker-reduced binders could also be tested as repair mortars.

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Author Contributions: Conceptualization, methodology, software, validation, formal analysis, investigation, resources, data curation, writing—original draft preparation and visualization, C.G.; writing—review and editing, supervision, C.G., R.A. and M.R. All authors have read and agreed to the published version of the manuscript.

7.8 REFERENCES

- [1] Deutsches Institut für Bautechnik (DIBt) Technische Regel - Instandhaltung von Betonbauwerken (TR Instandhaltung) - Teil 2: Merkmale von Produkten oder Systemen für die Instandsetzung und Regelungen für deren Verwendung. *Deutsches Institut für Bautechnik (DIBt)*, (2020) Berlin.
- [2] DIN EN 1504-9:2008. Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 9: General Principles for the Use of Products and Systems. *Beuth*, (2008) Berlin.

- [3] Deutsches Institut für Bautechnik (DIBt) Technische Regel - Instandhaltung von Betonbauwerken (TR Instandhaltung) - Teil 1: Anwendungsbereich und Planung der Instandhaltung. *Deutsches Institut für Bautechnik (DIBt)*, (2020) Berlin.
- [4] Vollpracht, A.; Lothenbach, B.; Snellings, R.; Haufe, J., The pore solution of blended cements: a review. *Materials and Structures* (2016) 49, 3341-3367. <https://doi.org/10.1617/s11527-015-0724-1>
- [5] Natkunarajah, K.; Masilamani, K.; Maheswaran, S.; Lothenbach, B.; Amarasinghe, D. A. S.; Attygalle, D., Analysis of the trend of pH changes of concrete pore solution during the hydration by various analytical methods. *Cement and Concrete Research* (2022) 156, 106780. <https://doi.org/10.1016/j.cemconres.2022.106780>
- [6] Lothenbach, B.; Winnefeld, F., Thermodynamic modelling of the hydration of Portland cement. *Cement and Concrete Research* (2006) 36, 209-226. <https://doi.org/10.1016/j.cemconres.2005.03.001>
- [7] Glawe, C.; Georget, F.; Raupach, M.; Matschei, T., Multi technique characterization of the carbonation affected zone uncluding non-destructive sindle sided ^1H NMR *Cement and Concrete Research* (2024) 178, 107438. <https://doi.org/10.1016/j.cemconres.2024.107438>
- [8] Castellote, M.; Fernandez, L.; Andrade, C.; Alonso, C., Chemical changes and phase analysis of OPC pastes carbonated at different CO_2 concentrations. *Materials and Structures* (2009) 42, 515-525. <https://doi.org/10.1617/s11527-008-9399-1>
- [9] Achenbach, R., Corrosion protection of steel reinforcement by alternative binder types. Ph.D. Thesis, RWTH Aachen University, (2024) 14.06.2024.
- [10] Glawe, C.; Raupach, M., Quantitative analysis of the alkali transport during achemical re-alkalization using laser-induced-breakdown spectroscopy. *Corrosion and Materials Degradation* (2025) 6, 43. <https://doi.org/10.3390/cmd6030043>
- [11] Glawe, C.; Raupach, M., Application of hybrid alkali-activated binders for chemical re-alkalization. *Materials and Structures* (2025) <https://doi.org/10.1617/s11527-025-02732-8>
- [12] García-Lodeiro, I.; Fernández-Jiménez, A.; Palomo, A., Variation in hybrid cements over time. Alkaline activation of fly ash–portland cement blends. *Cement and Concrete Research* (2013) 52, 112-122. <https://doi.org/10.1016/j.cemconres.2013.03.022>
- [13] Detphan, S.; Hanjitsuwan, S.; Pangdaeng, S.; Phoo-ngernkham, T.; Damrongwiriyanupap, N.; Wongsas, A.; Sukontasukkul, P.; Chindaprasirt, P., Hybrid alkali-activated fly ash-Portland cement binders with modified polymer as patch repair. *Construction and Building Materials* (2024) 436, 136776. <https://doi.org/10.1016/j.conbuildmat.2024.136776>

- [14] Lothenbach, B.; Scrivener, K.; Hooton, R., Supplementary cementitious materials. *Cement and Concrete Research* **(2011)** 41, 1244-1256.
<https://doi.org/10.1016/j.cemconres.2010.12.001>
- [15] Haardt, P.; Hilsdorf, H. K., **(1993)** Realkalisierung karbonatisierter Betonrandzonen durch großflächigen Auftrag zementgebundener Reparaturschichten. . *Internationales Kolloquium zum Thema Werkstoffwissenschaften und Bausanierung*. 666-684.
- [16] Guse, U.; Hilsdorf, H. K.; Haardt, P., Realkalisierung carbonatisierter Betonrandzonen durch den Auftrag zementgebundener Mörtel. *Kurzberichte aus der Bauforschung* **(1994)** 36,
- [17] Bier, T. A., Carbonation and realkalization of cement paste and concrete. Ph.D. Thesis, Universität Fridericiana zu Karlsruhe, **(1988)** Karlsruhe, 23.12.1987.
- [18] DIN EN 1992-1-1: 2011-01 Eurocode 2: Bemessung und Konstruktion von Stahlbeton- und Spannbetontragwerken - Teil 1-1: Allgemeine Regeln und Regeln für Hochbauten, Brücken und Ingenieurbauwerke; Deutsche Fassung EN 1992-1-1:2023. *Beuth*, **(2025)** Berlin.
- [19] Merkel, M., Realkalisierungspotenzial von zementgebundenen Werkstoffen im Trinkwasserbereich. Ph.D. Thesis, Technische Universität Kaiserslautern, **(2021)** Kaiserslautern, 15.07.2021.
- [20] Rucker, P.; Beddoe, R. E.; Schießl, P., Wasser-und Salzhaushalt im Gefüge zementgebundener Baustoffe–Modellierung der auftretenden Mechanismen. *Beton-und Stahlbetonbau* **(2006)** 101, 402-412. <https://doi.org/10.1002/best.200600483>
- [21] Przondziono, R.; Timothy, J. J.; Nguyen, M.; Weise, F.; Breitenbücher, R.; Meschke, G.; Meng, B., Vorschädigungen in Beton infolge zyklischer Beanspruchungen und deren Auswirkung auf Transportprozesse im Hinblick auf eine schädigende AKR. *Beton-und Stahlbetonbau* **(2015)** 110, 3-12. <https://doi.org/10.1002/best.201400095>
- [22] Kraft, B.; Achenbach, R.; Ludwig, H.-M.; Raupach, M., Hydration and Carbonation of Alternative Binders. *Corrosion and Materials Degradation* **(2022)** Volume 3, 19-52. <https://doi.org/10.3390/cmd3010003>
- [23] Bernal, S. A.; Provis, J. L., Durability of alkali-activated materials: progress and perspectives. *Journal of the American Ceramic Society* **(2014)** 97, 997-1008. <https://doi.org/10.1111/jace.12831>
- [24] Réus, G. C.; Salvador, R. P.; Hoppe Filho, J.; De Souza, D. J.; de Medeiros, M. H. F., Chemical realkalization of carbonated concrete: Influence of cement composition on alkalinity restoration and portlandite formation. *Buildings* **(2025)** 15, 1318. <https://doi.org/10.1016/j.conbuildmat.2025.143622>

- [25] Zajac, M.; Song, J.; Ullrich, P.; Skocek, J.; Ben Haha, M.; Skibsted, J., High early pozzolanic reactivity of alumina-silica gel: A study of the hydration of composite cements with carbonated recycled concrete paste. *Cement and Concrete Research* (2024) 175, 107345. <https://doi.org/10.1016/j.cemconres.2023.107345>
- [26] Raupach, M.; Achenbach, R.; Ludwig, H.-M.; Kraft, B. I. E., Zur Anwendbarkeit des Formationsfaktors als Gefügekennwert für Mörtel aus verschiedenen alternativen Bindemittelsystemen. *ce/papers* (2023) 6, 1324-1333. <https://doi.org/10.1002/cepa.2925>
- [27] Georget, F.; Sui, S.; Wilson, W.; Scrivener, K. L., Reconciliation of pore structure characterization methods: The simple case of PC-limestone cement pastes. *Cement and Concrete Research* (2024) 184, 107624. <https://doi.org/10.1016/j.cemconres.2024.107624>
- [28] Munsch, S.; Schmidt, W.; Lorenzoni, R.; Telong, M.; Grobla, L.; Lauinger, R.; Kruschwitz, S., Investigation of the hydration of clinker-reduced cementitious binders by ^1H NMR relaxometry. *Materials and Structures* (2025) 58, 137. <https://doi.org/10.1617/s11527-025-02632-x>
- [29] Schulte-Holthausen, R., Evaluation of the pore structure of concrete using single-sided ^1H nuclear magnetic resonance relaxometry. Ph.D. Thesis, RWTH Aachen, (2019)
- [30] Rucker-Gramm, P., Modellierung des Feuchte-und Salztransports unter Berücksichtigung der Selbstabdichtung in zementgebundenen Baustoffen. Ph.D. Thesis, Technische Universität München, (2008) 11.11.2008.
- [31] Réus, G. C.; Medeiros, M. H. F., Chemical realkalization for carbonated concrete treatment: Alkaline solutions and application methods. *Construction and Building Materials* (2020) 262, 120880. <https://doi.org/10.1016/j.conbuildmat.2020.120880>
- [32] Bier, T. A.; Kropp, J.; Hilsdorf, H., Carbonation and realcalinisation of concrete and hydrated cement paste. *Durability of construction materials* (1987) 3, 927-934.
- [33] Glawe, C.; Raupach, M., Basics and new opportunities for chemical re-alkalisation of carbonated concrete, including alkali-activated binders. *Magazine of Concrete Research* (2024) 76, 1185-1197. <https://dx.doi.org/10.1680/jmacr.24.00026>

8. CONCLUSIONS AND RECOMMENDATIONS

The present thesis includes an analytical examination of the mechanisms of chemical re-alkalization and the application of clinker-reduced, alkali-activated binders to determine the limits and future prospects of this repair method. In addition to a thorough review of the current state of the art, novel methods for analyzing chemical re-alkalization were applied to gain a deeper understanding of the re-alkalization process. Based on the adaptation of existing models, the course of chemical re-alkalization could be depicted and the material-related influences on the different states of the process quantified.

The results allow for the formulation of implications for practical application in construction as well as limitations of the presented research.

8.1 SUMMARY OF THE MAIN FINDINGS IN RESPONSE TO THE RESEARCH QUESTIONS

The following section answers the research questions listed in the introduction based on the findings of this study. Since CRA consists of an interaction between many processes, the research questions are not answered individually, so that connections between the results of this work can be formulated.

The present investigations have demonstrated that under the described conditions of cyclic irrigation in the case of highly porous concrete, a re-alkalization depth of 33 mm can be achieved, which supplements previous investigations on a maximum re-alkalization depth of 14 mm. Within the 90-day re-alkalization period, this was possible with the help of repair mortars that have an initial pH value greater than 14. The decisive factor here is the suction phase within the first 24 hours, during which these highly alkaline mortars already achieve 50% of the final re-alkalization depth. Sufficient alkalinity of the repair mortar can be achieved in the case of the examined HAAB with substitution rates of up to 50 % with calcined clay through alkali activation using KOH solutions. However, the compressive strength of the mortar must also be taken into account, as this prevents the addition of an arbitrary amount of alkali. Even though the regulations assume rear-sided re-alkalization in order to achieve re-alkalization depths of up to 40 mm, this phenomenon could not be explicitly observed in any of the cases examined in this study. Under the conditions mentioned, re-alkalization by the repair mortar alone enables chemical re-alkalization up to 33 mm.

The effectiveness and limitation of the CRA were shown to depend strongly on the properties of the applied repair material. While different materials such as alkaline solutions, highly alkaline hydrogels and cement-based mortars can in principle introduce alkalis into the concrete, only

cement-based mortars are currently regulated for application on site. Besides they all offer the possibility to introduce alkalis into the concrete to rebuild the pH of the pore solution in the carbonated area, cement-based repair mortars also act as a protective layer against re-carbonation of the re-alkalized area which advantage is not given when using alkaline solutions or hydrogels. At the same time, clinker-reduced mortars with high substitution rates and without additional alkali activation may exhibit insufficient alkalinity, thereby limiting the application as repair mortar for CRA. However, it was primarily due to the high availability of alkalis, which was ensured in this study by the addition of KOH, that the mortars examined showed their sensitivity to leaching. Although significant leaching was observed during the investigated time period due to cyclic irrigation, no effects on the CRA could be quantified, as the concentration gradient within and near the interfacial zone between mortar and concrete is decisive for progress in the later course of CRA.

The carbonation was shown to fundamentally alter the microstructural and mineralogical properties of the substrate concrete such as the reduction of C-S-H phases, the formation of carbonates and the decrease of the overall porosity with a shift to coarser pores. The decomposition of the C-S-H phases during the carbonation in form of the decalcification also leads to the formation of a porous silica gel. Although this could not be explicitly proven in the present study, existing literature suggests that carbonation led to the formation of the silica gel. This gel is attributed with pozzolanic reactivity, which has so far been proven primarily in contact with Ca(OH)_2 . Such reactivity of carbonated concrete was in turn demonstrated by LIBS investigations, which showed a significant enrichment of potassium in the carbonated area of the concrete, leading to a potassium concentration in this area that exceeds the equilibrium concentration between mortar and concrete. Such binding of alkalis when using alkaline solutions has already been demonstrated in other research work. The alkalis bound in carbonated concrete are no longer available for CRA in the further course of the process, which has an inhibiting effect, especially in repair mortars with lower alkali reserves.

The temporal evolution shows the CRA as a process consisting of two distinct transport phases. The initial suction phase is governed by a substantial portion of the total alkali transport from the mortar into the concrete within 24 hours. This phase is driven by the high pH and moisture differences between the mortar and the concrete in the interfacial area. The subsequent diffusion phase is characterized by a progressive deceleration of the alkali transport as a result of a decreasing alkali concentration gradient.

Based on the experimental findings, a semi-empirical modelling framework was developed to parameterize the CRA process. The deviation from ideal diffusion, as defined by Fick's second law

of diffusion, were quantified using a time-dependent attenuation factor for each of the investigated repair mortars. The introduction of a suction factor a and a deceleration factor b enabled a differentiated description of the suction and diffusion phase and allowed the material- and time-dependent re-alkalization behavior to be captured within an analytical framework (compare Figure 8-1).

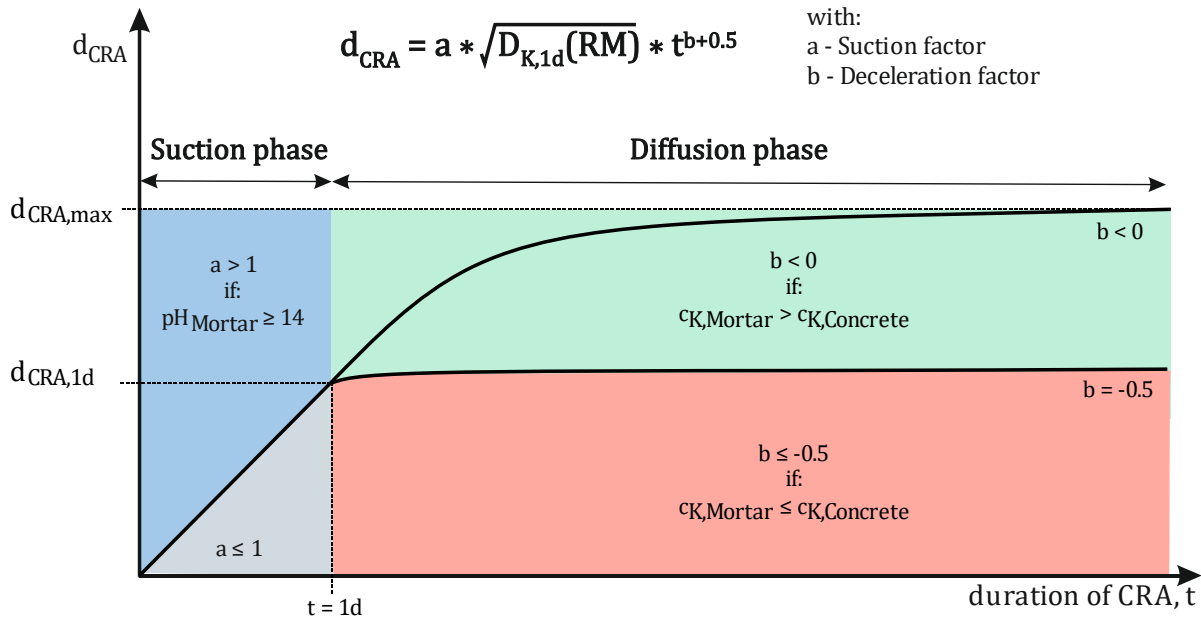


Figure 8-1: Schematic summary of the semi-empirical model of the CRA and the material-related influences on the suction factor a and the deceleration factor b .

The suction factor was found to be primarily controlled by the alkalinity of the mortar pore solution, with pH values above 14 leading to pronounced early-state re-alkalization. Importantly, a strong suction phase did not necessarily result in a strong deceleration during the diffusion phase, as high initial alkali concentrations maintain the concentration gradient over the investigated period. By correlating the model parameter, a and b with mortar- and concrete-related properties, the developed framework enables a comparative assessment of different re-alkalization materials. With the help of the specific material-dependent temporal deviation of the CRA from an ideal diffusion process, it was possible, for example, to use the measured re-alkalization depths after 28 days to better predict the expected re-alkalization depth after 90 days than with the previously common calculation using the re-alkalization coefficient k_{CRA} . Although the model is not intended to provide absolute predictions of re-alkalization depth, it provides a robust basis for interpreting experimental results and for systematically comparing CRA systems

under varying boundary conditions. The added value of the developed model is clearly illustrated in Figure 8-2, which concludes with a comparison of the re-alkalization potential of different materials based on the re-alkalization coefficient. Within this work, the re-alkalization coefficient was previously determined on the basis of the available literature using a standard linear regression in which the linear regression does not pass through the origin. This was chosen primarily to reflect the long-term behavior of the mortars after the suction phase, as this is minimal in mortars according to the origin state of research.

This contrasts with the investigations in this work and those by the latest work of Moraes et al. [1] and the research of Réus et al. [2], in which the use of HAAB or alkaline solutions shows significantly more pronounced suction phases. To represent this in the re-alkalization coefficient k_{CRA} , a linear regression through the origin was again performed using all studies on CRA available in the literature. The studies by Merkel [3] are excluded here, as they refer to the use of CRA in drinking water containers in the case of leached concrete.

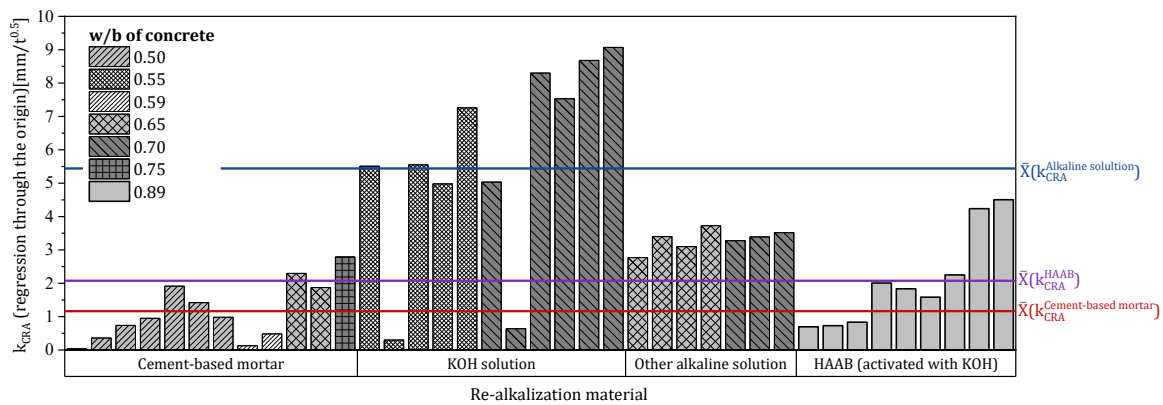


Figure 8-2: Summary comparison of the investigated materials (HAAB) with previous research on CRA based on paper I using the re-alkalization coefficient k_{CRA} .

Here, HAABs show only a slightly higher re-alkalization coefficient compared to conventional cement-based mortars, although these materials have shown significantly higher re-alkalization rates, especially in the suction phase, based on the available results. This once again underlines the relevance of the quantitative differentiation between the two phases of re-alkalization, as made possible by the newly developed model.

Due to a lack of data in the literature on values of re-alkalization depth after one day, it was unfortunately not possible to compare the suction and deceleration factors of all studies.

8.2 SCIENTIFIC CONTRIBUTION - POSITIONING THE RESULTS WITHIN EXISTING RESEARCH

This thesis deals with chemical re-alkalization, a repair method that has been in use for many years and was first investigated on a scientific level in a thesis by Bier in 1988 [4]. While the fundamental principle of chemical re-alkalization has been known for several decades, both the boundary conditions and the available analytical tools have changed significantly. On the one hand, the construction industry is currently undergoing a fundamental shift in requirements due to the increasing demand for clinker-reduced, low-carbon binders. On the other hand, modern analytical methods offer new possibilities for investigating the underlying scientific phenomena in greater detail.

Despite the fact that the use of novel binders is known to pose new challenges in terms of durability, only very limited research has been conducted on the influence of clinker-reduced binders on the possibilities and limitations of chemical re-alkalization. When reviewing the existing literature, it was particularly striking that the application limits for the chemical re-alkalization formulated to date, which according to regulations can currently be applied at a carbonation depth of up to 40 mm, are not based on any discernible research. Overall, the formulations for the requirements regarding the substrate concrete and the mortars that can be used as repair materials are very general.

This lack of specificity becomes particularly a problem, especially in context of clinker-reduced binders, where the alkalinity of the resulting repair mortar is reduced to such an extent that no longer allows for effective chemical re-alkalization. To date, alkalinity has been ensured through the use of Portland cement-based binders, but their use will be heavily regulated in the future due to their high carbon footprint. With regard to these challenges, the present study makes a fundamental contribution by systematically investigating mortar mixtures with reduced clinker content, both with and without alkali activation. The results allow for clearer formulation of requirements and suggest that a high substitution rate ($> 25\%$) in the repair mortar without additional alkali activation can lead to the mortar's alkalinity no longer being sufficient to ensure chemical re-alkalization of the concrete.

In addition, significantly higher carbonation depths of concrete were investigated in this thesis compared to the literature (maximum carbonation depth approx. 14 mm) in order to approach the verification of the basic feasibility of chemical re-alkalization of 40 mm. Here, it was shown

that a carbonation depth of 33 mm can be achieved under cyclic irrigation when using hybrid alkaline-activated binders. These binders offer a particular advantage due to their high pH value, which, at over 14, even exceeds that of OPC-based binders. Compared to existing studies such as those by Bier or Merkel, this work was limited to variations in mortar in order to clearly determine the material-based influences [3, 4].

Furthermore, most of the results of these past studies are based on the analysis of the CRA using the phenolphthalein test as this represents the common method to determine the re-alkalization depth on site. While this method displays the corrosion-relevant pH threshold of 9, no further details about the processes of the chemical re-alkalization such as the alkali transport can be derived from this test. In contrast, the present work has shown that alkali transport in the composite system can be quantified using laser-induced breakdown spectroscopy. This provides the possibility to monitor the temporal course of the chemical re-alkalization and simultaneously to investigate the effects on the repair mortar.

Based on the results, a model could be derived that, in comparison to Merkel's model, primarily takes into account initial alkalinity of the mortar and the concentration gradient between mortar and concrete [3]. In contrast to previous studies, both parameters were quantified in the present work. Using the model as an analytical framework, the material-based influences on the two phases, the absorption and diffusion phases, could be differentiated. This work thus complements the results of Merkel, who characterized the two phases of chemical re-alkalization primarily based on ambient humidity and the resulting component moisture in a more descriptive manner. In comparison to Merkel, who investigated the re-alkalization potential of cement-based mortars in drinking water applications, resulting in permanent water saturation of the composite system, this thesis illustrates the potential of CRA in building construction.

As already outlined in the introduction to the thesis, research results by Réus et al. on the use of alkaline solutions as re-alkalization materials are also available [2]. Although these materials are already being used in practical construction applications such as repairs in Australia, German regulations continue to prescribe the use of repair materials in the form of mortars. Nevertheless, the investigations provide a valuable complementary perspective, as the introduction of alkalis into the substrate occurs in both cases.

In Particular, the observations that alkalis introduced into the concrete are partially bound promoting further transport of alkalis from the repair mortar into the concrete in order to achieve equilibrium in the pore solution, the present work complements the results reported by Réus et al. Although the binding mechanisms and the resulting reaction products were not investigated in

detail within this thesis, the underlying assumption is supported by the findings of by Réus' et al [2].

8.3 IMPLICATIONS FOR CONSTRUCTION PRACTICE

The CRA was presented as a suitable repair method to maintain or rebuild the alkalinity in carbonated concrete by the application of alkaline mortars under specific conditions. Using mortars based in HAAB, a maximum re-alkalization depth of 33 mm was achieved within the investigation period. However, this high re-alkalization depth was only achieved when using high portions of KOH-solutions, which would be rather unsuitable for the construction site for safety reasons. Efforts should therefore be made to ensure that the materials are produced using ready-mixed compounds to which only water needs to be added.

With regard to the preparation of the concrete substrate, it was found that the absorbency of the concrete can be increased by pre-wetting the concrete surface shortly before applying the mortar. This promotes increased piggyback transport.

Since this study determined that the suction phase is the phase in which CRA progresses most rapidly, particular attention should be paid to appropriate follow-up treatment in order to ensure the best possible piggyback transport. Ideally, the surface should also be watered regularly in the days following the hardening of the mortar. Daily watering for one hour, as used in the present studies, cannot be recommended without reservation due to the severe leaching in the area close to the surface. To counteract the leaching of the mortar and the associated loss of the alkali buffer, which is also relevant for the carbonation resistance of the material, a hydrophobic coating could also be added at a later stage.

When selecting the materials, it is essential to clarify in advance the actual alkalinity of the mortar. In addition, the other advantages and disadvantages of the potential repair material should be taken into account. A summary of the identified practical properties is provided in Table 8-1.

Table 8-1: Summary of the practice-relevant features of the currently known re-alkalization materials.

	Main advantages	Limitations	Requirements for successful CRA	Handling and safety	Durability
OPC-based mortars	- Regulated and widely accepted in construction practice - Good compatibility with existing concrete substrates - Acts as a protective layer against re-carbonation	- slow re-alkalization over a long period of time - High clinker content associated with high CO₂ footprint - Reduced alkalinity when clinker content is significantly lowered	- Continuous moisture supply required to enable alkali transport over long time periods - Curing conditions during the first days after application are critical	- Dust exposure during mixing - Standard PPE sufficient	- Proven durability in practice - Suitable for CRA under moderate carbonation depths - Limited suitability for deep carbonation without modified binder systems
HAAB-based mortars	- Increased re-alkalization rate especially directly after application - Re-alkalization depth up to 33 mm proven - Potential for reduced clinker content - Can provide protection against re-carbonation	- Limited practical experience compared to OPC-based systems - Regulatory framework not yet fully established - Sensitive to leaching	- Continuous moisture supply for very high re-alkalization depths but no fundamentally higher compared to OPC-based materials	- Handling of highly alkaline materials - Increased requirements for PPE (skin and eye protection)	- Promising durability, but long-term field data still limited - Leaching can limit the durability or needs to be limited by further measures, e.g. hydrophobic treatment
Alkaline solutions	- High immediate alkali availability - High re-alkalization depths - Simple application methods	- No protective function against re-carbonation - High dependence on ambient moisture due to rapid drying - Not regulated in many countries	- Repeated application or sustained wetting often required - Immediate drying needs to be prevented to maintain process	- Handling of corrosive alkaline liquids - High risk of chemical burns and splashing - Strict safety measures required	- Risk of rapid re-carbonation - Only for special applications due to risk of leaching
Alkaline hydrogels	- Sustained release of alkalis - Potentially improved control over alkali transport - No permanent visual impact on components - Gel contains sufficient moisture to ensure continuous process	- No mechanical contribution or protective layer - Limited practical experience - Application and removal can be complex	- Sensitive to drying and environmental conditions	- Risk of skin contact and contamination of surrounding surface - Removal and disposal can pose practical challenges	- Durability highly dependent on boundary conditions - Currently more relevant for experimental or niche application - no information about long-term durability

A mortar with high initial alkalinity, such as HAAB, enables rapid initial re-alkalization, whereas cement-based mortars tend to re-alkalize over a longer period of time. This means that the necessary moisture supply would also have to be guaranteed over a significantly longer period of time, with Merkel, for example, specifying an average ambient humidity of at least 95 %. Particularly in the case of weakly alkaline mortars, which can occur mainly as a result of a high substitution rate, the combination of a low absorption phase, strong deceleration during the diffusion phase (even with high moisture supply) in combination with low carbonation resistance is one reason why such a material is not recommended for use in critical cases with regard to the risk of corrosion. However, if the mortar is only intended to maintain the alkalinity in the concrete in presence of low concrete carbonation, it is only necessary to ensure that the carbonation resistance is sufficiently high to guarantee the planned service life of the component.

8.4 LIMITATIONS OF THIS STUDY AND RECOMMENDATION FOR FUTURE RESEARCH

The present investigations have provided new insights into the potential of CRA as a repair method and the influence of the materials used. Nevertheless, there are limitations regarding the transferability of the present results to practical applications, which give rise to recommendations for further research.

Starting with carbonated concrete, which was artificially carbonated under accelerated conditions, it is possible that the initial state of the concrete is not entirely comparable to concrete used in the application. In addition, although the concrete class A2 was used as a reference, this was approximated primarily in terms of strength, resulting in a very high w/c ratio of 0.89 for the concrete. Due to the resulting high porosity of the concrete, it can be assumed that the transport processes were significantly intensified. Therefore, the strong characteristics of the suction phase should be verified on other concretes. Here, concretes with varying degrees of carbonation would also be important in order to investigate the inhibitory influence of carbonated concrete more precisely.

In addition, moisture supply should also be varied by increasing the intervals between the watering in order to approximate realistic environmental conditions. This would be particularly important for investigating the carbonation of the repair layer during and after CRA, as under the present conditions no carbonation could be observed, only leaching of the mortar.

With regard to leaching, no inhibitory effect on leaching could be determined in the 90-day period under consideration. Therefore, the period under consideration should be extended in order to

investigate the long-term behavior of the mortars. In this context, work should also be done to optimize the mortar formulations to such an extent that a pronounced suction phase is still guaranteed, but leaching is less pronounced after the mortar has hardened.

The development of the model is currently based on only six different material combinations, so its transferability to other material combinations should be verified. The basis for this is that in future studies, the re-alkalization depths will be determined at several points in time and, above all, after just one day.

Finally, and probably most importantly, the question of whether chemical re-alkalization leads to re-passivation of the steel reinforcement needs to be clarified. Tests have already been started within the scope of this work, whereby the defects between the steel reinforcement and the concrete have proven to be a source of misinterpretation of the results. Accordingly, the focus should be placed on the test specimen concept in order to achieve reliable results.

Overall, this thesis provides a basis for further research into chemical re-alkalization and the possibilities depending on the materials used, with a focus on the application of sustainable materials.

8.5 REFERENCES

- [1] Moraes, M.; Carasek, H.; de Castro, A.; Cascudo, O., Chemical realkalization in concretes subjected to natural carbonation over 20 years: Analysis of effectiveness and changes produced. *Construction and Building Materials* (2025) 495, 143622. <https://doi.org/10.1016/j.conbuildmat.2025.143622>
- [2] Réus, G. C.; Medeiros, M. H. F., Chemical realkalization for carbonated concrete treatment: Alkaline solutions and application methods. *Construction and Building Materials* (2020) 262, 120880. <https://doi.org/10.1016/j.conbuildmat.2020.120880>
- [3] Merkel, M., Realkalisierungspotenzial von zementgebundenen Werkstoffen im Trinkwasserbereich. Ph.D. Thesis, Technische Universität Kaiserslautern, (2021) Kaiserslautern, 15.07.2021.
- [4] Bier, T. A., Carbonation and realkalization of cement paste and concrete. Ph.D. Thesis, Universität Fridericiana zu Karlsruhe, (1988) Karlsruhe, 23.12.1987.