

Corrosion of Building Materials

Prof. Dr. Andreas Gerdes

Concrete and Mortar

Concrete and mortar is a mixture of...

- Portland Cement
- Aggregates
- Water
- Admixtures

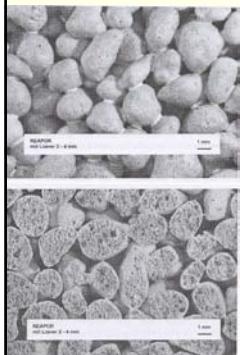


Aggregates I

Natural Aggregates	
Basalt	Mica
Gneiss	Opalit
Granite	Grauwacke
Quartz	Flint
Calcite	



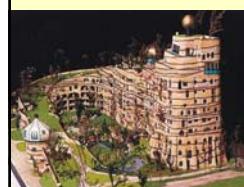
Aggregates



Industrial Aggregates

- Bims
- Blähton
- Geblähte Schlacke
- Geblähte Asche
- Geblähtes Glas

Aggregates III

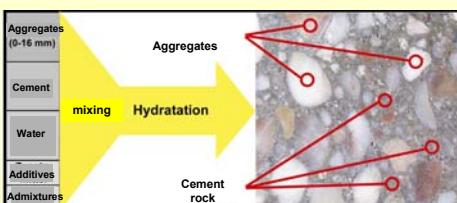


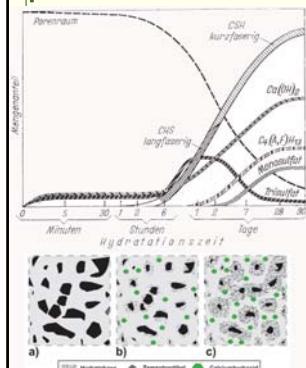
Recycling-Aggregates

- Excavation
(Gotthard-tunnel)
- FRANKA-Procedure
- Crusher
- Impact Mill

Properties of cement based materials

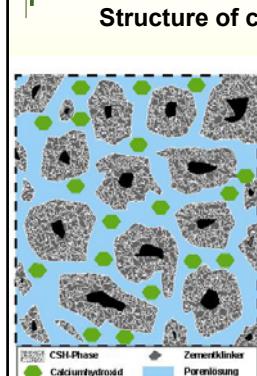
- Structure
- Chemical reactivity





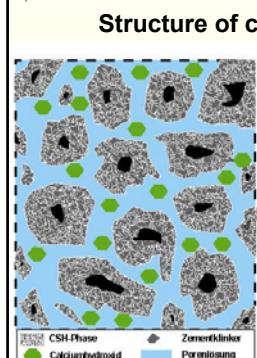
Structure build up due to hydration

- Formation of CSH-gel
- Decrease of pore volume
- Inclusion of calcium hydroxide in the pore volume / cement stone

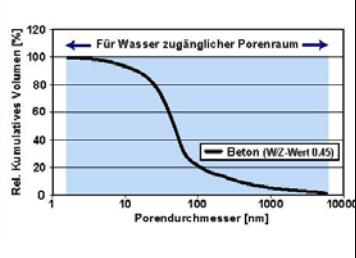


Structure of cement based materials

- Gel pores in CSH-Cluster
- Capillary pores between the Cluster



Structure of cement based materials



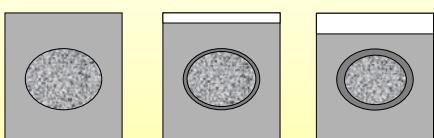
Pore classification

Concrete-techno-logical procedure	Pore type		Pore classification by Setzer	Pore classification by IUPAC
compacting	Compacting pores	Large pores	> 2 mm	-
Air entraining agents	Air pores	Micro-capillaries	50 µm – 2 mm	50 µm – 2 mm
W/C (water-cement-ratio)	Capillary pores	Capillaries	2 µm – 50 µm	2 µm – 50 µm
		Micro-capillaries	5 nm – 2 µm	5 nm – 2 µm
Hydration and type of cement	Gel pores	Mesopores	2 nm – 50 nm	2 nm – 50 nm
		Micropores	< 2 nm	< 2 nm

Pore size and Pore size distribution



Measuring of total porosity and pore size distribution by mercury pressure porosimetry



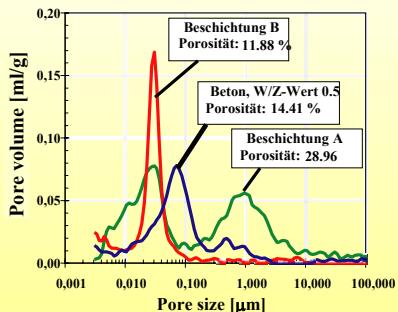
0 bar 1000 bar 2000 bar

Pressure is increased step by step up to 350 MPa

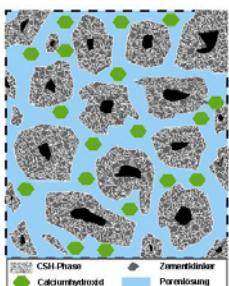
- Total mercury content is equivalent to total porosity
- With increasing pressure lower pore radii were filled



Pore size distribution of cement based materials



Composition of the pore solution

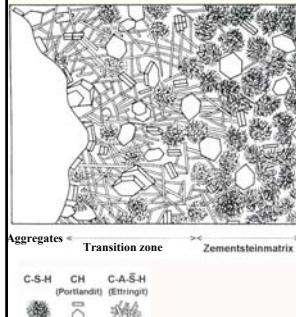


- Calcium hydroxide $[\text{Ca}(\text{OH})_2]$
- Potassium hydroxide $[\text{KOH}]$
- Sodium hydroxide $[\text{NaOH}]$
- Calcium sulfate $[\text{CaSO}_4]$

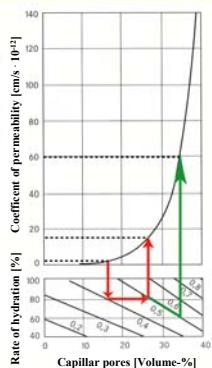
Saturated $\text{Ca}(\text{OH})_2$ -solution:
 $\text{pH } 12.3$

Pore solution of cement rock:
 $\text{pH } 12.3 - 13.0$

Microstructure of the phase boundary



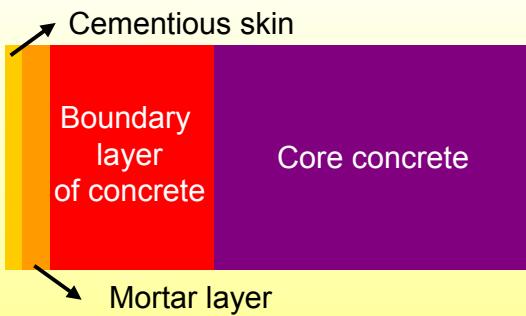
1. The phase boundary between aggregate and cement rock is 3.5 times more porous than the cement rock
2. Structure of the interface
 - Duplex film ($1 \mu\text{m}$ thick)
 - Crossover zone (approx. $50 \mu\text{m}$ thick)
3. Reasons for low strength
 - high porosity (high W/C-ratio)
 - Low crystalline bond of portlandite crystals
 - Hadley grains of hydration products



Permeability of cement based materials

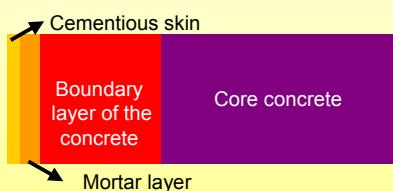
Researches made by
POWER's already made in the
1950's!!

The boundary layer of concrete



Influencing factors on the permeability of the boundary layer

- W/C-ratio
- Treatment after construction
- Used cement



Alkali-Silica-Reaction

1920 → Verification of a reaction between aggregates and alkaline chemicals

1965 → no danger in Germany

"Lachswehr"-bridge: built in 1965/66 , demolished in 1968



Mechanismen is well-known
since the 1970's

Alkali-Silica-Reaction (ASR)

1. Aggregate Reactivity

- Interferences in the grid structure
- Temperature
- Aggregate size
- pH-value of the solution



2. Influences on ASR

- Environment
- Temperature
- Humidity
- Amount and size of aggregates
- Permeability of the concrete
- Alkaline content of the cement
- Cement content

3. Counteractive measures

- Bond of alkaline content by puzzolanes
- Water repellent treatment

Damage processes

Carbonation



Carbonation of reinforced concrete

Brief historical abstract



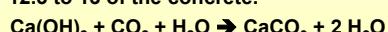
- 1879 Cement cover prevents iron from oxidizing (rust)
- 1908 Realisation that the alkaline ambience prevents this corrosion
- 1916 „Corrosion of highly importance because of security reasons“
- 1919 1.5 cm cover concrete shall be enough to prevent corrosion of the reinforcement

Carbonation of reinforced concrete

The reaction of the CSH-phases with CO₂ is called
CARBONATION



The Ca(OH)₂ (approx. 20 mass-%) which is build up by the hydration of cement and KOH & NaOH in the pore solution are responsible for the pH of approx. 12.3 to 13 of the concrete.

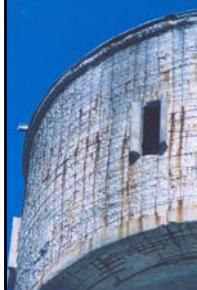


Reasons for damages by carbonation

- Low cement content
- Minor dimension of cover concrete
- CO₂-content of the air
- Additional pollutants (NO, NO₂, NO₃)
- Insufficient manufacture of the concrete

Reaction steps of the carbonation

**Carbonation is a coupled process:
Transport & chemical reaction**



- 1. Diffusion of CO₂ into the cement rock**
 - 2. Solution of CO₂ in the pore solution**

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow 2 \text{H}^+ + \text{CO}_3^{2-}$$
 - 3. Reaction of Ca(OH)₂ with H₂CO₃**

$$\text{Ca(OH)}_2 + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2 \text{H}_2\text{O}$$

Carbonation of the alkaline hydroxides

$$2 \text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$

$$\text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + 2 \text{NaOH}$$
 - 4. Decomposition of cement rock**

$$\text{C}_x\text{SH}_y + x\text{CO}_2 \rightarrow x\text{CaCO}_3 + \text{SiO}_2 + y\text{H}_2\text{O}$$

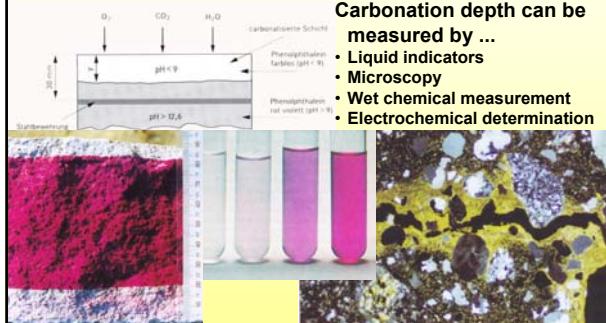
Consequences of carbonation

CARBONATION has positive & negative effects on reinforced concrete



- POSITIVE:
Increase in density of the concrete
($\Delta V=11\%$)
- NEGATIVE:
Decomposition of the protective layer
(approx. 50 nm) consisting of iron
hydroxides and oxides on the surface of
the reinforcement
→ Corrosion of the reinforcement

Determination of the depth of Carbonation



Calculation of carbonation depth

Carbonation is a diffusion controlled process:

1. Fick's law

$$\frac{dm}{dt} = D \cdot F \cdot \frac{dc}{dy} \quad dm = m_0 \cdot F \cdot dy$$

Mass balance

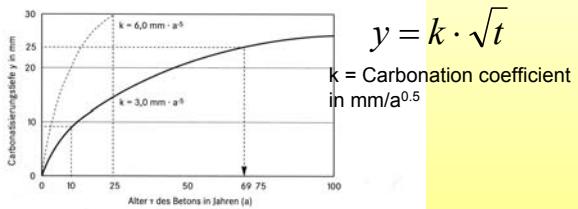
$$dm = m_0 \cdot F \cdot dy$$

m	=	CO ₂ mass transported through the concrete surface [kg]
t	=	Time of admission [a]
D	=	Diffusion coefficient [m ² /s]
c	=	CO ₂ concentration in the air and in the pore structure [kg/m ³]
y	=	Thickness of carbonated layer [m]
m_o	=	Absorbed CO ₂ mass per volume unit of concrete [kg]
F	=	Area of carbonating concrete [m ²]

Calculation of carbonation depth – \sqrt{t} -law

Solution of the diffusion equation:

$$y = \sqrt{\frac{2 \cdot D \cdot c_0}{m_0}} \cdot \sqrt{t}$$



Factors affecting the depth of carbonation



- Concentration of CO₂
 - Humidity
 - Concrete quality (W/C-ratio)
 - Type of cement
 - aftercare
 - Aggregates, additives, admixtures
 - Temperature

Factors affecting the depth of carbonation – CO₂-concentration

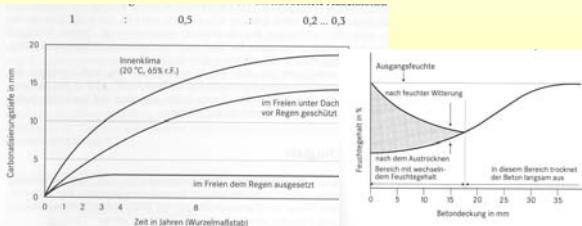
- CO₂ content in air is approx. 0.03% and almost constant.
 - Higher contents are a result of the type of use (e.g. basement garages or wine cellars)



Factors affecting the depth of carbonation -

Humidity

- High moisture content: lowers diffusion ($D \ll$)
 - Low moisture content: lowers reaction ($RG \ll$)
 - ➔ **Optimal value lies between 60% and 80% rel. humidity**

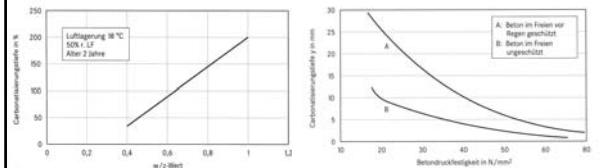


Factors affecting the depth of carbonation– W/C-ratio

- The Depth of carbonation is mainly determined by the permeability of the boundary concrete

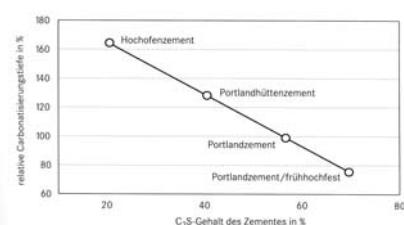
→ W/C-ratio

Depending on the W/C-ratio different final depth of carbonation can be detected



Factors affecting the depth of carbonation– Type of cement

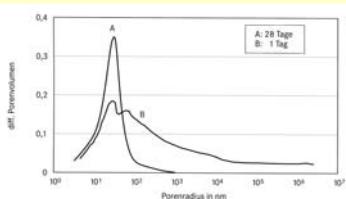
- Depending on the cement type different contents of $\text{Ca}(\text{OH})_2$ were build up and structure of different density were formed



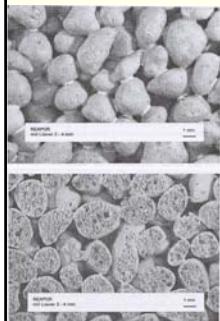
Factors affecting the depth of carbonation - Aftercare

- Adequate aftercare forms a denser concrete boundary layer
- Aftercare by keeping in the formwork, covering with foils or water storage meadows, aftercare additives, spraying with water

→ Increasing the carbonation resistance



Factors affecting the depth of carbonation – Aggregates, additives and admixtures



- Low weight aggregates (Perlite) result in an easier transport of water and CO_2
- Effect of admixtures is unexplained
- Additives form a denser concrete boundary layer; addition of up to 40% show no problem in the reaction with alkali

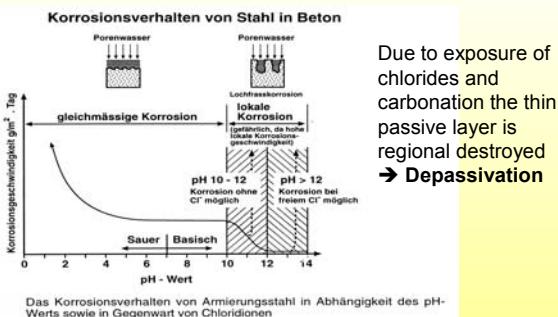
Corrosion of the reinforcement

Contrary to steel kept at the atmosphere a thin PASSIVE LAYER is formed in high alkaline medium

→ Low speed of corrosion



Destabilisation of the passive layer



Corrosion of the reinforcement

Conditions for reinforcement corrosion

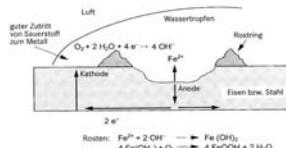
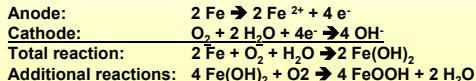
- Availability of an electrolyte
- „Break-down“ of the passive layer
- Adequate oxygen supply
- Formation of local potentials



Mechanism of reinforcement corrosion

The corrosion of the reinforcement is an electrochemical process

Electrochemical factors:

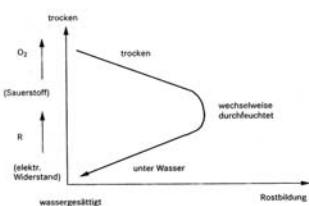


Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

Reinforcement corrosion – Affecting factors

The corrosion of the reinforcement is influenced by ...

- Oxygen supply (concrete quality, moisture content)
 - Electric resistance (moisture content, salt load)
 - ...

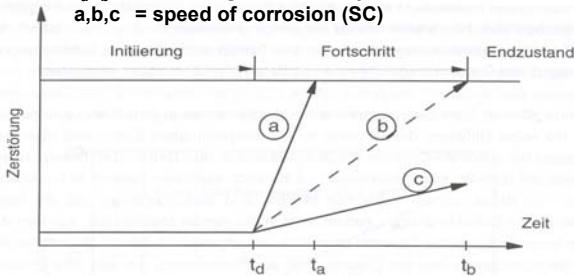


Devolution of the corrosion

t_d = point of depassivation

t_a, t_b = reaching final state by SC

a,b,c = speed of corrosion (SC)



Phase of Initiation

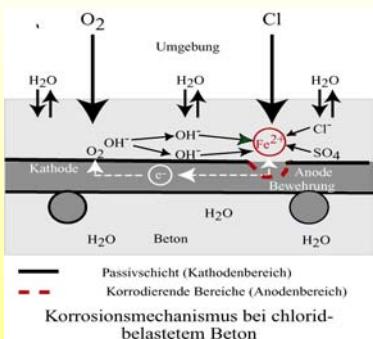
During the initiation phase aggressive compounds penetrate the boundary layer of concrete.

→ The period of initiation is determined by:

- ... Thickness of concrete cover
- ... Penetration speed of pollutants
- ... Concentration of pollutants

→ Calculation made by the civil engineer

Speed of corrosion



Characterising the process of corrosion

The process of corrosion can be expressed by the rate of degradation.

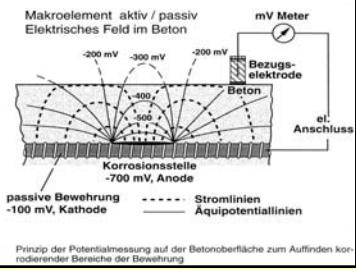
For example: 10-1000 µm per year

Methods to determine the corrosion

- Potential measurement ...
 - Electrical resistance of the concrete
 - Impedance measurement
- ... Allows fundamental evidence of
- Location and state of areas of corrosion
 - Actual state of the corrosion of the reinforcement

Corrosion potential of the reinforcement

Due to the current flow induced by the corrosion an electrical field is build up. The potential of the corrosion is representative for the actual state of the corrosion.



Prinzip der PotentialsMessung auf der Betonoberfläche zum Auffinden korrodierender Bereiche der Bewehrung

Phase II: Potential measurement



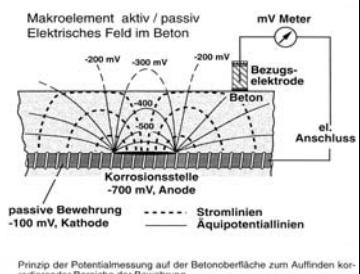
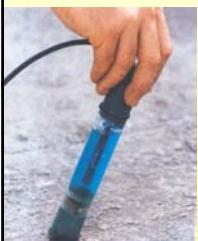
- After removal of the surface
- Up to 1000 m²/d



- In complex buildings
- Up to 1000 points/d

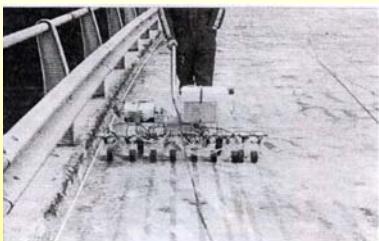
Implementation of the measurement

- Connecting the Cu/CuSO₄-electrode with volt meter
- Connecting reinforcement with volt meter
- Measurement of the corrosion potential

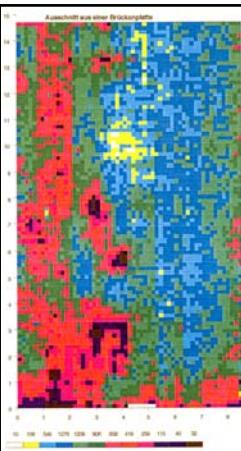


Performance of the measurement

Large areas can be scanned by wheel-electrodes. The results are evaluated by computers.



Das im Rahmen des Forschungsprojekts entwickelte IBWK-Messsystem für Potentialfeldmessungen mit acht Radenelektroden im praktischen Einsatz.

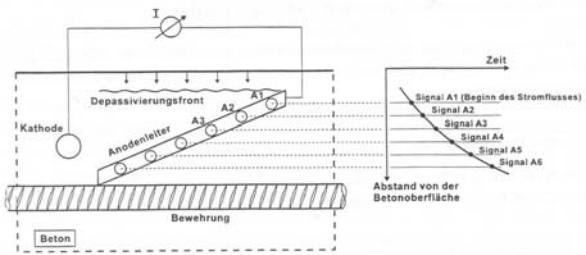


Typical results

Analysis is performed by computers. The output is given as „potential mappings“.

Test probe for monitoring

Assembly of the test probes in very exposed concrete members.



Condition analysis of a balcony plate

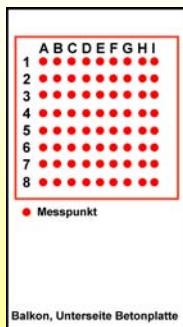
Balcony – State of repair



Balcony – State of repair



Results of balcony analysis



Results of balcony analysis



Results of balcony analysis



Results of balcony analysis



Results of balcony analysis

9 7 22 30 32 11 14

Results of balcony analysis

Adlerstrasse Nr. 42 - 4. OG										
Bewehrungsüberdeckung in mm										
A	B	C	D	E	F	G	H	I	Mittelwert	Standardabw.
30	28	25	24	10	5	9	5	-	17,0	10,7
29	30	25	23	6	7	27	8	-	19,3	10,7
21	15	12	15	10	7	11	5	-	12,1	5,0
22	19	16	19	12	8	-	-	-	16,1	5,1
34	20	28	31	23	8	-	-	-	24,0	9,4
38	30	22	14	15	9	8	-	-	19,4	11,2
32	24	18	15	18	15	9	8	-	17,4	7,8
Mittelwert Bewehrungsüberdeckung/Standardabweichung:										
Carbonatisierungstiefe										
Bohrkern 1	Bohrkern 2	Bohrkern 3	Mittelwert Carbonatisierungstiefe							

17,0 8,6

Carbonatisierungstiefe

Results of balcony analysis

Adlerstrasse Nr. 42 - 5. OG											
Bewehrungsüberdeckung in mm											
Position	A	B	C	D	E	F	G	H	I	Mittelwert	Standardabw.
1	29	22	17	16	15	13	5	-	-	16,7	7,4
2	20	8	19	18	32	25	5	-	-	15,1	9,3
3	15	11	11	18	30	5	-	-	-	14,5	8,4
4	15	10	10	12	12	5	5	-	-	13,5	4,4
5	11	10	10	11	13	26	5	-	-	12,3	6,6
6	22	19	14	21	15	19	7	-	-	16,7	6,2
7	21	38	22	18	17	7	7	-	-	16,6	10,6
8	-	-	-	-	-	-	-	-	-	-	-
Mittelwert Bewehrungsüberdeckung/Standardabweichung:											15,6 7,4
Carbonatisierungstiefe											
Bohrkern 1	Bohrkern 2	Bohrkern 3	Mittelwert Carbonatisierungstiefe								6,7

15,6 7,4

Carbonatisierungstiefe

Results of balcony analysis

Steinstrasse Nr. 19 - 4. OG											
Bewehrungsüberdeckung in mm											
Position	A	B	C	D	E	F	G	H	I	Mittelwert	Standardabw.
1	37	28	17	19	20	5	5	-	-	18,7	11,6
2	32	30	22	20	15	8	5	5	-	17,1	10,7
3	37	36	24	31	29	22	16	-	-	27,3	10,0
4	30	33	30	21	17	16	14	-	-	23,8	12,0
5	39	32	17	11	21	19	7	-	-	20,5	11,3
6	43	42	41	39	38	27	7	5	-	30,3	16,8
7	32	23	11	5	9	7	5	7	9	12,4	9,9
8	-	-	-	-	-	-	-	-	-	-	-
Mittelwert Bewehrungsüberdeckung/Standardabweichung:											21,5 11,3
Carbonatisierungstiefe											
Bohrkern 1	Bohrkern 2	Bohrkern 3	Mittelwert Carbonatisierungstiefe								18,0

21,5 11,3

Carbonatisierungstiefe

Results of balcony analysis

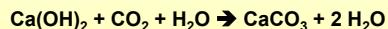
Position	Steinstraße Nr. 19, 5. OG									Mittelwert	Standardabw.
	A	B	C	D	E	F	G	H	I		
1	37	28	28	28	28	21	17	-	-	24.6	6.0
2	31	33	29	22	37	35	19	-	-	29.8	9.9
3	34	17	34	34	23	12	19	-	-	24.7	9.3
4	35	11	32	34	32	32	22	-	-	29.3	6.7
5	37	34	28	29	34	26	-	-	-	29.9	6.5
6	36	36	33	25	17	23	-	-	-	29.5	7.8
7	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-
										Mittelwert Bewehrungsüberdeckung/Standardabweichung:	27.6 7.9
										Carbonatisierungsdicke	
	Bohrkern 1	Bohrkern 2	Bohrkern 3	Mittelwert	Carbonatisierungsdicke						
	20	20	15	18.3							

Carbonation of reinforced concrete

The reaction of the CSH-phases with CO₂ is called
CARBONATION



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- Low cement content
- Minor dimension of cover concrete
- CO₂-content of the air
- Additional pollutants (NO, NO₂, NO₃)
- Insufficient manufacture of th concrete

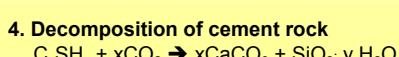
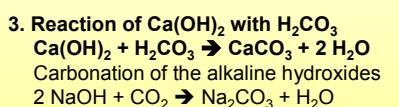
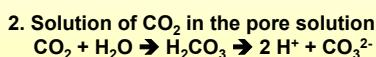
Reaction steps of the carbonation

Carbonation is a coupled process:

Transport & chemical reaction



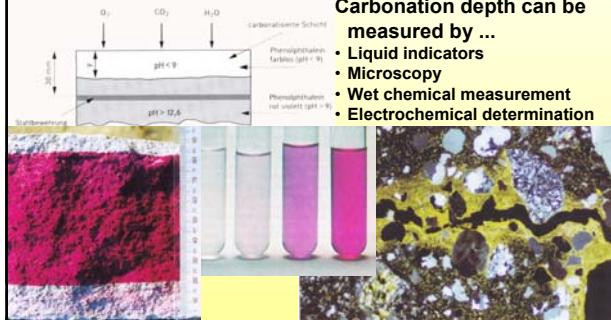
1. Diffusion of CO₂ into the cement rock



Determination of the depth of Carbonation

Carbonation depth can be measured by ...

- Liquid indicators
- Microscopy
- Wet chemical measurement
- Electrochemical determination



Calculation of carbonation depth

Carbonation is a diffusion controlled process:

1. Fick's law

$$\frac{dm}{dt} = D \cdot F \cdot \frac{dc}{dy}$$

Mass balance

$$dm = m_0 \cdot F \cdot dy$$

m	=	CO ₂ mass transported through the concrete surface [kg]
t	=	Time of admission [a]
D	=	Diffusion coefficient [m ² /s]
c	=	CO ₂ concentration in the air and in the pore structure [kg/m ³]
y	=	Thickness of carbonated layer [m]
m₀	=	Absorbed CO ₂ mass per volume unit of concrete [kg]
F	=	Area of carbonating concrete [m ²]

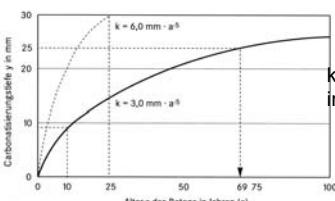
Calculation of carbonation depth – \sqrt{t} -law

Solution of the diffusion equation:

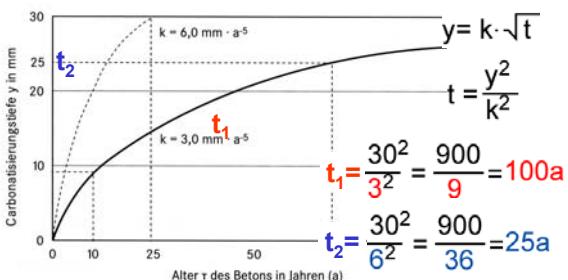
$$y = \sqrt{\frac{2 \cdot D \cdot c_0 \cdot t}{m_0}}$$

$$y = k \cdot \sqrt{t}$$

k = Carbonation coefficient
in mm/a^{0.5}



Calculation of the life span of a carbonating concrete member



Damage mechanism

- Sulfidation
- Sulfate attack

Sulfidation of concrete

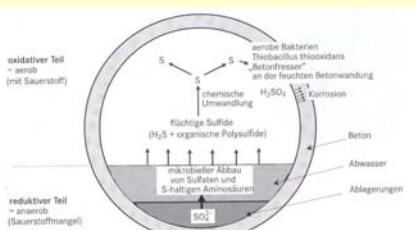
Emissions (e.g. fuel) in the air are oxidised to SO_2 or SO_3 . By reaction with rain „sulphurous acid“ and „sulphuric acid“ is formed

→ Reactions of these acids with cement rock form gypsum
 $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$

But no high penetration depth → surface near effect

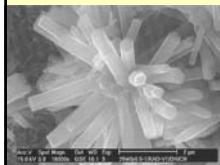
Sulfidation of concrete

In presence of micro organisms gaseous sulfur compounds can also be formed which attack and destroy the concrete.



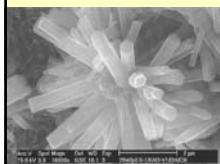
Sulfate attack on concrete

- Important damage mechanism
- Known since 1877 (Michaelis)
 - Structural damage due to the formation of complex compounds ($3 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{ CaSO}_4 \cdot 32 \text{ H}_2\text{O}$)
 - Damage event: 1890 in Magdeburg. Spring water with 2000 mg/l sulfate → 8 cm expansion in 2 years



Influence of sulfate – Attack through expansion

- Sulfate attack results in expansion
- Compounds of cement rock react together (**INTERNAL ATTACK**) or together with penetrating chemical agents (**OUTER ATCK**)



Portland cement – Hydration of C₃A

Addition of water: $2\text{C}_3\text{A} + 21\text{ H} \rightarrow \text{C}_4\text{AH}_{13} + \text{C}_2\text{AH}_8$
 Conversion: $\text{C}_4\text{AH}_{13} + \text{C}_2\text{AH}_8 \rightarrow 2\text{ C}_3\text{AH}_3 + 3\text{ CH}$



- In absence of sulfate C₃A hydrates in thin plates (calciumaluminate- hydrates)
- ➔ **Result:** quick stiffening of the material

Portland cement – Hydration of C₃A in presence of CaSO₄

Formation of ettringite

Addition of water: $\text{C}_3\text{A} + 3\text{CSH}_2 + 26\text{ H} \rightarrow \text{C}_3\text{A}-3\text{CS} \cdot 32\text{ H}$ ettringite

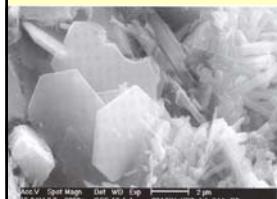


- In presence of gypsum the water-rich compound ettringite is formed
- ➔ **needle-structure**
- Result:** Decrease of the reactivity of the C₃A-Phase

Portland cement – Hydration of C₃A in presence of CaSO₄

Formation of monosulfate

Conversion: $\text{C}_3\text{A}-3\text{CSH}_{32} + 2\text{ C}_3\text{A H} \rightarrow 3\text{C}_3\text{ACSH}_{12}$
 Monosulfat



- The layer get more porous and the reaction starts again.

Types of sulfate attack

Inner sulfate attack:

- Excessive gypsum content in Portland cement
- Cement mortar in contact with gypsum
(e.g. reconstruction of brickwork with mortars containing gypsum)

Outer sulfate attack:

- Sulfate containing waters and soils

Inner/Outer attack – Reaction process

Inner sulfate attack:

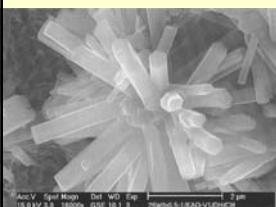
- Comparative quick reaction
- Speed of reaction decreases by time

Outer sulfate attack:

- Time-dependent because of transport process
- High sulfate concentration is necessary
- Speed of reaction increases
- Cation determines speed and amount of reaction too

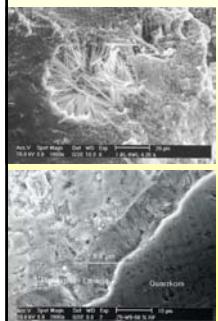
Properties of sulfate attack

C_3A resp. calciumaluminate hydrates react with gypsum under formation of ettringite
→ 8 times increase in mol volume



Acc.V Spd.10μm Dist. WD Exp. 29W1025-XRD-V105FCR
15.0 kV 3.0 1000x 0.25 10.1 3

Properties of sulfate attack

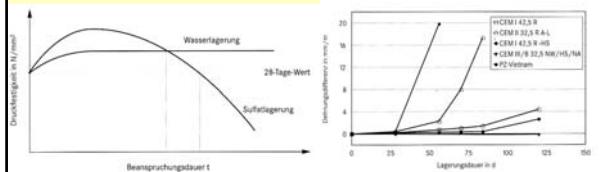


Formation of ettringite in pores and phase boundary layers

Reason:
**Large pore area is accessible
for precipitation products**

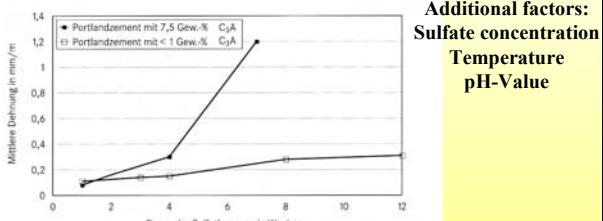
Effect on concrete structure

- Formation of ettringite firstly results in higher strength
 - Formation of micro cracks → expansion!!
 - Total demolition of the structure



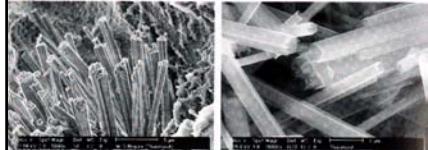
Factors determining the sulfate resistance – C₃A-content

- Sulfate resistance is mainly depending on C₃A-content



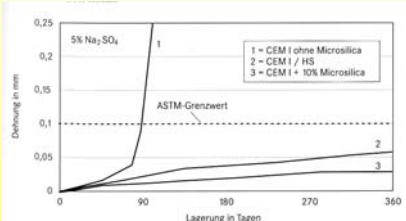
Factors determining the sulfate resistance – Low C₃A-content cements

- Even cements with low C₃A-content can be attacked by sulfate → formation of thaumasite
- Mechanism:
 1. Sulfate exposure to C₃A → Ettringite (actuator)
 2. CO₂/CO²⁻ (water) and SiO₂ (CSH-Gel) transform ettringite to THAUMASITE
- Pre-condition: temperature < 10 °C, even better < 5 °C



Factors determining the sulfate resistance – Influence of additives

- Fly ash, sands und micro silica (Puzzolane) improve sulfate resistance → higher density
- This effect is increased when C₃A-content decreases



Type and Concentration of sulfate solution



- (NH₄)₂SO₄ > MgSO₄ > Na₂SO₄ > CaSO₄
- E.g. combination of dissolving and expanding attack
- Degree of attack depends on concentration (up to 10 000 mg/l)
 - up to 1000 mg/l: Formation of AFt und AFm
 - up to 1000 mg/l: Formation of gypsum

Grenzwerte für die chemischen Merkmale der Expositionsklassen XA1-XA3 nach DIN EN 206-1				
Chemisches Merkmal	Referenz-prüfverfahren	XA1	XA2	XA3
Grundwasser				
SO ₄ ²⁻ mg/l in Wasser	EN 196-2	≥ 200 und ≤ 600	> 600 und ≤ 3000	> 3000 und ≤ 6000
pH-Wert	ISO 4316	≤ 6,5 und ≥ 5,5	< 5,5 und ≥ 4,5	< 4,5 und ≥ 4,0
CO ₂ mg/l angreifend	PrEN 13577	≥ 15 und ≤ 40	> 40 und ≤ 100	> 100 bis zur Sättigung
NH ₄ ⁺ mg/l	ISO 7150-1 oder ISO 7150-2	≥ 15 und ≤ 30	> 30 und ≤ 60	> 60 und ≤ 100
Mg ²⁺ mg/l	ISO 7980	≥ 300 und ≤ 1000	> 1000 und ≤ 3000	> 3000 bis zur Sättigung
Boden				
SO ₄ ²⁻ mg/kg insgesamt	EN 196-2 ²⁾	≥ 2000 und ≤ 3000 ³⁾	> 3000 ³⁾ und ≤ 12.000	> 12.000 und ≤ 24.000
Säuregrad in ml/kg	DIN 4030-2	> 200	in der Praxis nicht anzutreffen	

¹⁾ Tonböden mit einer Durchlässigkeit von weniger als 10^{-1} m/s dürfen in eine niedrigere Klasse eingestuft werden.

²⁾ Das Prüfverfahren beschreibt die Auslösung von SO₄²⁻ durch Salzsäure. Wasserauslösung ist nicht zulässig, da diese nicht erlaubt werden, wenn am Ort der Verwendung des Betons Erfahrung hierfür vorhanden ist.

³⁾ Falls die Gefahr der Ablösung von Sulfatonen im Beton - zurückzuführen auf wechselndes Trocknen und Feuchtigkeitswechsel kapillares Saugen - besteht, ist der Grenzwert von 3000 mg/kg auf 2000 mg/kg zu vermindern.

Critical value, defined by DIN EN 206-1

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Influence of concrete quality on sulfate corrosion

- Low W/C-ratio
- high Portland cement content → Increase of sulfate resistance
- Low cement content
- Addition of puzzolanes

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Examples for highly endangered buildings

Bridges

Industrial facilities

Tubes

Drinking water reservoir

Waste water treatment plant

	Belebungsbecken Sohle, Wände	Nachklärbecken Kronenbereich Laufbahn	FH Karlsruhe UNIVERSITY OF APPLIED SCIENCES HOCHSCHULE FÜR TECHNIK	
Anforderungen	B 35 / Wasserundurchlässigkeit: hoher Frostwiderstand; hoher Widerstand gegen starken chemischen Angriff (1000 mg SO ₄ ²⁻ /l im Grund- wasser/Baugrund) ¹⁾	hoher Frost-Tausalz-Wider- stand		
Beton	Kiesbeton 0/32 mit Pumpförderung	Konsistenz KR LP-Beton ($\epsilon = 5 \pm 0,5$ Vol.-%) Konsistenz KP		
Zementart	CEM III/A 32,5-NW/NA	CEM I 32,5 R		
Zementgehalt z	kg/m ³ 345	370		
SFA f	kg/m ³ 50 ²⁾	-		
Wassergehalt w	kg/m ³ 180	170		
w/z	0,52	0,46 < 0,50		
w/(z + 0,4f)	0,49 < 0,50	-		
Größtkorn mm	32	32		
Zusammensetzung g	kg/m ³ 1728	1710		
Körnungen bei Sieblinie im Bereich AB M-%	0/2a = 34	2/8 = 18	8/16 = 24	16/32 = 24
Zusatzzmittel	BV	BV, LP		
Druckfestigkeit N/mm ²	42,8 / 50,2 ²⁾	43,0 / -		
d = 28 / 56 Tage				
Wassereindringung mm	22 < 30	20 < 30		
tiefe ϵ_{28}				
CDF-Test	-	Bestanden		

¹⁾ Nach BILZ DAISIb 09/96 „Verwendung von Flugasche nach DIN EN 450 im Betonbau“ gilt:
 $f_z + f_f \geq 0,10$ bei Einsatz von CEM II/A
²⁾ Vereinbartes Nachweisalter beim Beton mit CEM III/A ist d = 56 Tage

Case study: concrete for waste water treatment plant

Waste water treat-
ment plant



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Cement based materials in permanent contact with water



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Why are drinking water reservoirs coated?



- Hygienic storing
- Repairing of entraptments (e.g. cracks)
- Abrasion layer against chemical and mechanical influences
- Easier cleaning
- appearance

Corrosion of mineral materials

Characterisation of the damage

- Appearance
- Mechanical properties
- Chemical composition
- Kinetics



Damage characterisation

Appearance

- Circular damage spots (diameter up to 5 cm)
- Often brown discolouration
- Often vertical, horizontal or orthogonal archetypes



Damage characterisation

Mechanical properties

- Defect material is softened
- Material can be easily removed, e.g. by cleaning



Damage characterisation

Chemical composition

- $\text{Ca}(\text{OH})_2$ -content equals zero
- Increased CaCO_3 -content



Damage characterisation

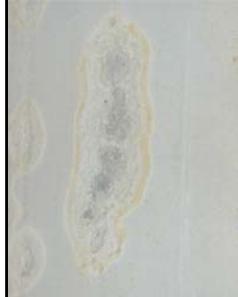
Kinetic

- High speed and local increase in corrosion
- Damage appears already six month after application



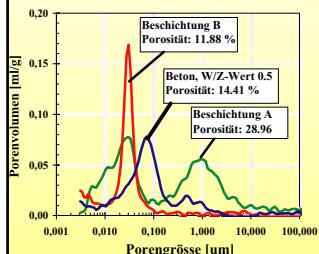
Possible causes for that damage

- Water attacks chemically
- Microorganismn
- Acidic cleaners
- Hydrolysis of the cement based material



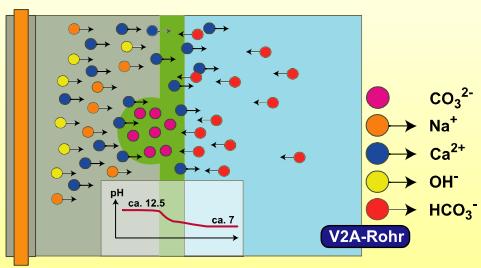
Mechanism of hydrolysis

1. Reaction step: Ion-transport
 - intake of HCO_3^- -ions
 - export of Na^+ , K^+ and Ca^{2+} -ions



- diffusion controlled
- transport resistance is structure dependent
(total porosity, content capillary pores)
- accelerated by electric fields

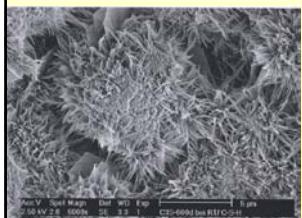
Schematic demonstration: Hydrolysis of cement based materials



Hydrolysis mechanism

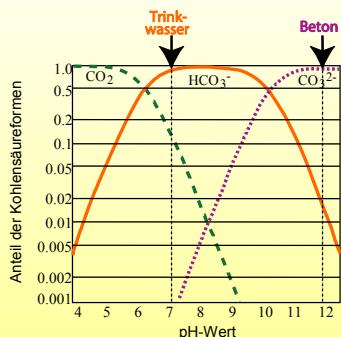
- 2. Reaction step: chemical reaction**

 - pH-dependent transformation of HCO_3^- ions in CO_3^{2-} ions
 - Precipitation of CaCO_3 by consuming $\text{Ca}(\text{OH})_2$
 - degradation CSH-phases to SiO_2 , Al_2O_3 and CaCO_3



Hydrolysis is a coupled process of transport and chemical reaction

„Lime-carbonic acid“-balance



Anteil der Kohlensäureformen

Trink-
wasser

Beton

pH-Wert ca. 7:
es liegt praktisch HCO_3^- vor

pH-Wert ca. 12:
es liegt praktisch nur CO_3^{2-} vor

Concept for quality insurance „Coatings for drinking water reservoirs“ in Switzerland

Tests:

1. Step: withdrawal of drilling core (\varnothing 50 mm)
2. Step : Determination of **layer thickness**
3. Step : Measurement of **total porosity** and **pore size distribution** (Hg-porosimetry)
4. Step: Determination of **calcium carbonate**- and **calcium hydroxide**-content

Concept for quality insurance „Coatings for drinking water reservoirs“ in Switzerland

Demands:

Layer thickness > 10 mm

Total porosity: < 15% ($p=2500$ bar)

1. Maximum in pore size distribution: < 0.1 μm

Chemical analysis: -