



Ins & outs of carbonation of concrete

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Ins & outs of carbonation of concrete

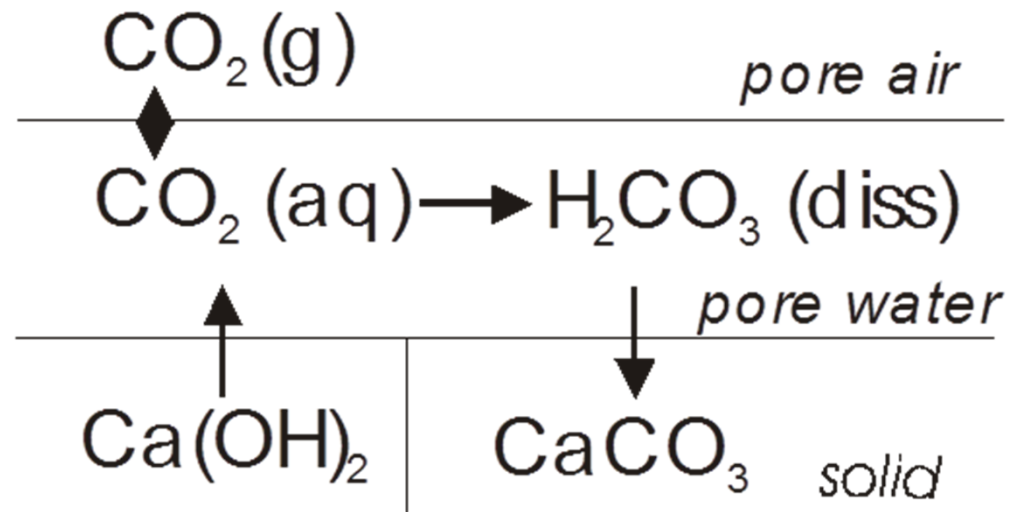
Contents:

1. Introduction: what is carbonation and why should we worry about it?
2. The carbonation mechanism
3. Testing the resistance against carbonation of concrete
 - influence of the humidity conditions
 - natural versus accelerated testing (CO_2 concentration)
 - Choice of cements
4. Designing for sufficient resistance against carbonation:
 - Service life design
 - Design by testing
 - Trading cover thickness for resistance or rather making a green deal?
5. Conclusions



1. Introduction: what is carbonation?

- **Carbonation** is the chemical reaction of the binder paste ('cement stone') with the CO_2 in the air
- Carbonation starts with **diffusion of CO_2 -molecules**
- It **dissolves** in the pore water and forms CO_3^{2-} ions
- It is instantly **consumed by Ca^{2+}** in the pore fluid

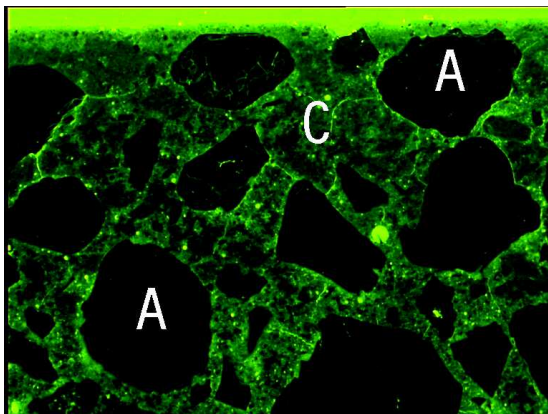




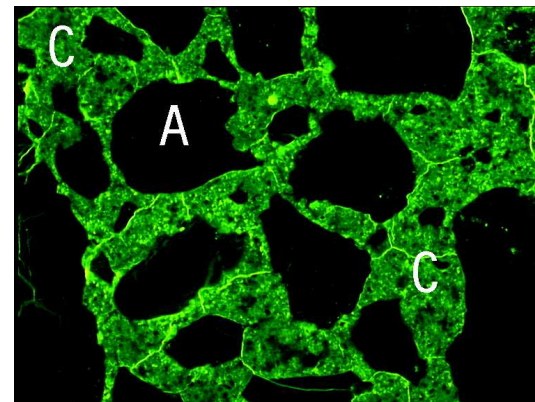
1. Introduction: why should we worry about carbonation?

- Carbonation lead to **a change in the cement paste** (e.g. Ca(OH)_2 into CaCO_3)
- Carbonation leads to **a change in the pore structure** (e.g. more dense for OPC, more porous for BFSC)
- Carbonation leads to a **change in the pH** of the cement stone below $\text{pH} < 9$; this breaks the passivation of the reinforcement when the carbonation front reaches it, leading to **corrosion**

non-carbonated BFSC



carbonated BFSC





1. Introduction: why is carbonation important?

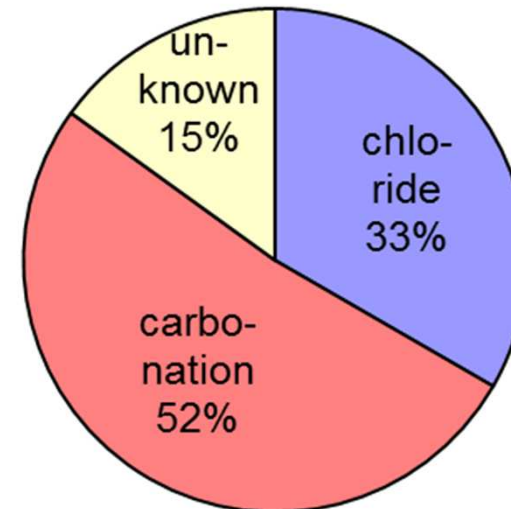
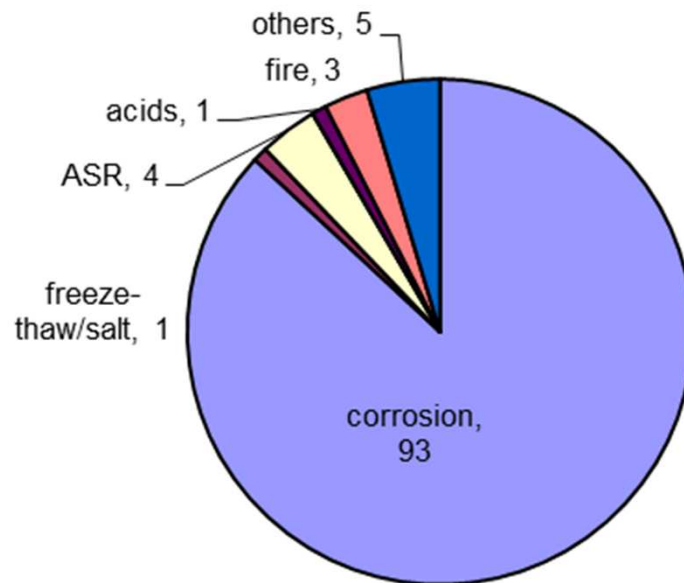
- Corrosion = the **rusting** of the reinforcement
- **Corrosion Initiation** = the breaking of the passivation (either by a drop in pH or due the presence of chlorides)





1. Introduction: why is carbonation important?

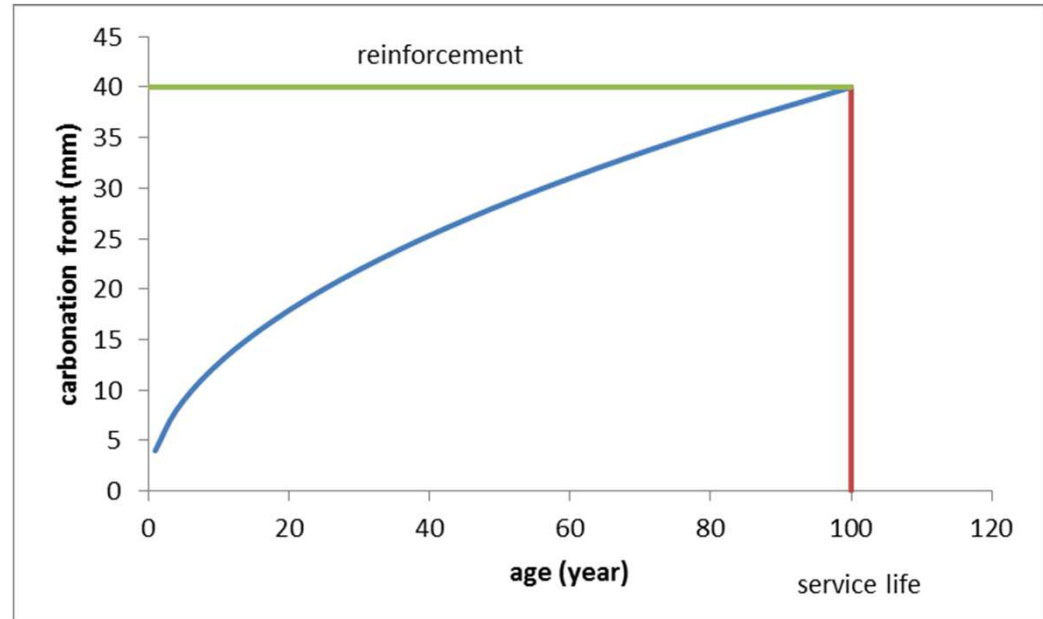
- **Corrosion** of the reinforcement may lead to damage (it is the most often encountered degradation)
- **Damage** include spalling & cracking and loss of rebar diameter
- This may lead to extensive repair & costs or even early **end of service life**





1. Introduction: why is carbonation important?

- **Service life** = time that a structure fulfils its performance demands
 - A performance demand may be: no corrosion within 100 year
 - Degradation will reduce the performance of the structure
 - When it fails to meet its demands the service life is said to be finished
-
- **We then need to take measures!**





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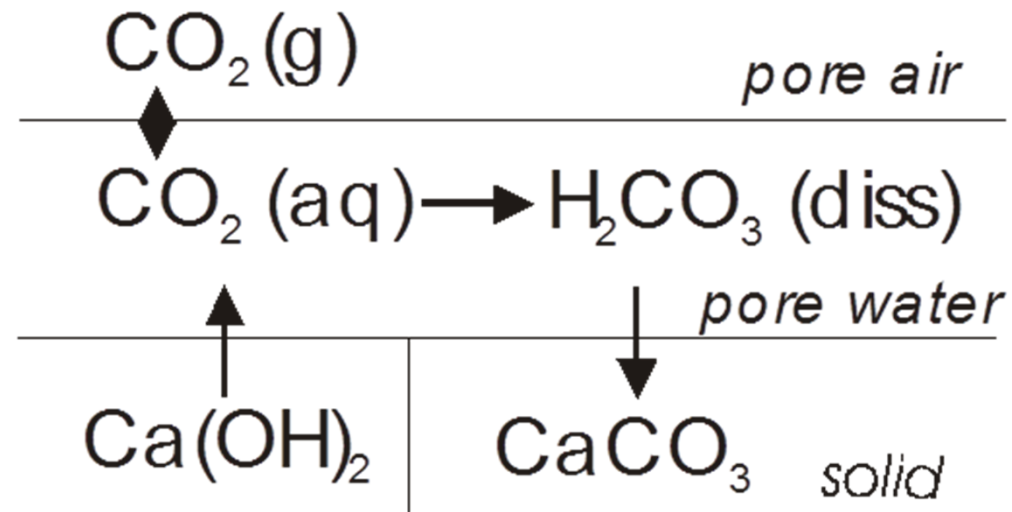
1. Introduction: what is carbonation and why is it important?
2. **The carbonation mechanism**
 - Chemical equilibrium of CO_2 in pore water
 - Stability of the cement phases
 - Buffering capacity of the cement phases
 - Transient effects in carbonation
3. Testing the resistance against carbonation of concrete
4. Designing for sufficient resistance against carbonation
5. Conclusions



2. The carbonation process

› *Chemical equilibrium:*

- › *Transport of CO₂ due to concentration difference*
- › *Dissolution of CO₂ in pore water and formation carbonic acid and dissociated (H₂CO₃, HCO₃⁻, CO₃²⁻)*
- › *Precipitation CaCO₃ - dissolution Ca(OH)₂*

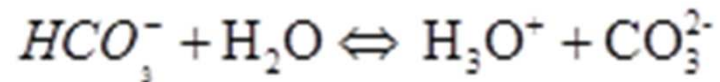




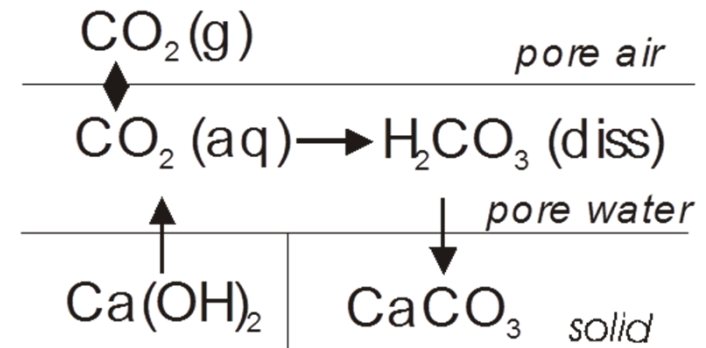
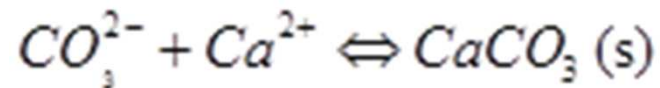
2. Carbonation mechanism: chemical equilibrium

› *Chemical equilibrium – in detail:*

› *Dissociation is acidification process*

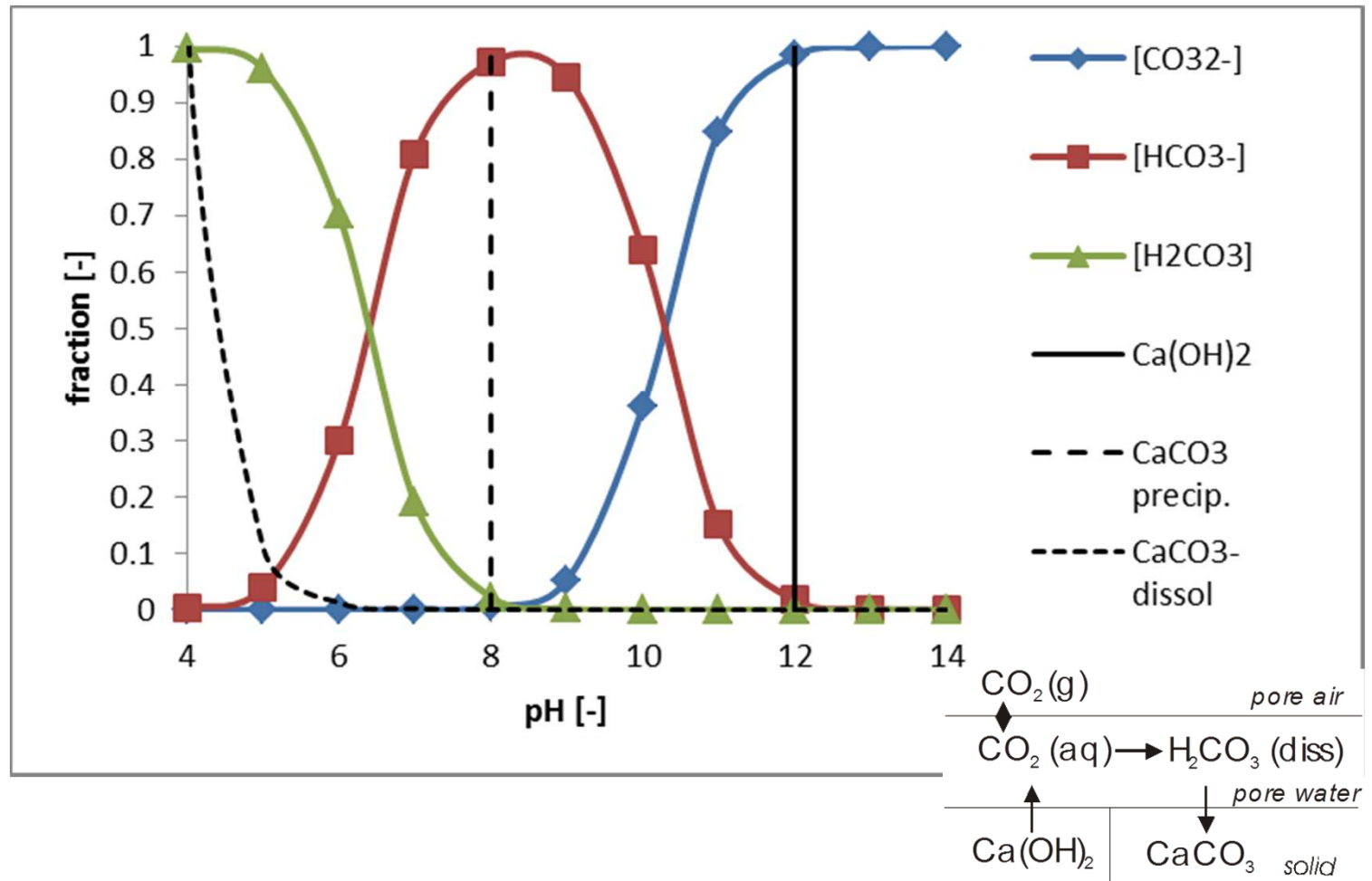


› *Precipitation of Ca^{2+} goes to completion:*





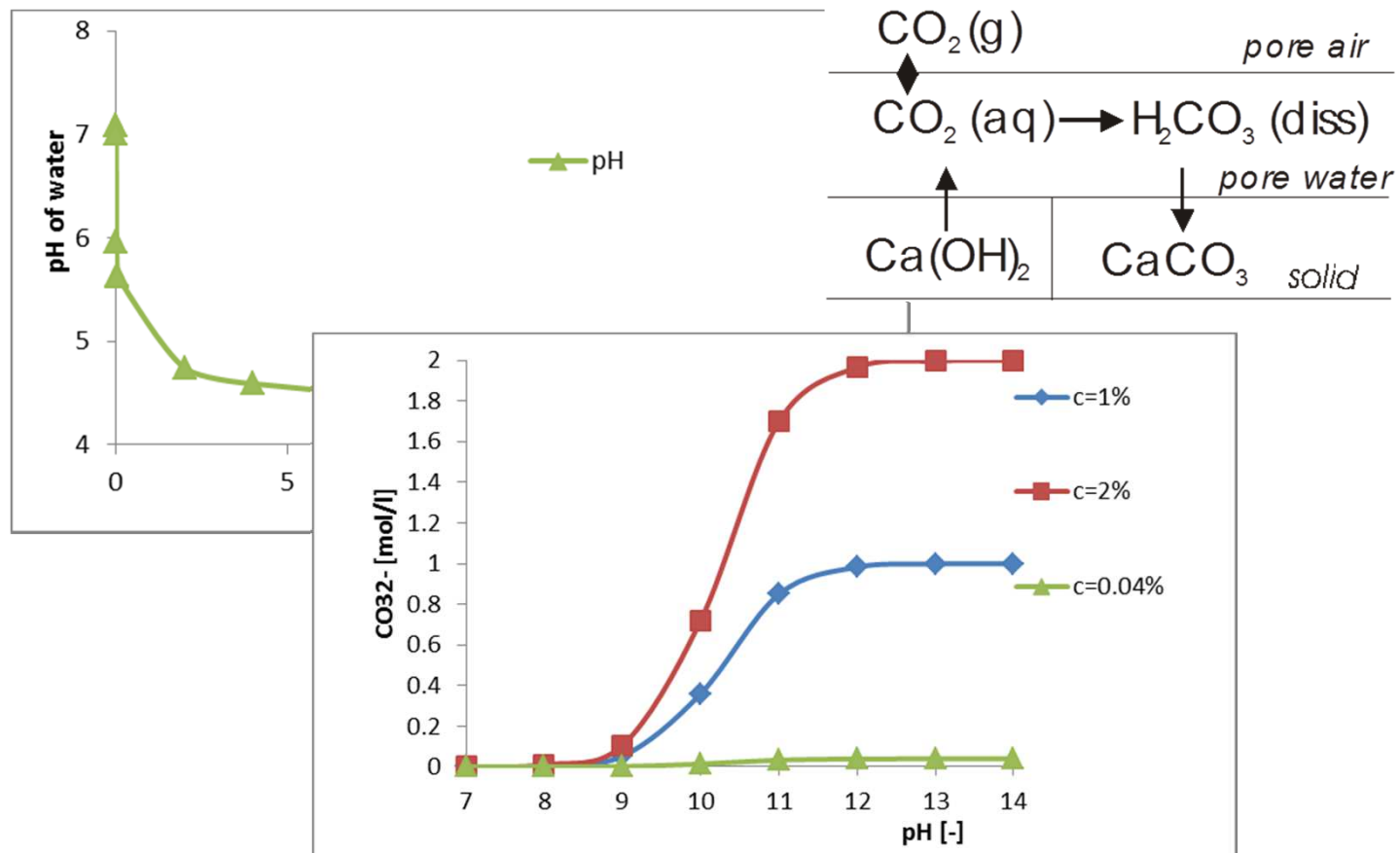
2. Carbonation mechanism: chemical equilibrium





2. Carbonation mechanism: chemical equilibrium

- *Equilibrium pH depending on CO₂ concentration*





2. Carbonation mechanism: stability of the cement phases

- *Stability & pH*

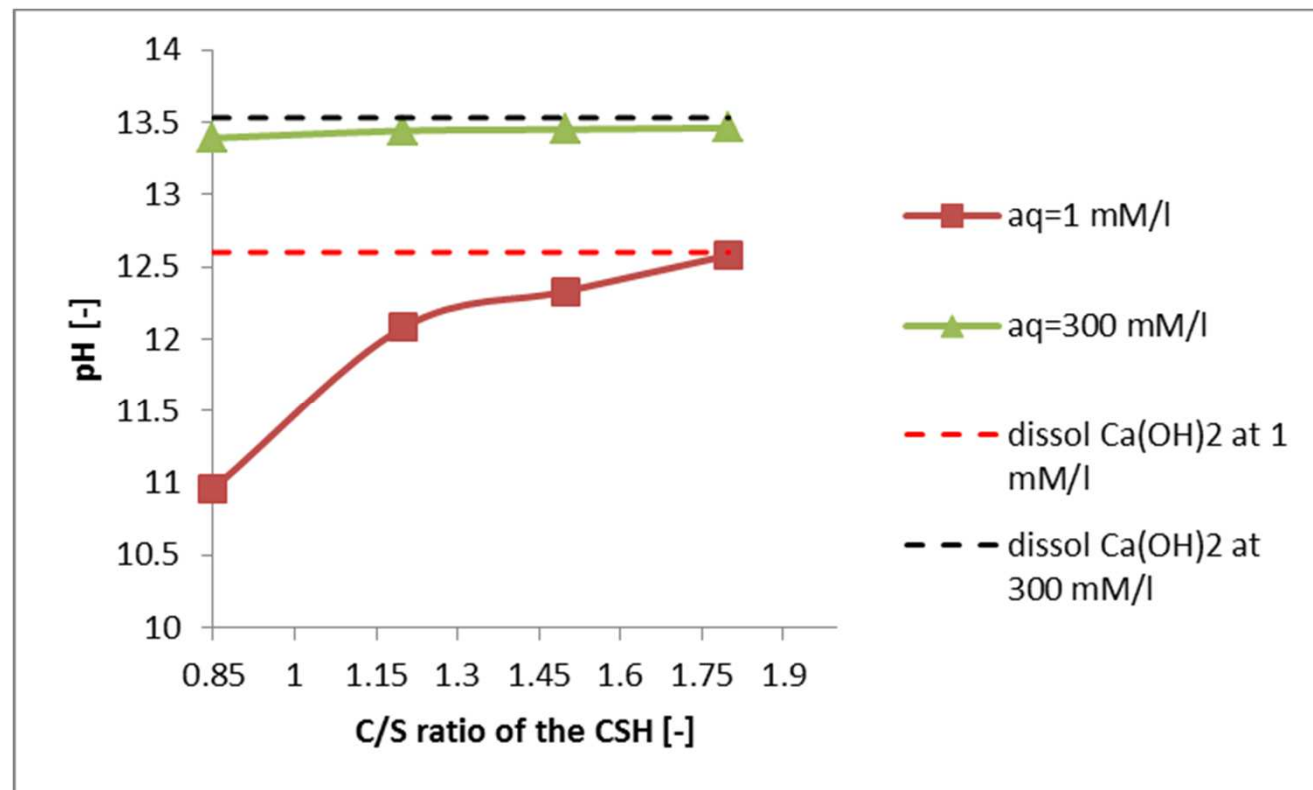
Stage	pH	stable phases
1 (non-carbonated)	>12.6	Ca(OH)_2 , CSH (Ca/Si > 1.8 or at high common ion effect), AFt, AFm
2	11.6 – 12.6	CSH (Ca/Si< 1.8), AFt, AFm
3	10.5 – 11.6	CSH (Ca/Si< 1.05), AFt, Al(OH)_3
4	10.0 – 10.5	CSH (Ca/Si< 0.85), Fe(OH)_3 , Al(OH)_3
5 (fully carbonated)	< 10	SiO_2 with some CaO, Fe(OH)_3 , Al(OH)_3

Data from literature, mostly from Lagerblad, 2005



2. Carbonation mechanism: stability of the cement phases

- *Cascading degradation of CSH*



Data CSH from Hong and Glasser, 1999



2. Carbonation mechanism: stability of the cement phases

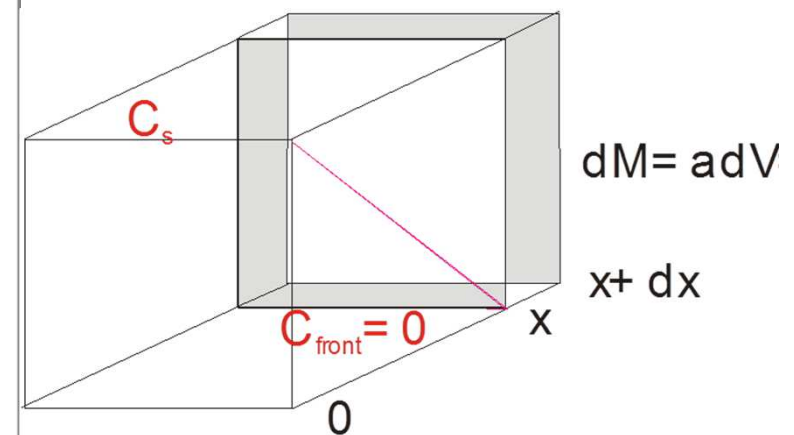
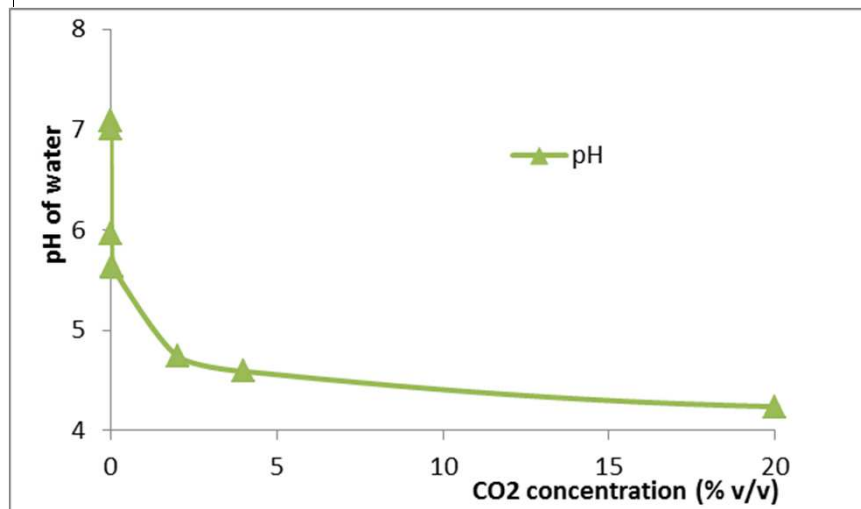
- *Buffering capacity of the other cement phases is likewise 100% - no further progress of carbonation until phases are 'consumed'*
- *Each does so at its own equilibrium pH*

Stage	pH	stable phases
1 (non-carbonated)	>12.6	Ca(OH) ₂ , CSH (Ca/Si > 1.8 or at high common ion effect), AFt, AFm
2	11.6 – 12.6	CSH (Ca/Si< 1.8), AFt, AFm
3	10.5 – 11.6	CSH (Ca/Si< 1.05), AFt, Al(OH) ₃
4	10.0 – 10.5	CSH (Ca/Si< 0.85), Fe(OH) ₃ , Al(OH) ₃
5 (carbonated)	< 10	SiO ₂ with some CaO, Fe(OH) ₃ , Al(OH) ₃



2. Carbonation mechanism: transient effects

- Carbonation starts with **diffusion of CO₂-molecules**
- At the carbonation front, it **dissolves in the pore water**
- It is instantly **consumed by Ca²⁺ in the pore fluid**
- Buffer capacity of cement phases **releases new Ca²⁺**
 - First Ca(OH)₂ & high Ca CSH, next the other phases at succ. Lower pHs
- Concentration CO₂ at the front remains 0 until no more buffer





2. Carbonation mechanism: conclusions

- › Carbonation of each cement phase occurs at **phase stability pH**
- › **No cement phase is stable** below $\text{pH} = 7$ ($c(\text{CO}_2)$ approx. 0)
- › All cement phases react in a neutral way so can **go to completion**
- › **All calcium is consumed**: buffer capacity = Ca content of cement





Ins & outs of carbonation of concrete

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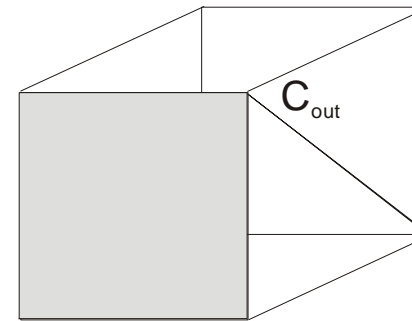
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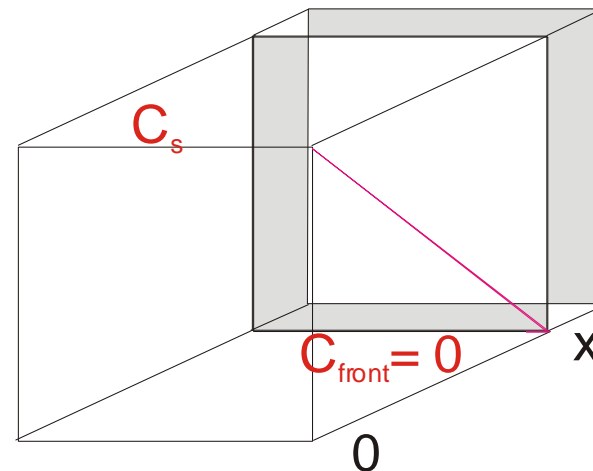
3. Testing the resistance against carbonation of concrete: designing a test method

- **Modeling** preferentially by (chemi-) physics
- By **Ficks first law**, under assumption that the front cannot progress until all carbonatable matter is consumed

$$x_c = \sqrt{2Dc_s t / a}$$
$$= \sqrt{2c_s t / R}$$



carbonation front
 $C_{\text{front}} = 0$



$dM = a dV = a A dx$

$x + dx$

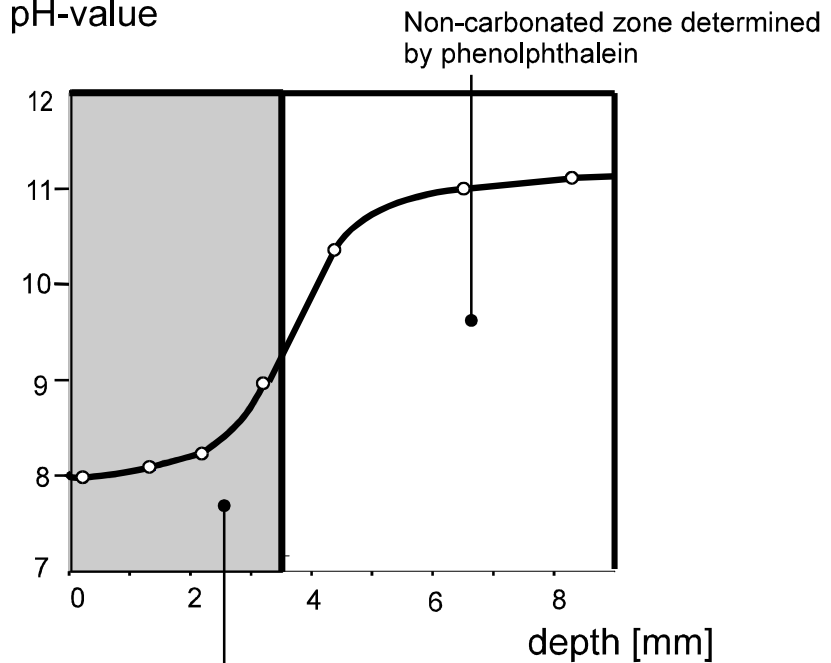


3. Testing the resistance against carbonation of concrete: designing a test method

- (Natural) carbonation test with colour reaction to measure $x_c - t$ (at favourable conditions for carbonation)



pH-value

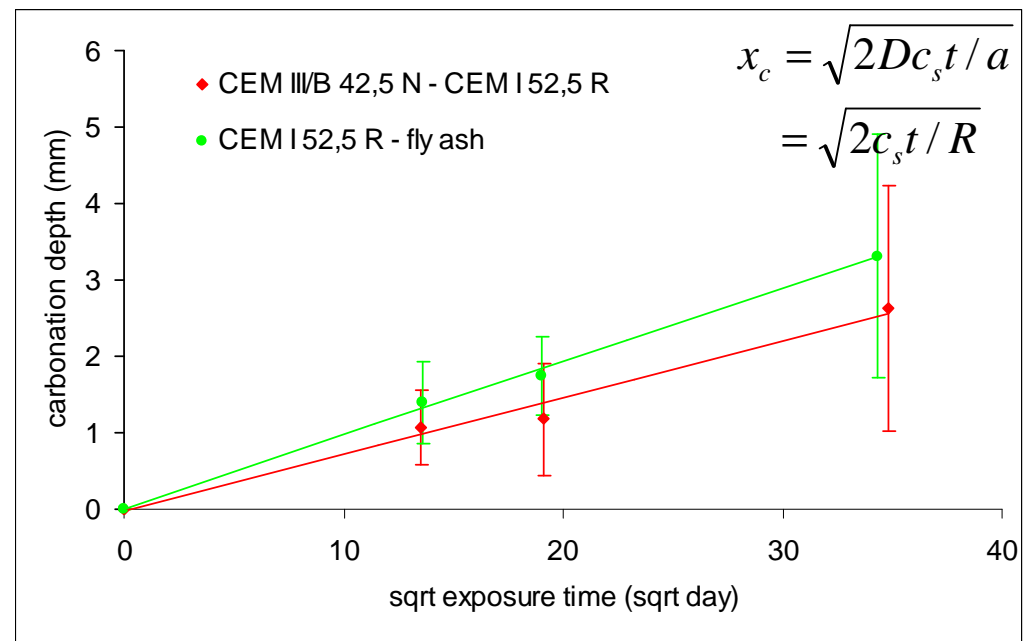


Carbonated zone determined by phenolphthalein



3. Testing the resistance against carbonation of concrete: designing a test method

- (Natural) carbonation test with colour reaction to measure $x_c - t$ (at favourable conditions for carbonation)





3. Testing the resistance against carbonation of concrete: accelerating the test

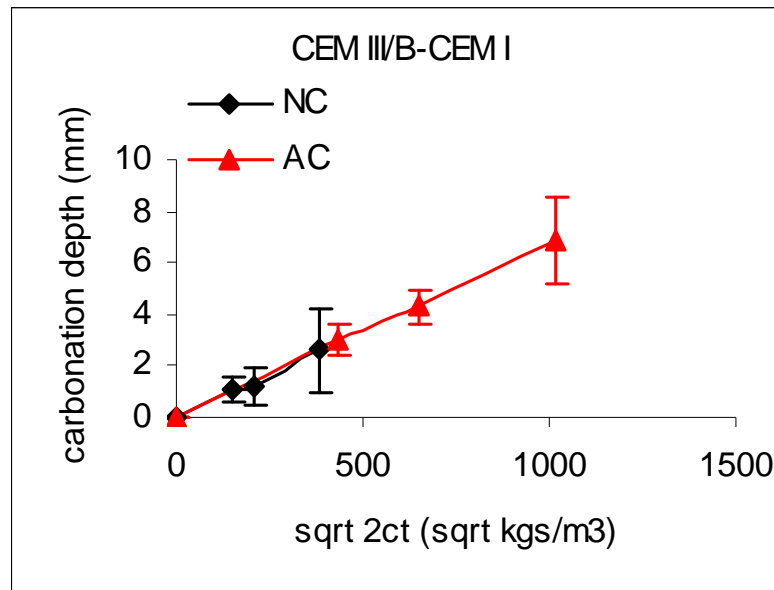
- › Carbonation is a **very slow process**
 - › Testing taking often a year to obtain reliable results
 - › In a design-by-testing a year is too long
 - › Acceleration of the test would be ideal

- › **How** to accelerate tests?
 - › Increase driving force (T, c, p)
 - › Compress time
 - › Chose equivalent mechanism with a linear relationship



3. Testing the resistance against carbonation of concrete: accelerating the test

- › Accelerated test in concentration versus natural tests:
 - › Start test **at same age** (28 days) after **same curing** (of which 7 days fog room and 21 days at 20/65)
 - › Concentration at **2 %** instead of natural (0.04) (=50 x increase in concentration)



$$x_c = \sqrt{\frac{D}{a}} \sqrt{2ct} = \sqrt{1/R_{carb}} \sqrt{2ct}$$

E.g.

Acceleration concentr.: $c = 2\%$

Natural concentration: $c = 0.04\%$

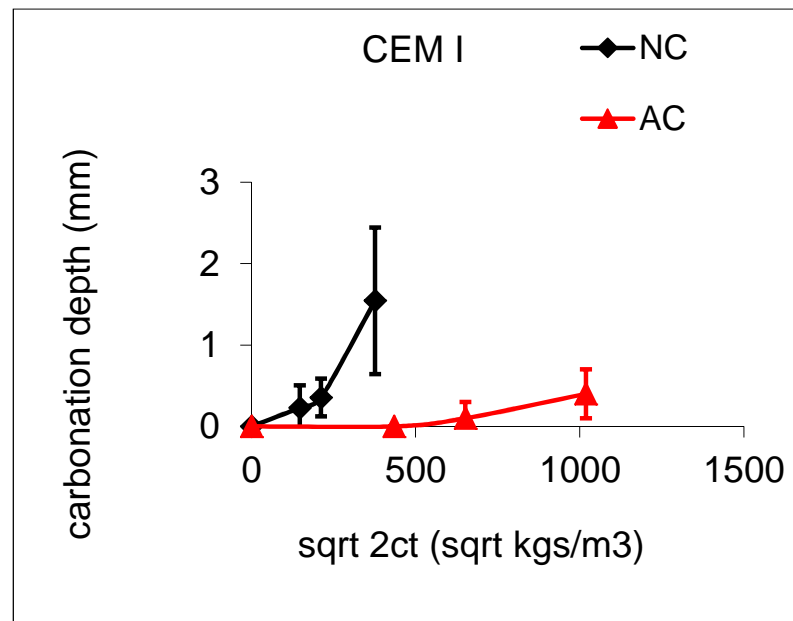
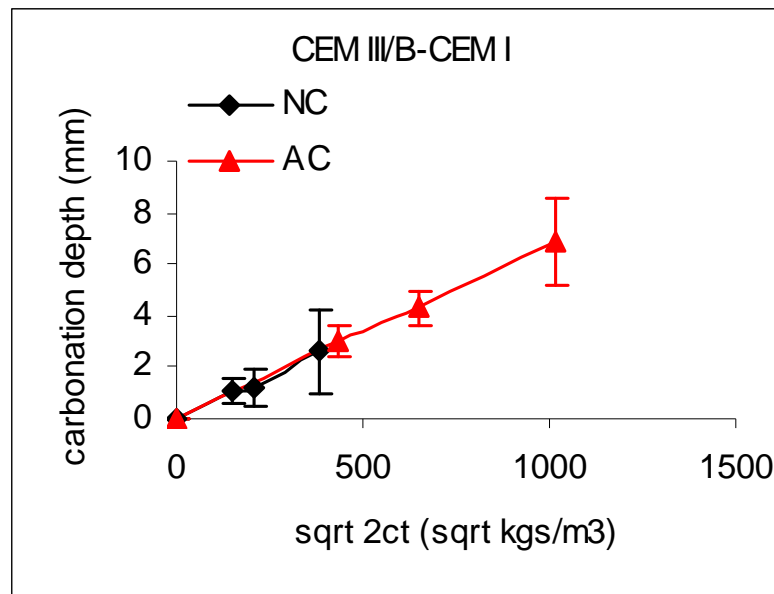
Acceleration = $2/0.04 = 50x$



3. Testing the resistance against carbonation of concrete: accelerating the test

- › Draw back of the accelerated tests?
- › Other mechanisms may become important

This may remain unnoticed!!!





3. Testing the resistance against carbonation of concrete: accelerating the test

concrete	binder	NC	AC
fine OPC	CEM I 52.5 R	$1.2 \cdot 10^{-2}$? (not linear)
FAC	CEM I 52.5 R – 30 % fly-ash	$4.2 \cdot 10^{-4}$	$4.5 \cdot 10^{-4}$
BFS	CEM III/B 42.5 – CEM I 52.5 R (50 % slag)	$6.8 \cdot 10^{-4}$	$7.0 \cdot 10^{-4}$



3. Testing the resistance against carbonation of concrete: accelerating the test

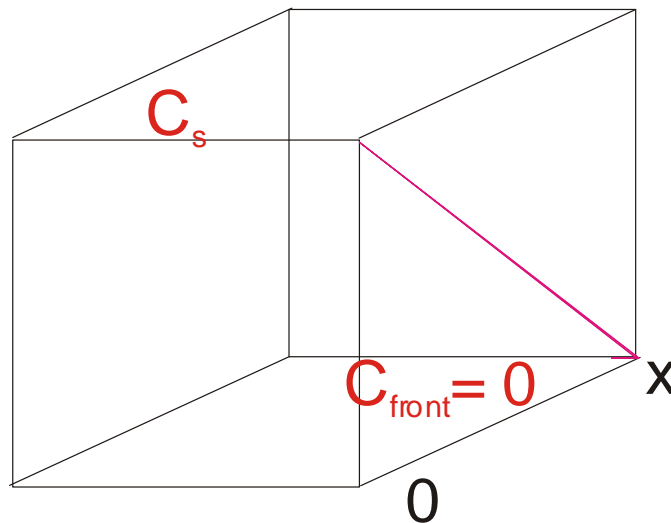
Possible causes for misfit for fine OPC:

1. carbonation mostly due by Ca(OH)_2
 - › precipitation CaCO_3 in pore space
 - › leading to densification and reduction average pore size
2. water is formed during carbonation:
 - › $\text{Ca(OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$
 - › Can drying (evaporation) become dominant?
The carbonation cannot proceed until evaporation is (partly complete)
 - › **Change the model!**



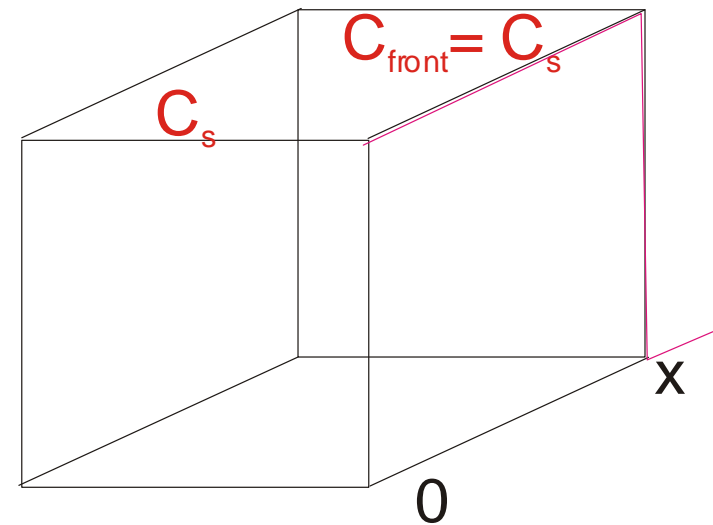
3. Testing the resistance against carbonation of concrete: accelerating the test

› Model 1: all CO₂ is instantly consumed at the carbonation front



$$q = DA(c_s - c_{front}) / x$$

› Model 2: consumption is so slow the concentration of CO₂ is constant (1st Fick over a membrane)



$$q = DA(c_s - c_{front})$$



3. Testing the resistance against carbonation of concrete: accelerating the test

› Model 1: all CO₂ is instantly consumed at the carbonation front

› Model 2: consumption is so slow the concentration of CO₂ is constant (1st Fick over a membrane)

$$x_c = \sqrt{2c_s t / R} \quad x_c = \text{Offset} + c_s t / R_{carb}$$

› Square root-behavior
(with offset = 0)

› Linear behavior
(offset non-negligible)



3. Testing the resistance against carbonation of concrete: accelerating the test

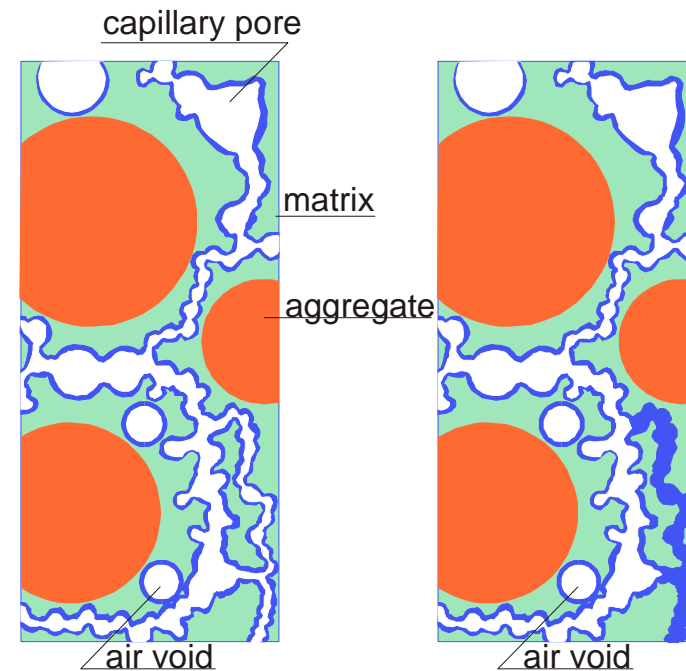
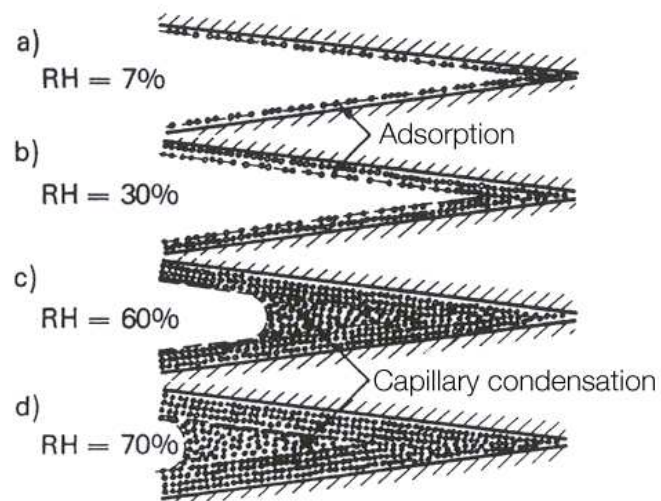
› Change in model lead to consistent result:

concrete	binder	NC (sqrt t) CO ₂ dominant	AC (linear t) H ₂ O dominant
fine OPC	CEM I 52.5 R	1.2 10 ⁻²	1.2 10 ⁻²



3. Testing the resistance against carbonation of concrete: test conditions

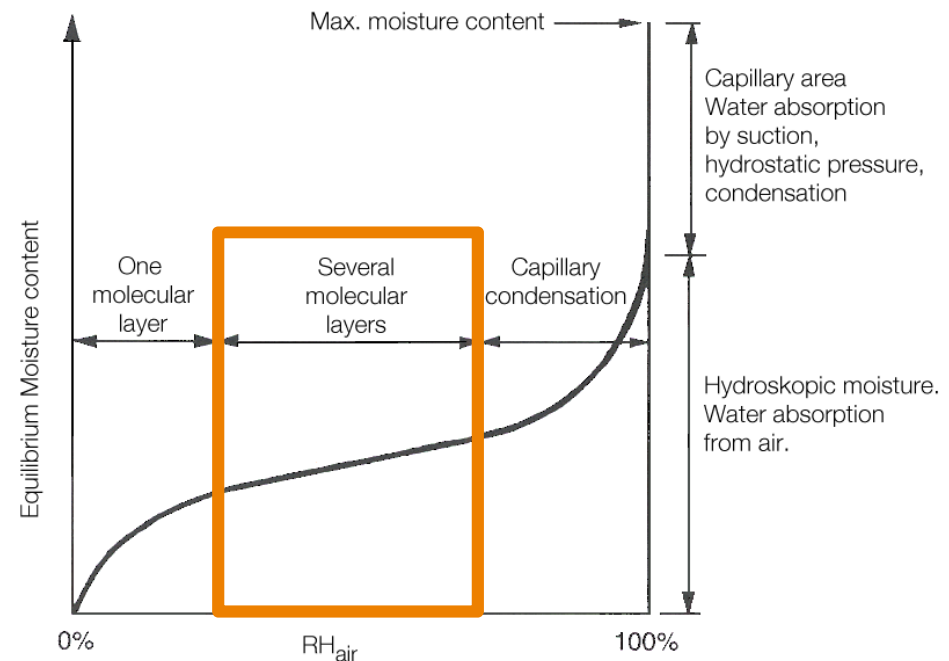
- › Carbonation can only take place when
 - › When the CO₂ can penetrate (sufficient dry)
 - › When the CO₂ can dissolve (sufficient wet)





3. Testing the resistance against carbonation of concrete: test conditions

- › Carbonation can only take place:
 - › When the CO₂ can penetrate (sufficient dry)
 - › When the CO₂ can dissolve (sufficient wet)
- › This condition applies if $S < S_{crit}$
- › Best is to take RH **before capillary condensation**
- › Normally taken constant at RH = 65%
- › Model adjusted with k_e which is 1 at RH = 65%



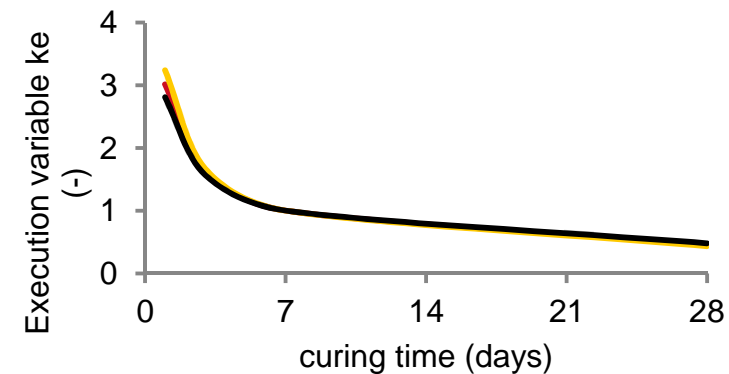
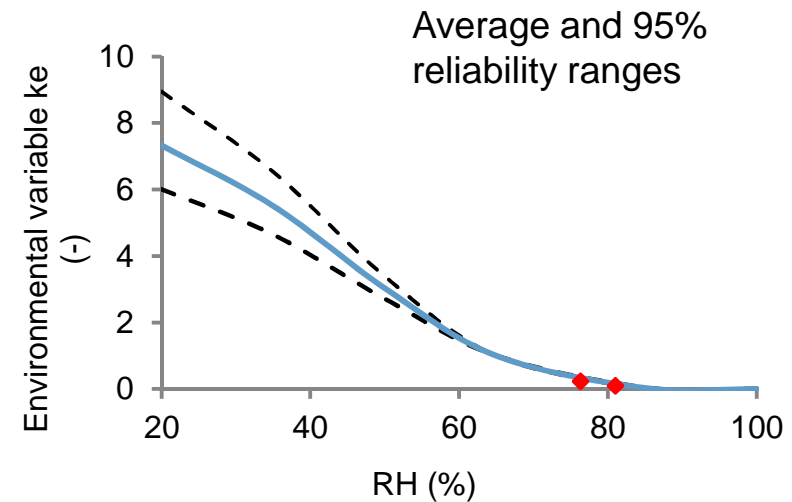
$$x_c = \sqrt{2k_e c_s t / R}$$



3. Testing the resistance against carbonation of concrete: test conditions

- › Environmental parameter k_e
also depends of T)
- › Curing can be a steering parameter
 - › (longer curing usually means better quality (higher density)
 - › Has therefor its own influence parameter k_c

$$x_c = \sqrt{2k_c k_e c_s t / R}$$





3. Testing the resistance against carbonation of concrete: conclusions

- › A good model is available
- › Influence of environment (RH) and curing can be included
- › Acceleration is possible, care must be taken!





3. Testing the resistance against carbonation of concrete: conclusions

- › A high CO₂ concentration has **no effect** on the carbonation process
- › The only effect is **faster transport** to the carbonation front
- › Side effects can occur, e.g. coating of Ca(OH)₂ crystals with CaCO₃ and drying out becoming dominant transport





Ins & outs of carbonation of concrete

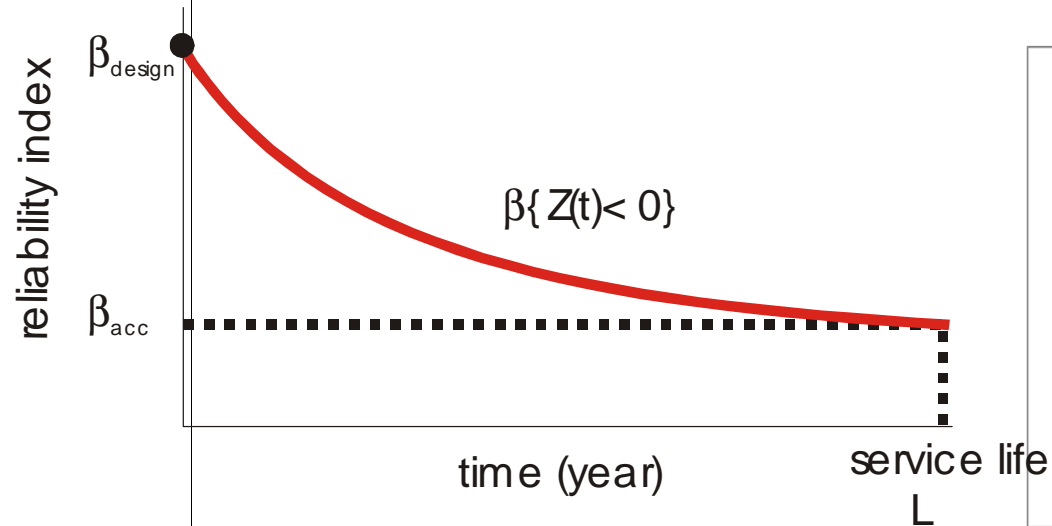
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 - Service life design
 - Design by testing
 - Trading cover thickness for resistance or rather making a green deal?
 - Choice of cements
5. Summary and conclusions



4. Designing for sufficient resistance against carbonation: Service life design

- › A service life design consists of:
 1. A (time dependent) behaviour model $Z(t)$,
with $Z(t) = \text{resistance } R(t) - \text{load } S(t)$, (e.g. progress carbonation front)
 2. A predefined acceptable reliability index β (“risk of failure”)
 3. A predefined service life L (e.g. 50, 100, 200 years)



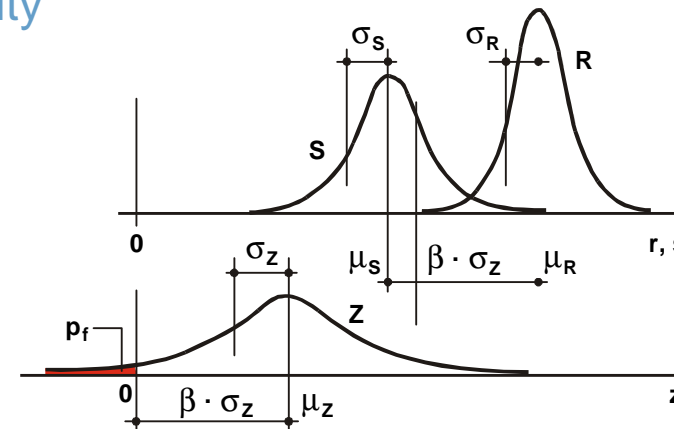


4. Designing for sufficient resistance against carbonation: Service life design

› Reliability and failure probability

$$Z = R - S$$

Z — Reliability
 R — Resistance
 S — (Environ.) Load



$$p_f = \Phi \left(-\frac{\mu_Z}{\sigma_Z} \right) = \Phi (-\beta), \text{ with } \mu_Z = \mu_R - \mu_S, \sigma_Z = \sqrt{\sigma_R^2 + \sigma_S^2}$$

$\Phi(\cdot)$ — Normal Distribution
 β — Reliability Index
 p_f — Failure Probability



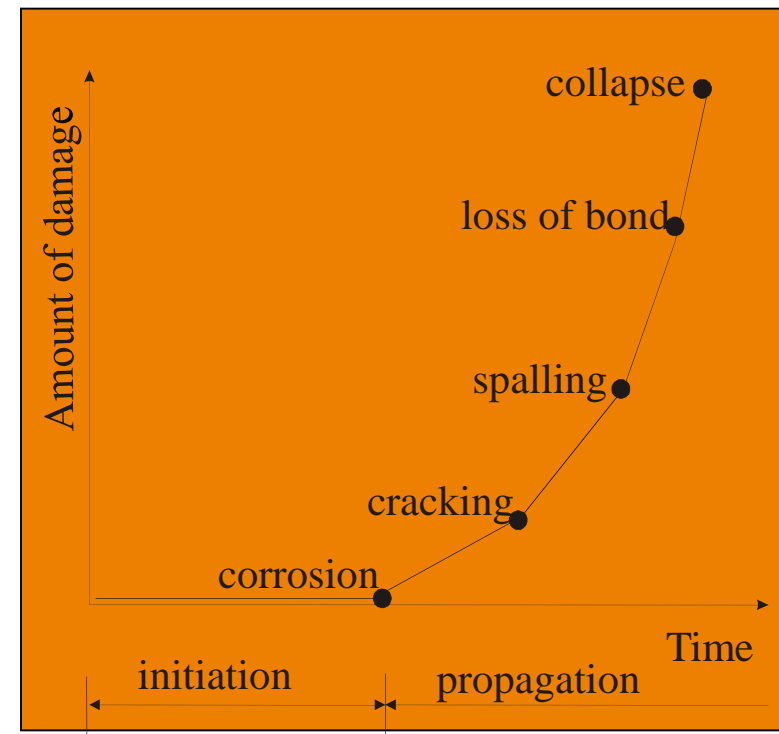
4. Designing for sufficient resistance against carbonation: Service life design

- Condition for the design: the carbonation front should not reach the reinforcement before the end of the service life (no corrosion initiation):

$$P\{x_c(t) < d_c\}_L < \beta_{acc}$$

with d_c = cover thickness
and

$$x_c(t) = \sqrt{2k_c k_e c_s t / R}$$





4. Designing for sufficient resistance against carbonation: Service life design

› First service life design for carbonation

	variables
Performance demand: $P\{x_c(t = L) \leq d_c\} \leq \Phi(\beta)$	x_c = carbonation depth d_c = concrete cover t = time since exposure L = service life (def) β = reliability index (def)
Behavioral model for carbonation: $x_c(t) = \sqrt{2k_c k_e c_s t / R}$	c_s = surface CO ₂ concentration k_e = environmental factor k_c = curing factor R = resistance against carbonation



4. Designing for sufficient resistance against carbonation: Service life design

- **Determine ALL** variables in the model (e.g. by field or lab measurements):
 - Determination of the material resistance in compliance test (standard tests under standard conditions, e.g. temperature, concentrations and rh)
 - Determine the environmental factor k_e (or take it from a database)
 - Determine the curing factor k_c (id)

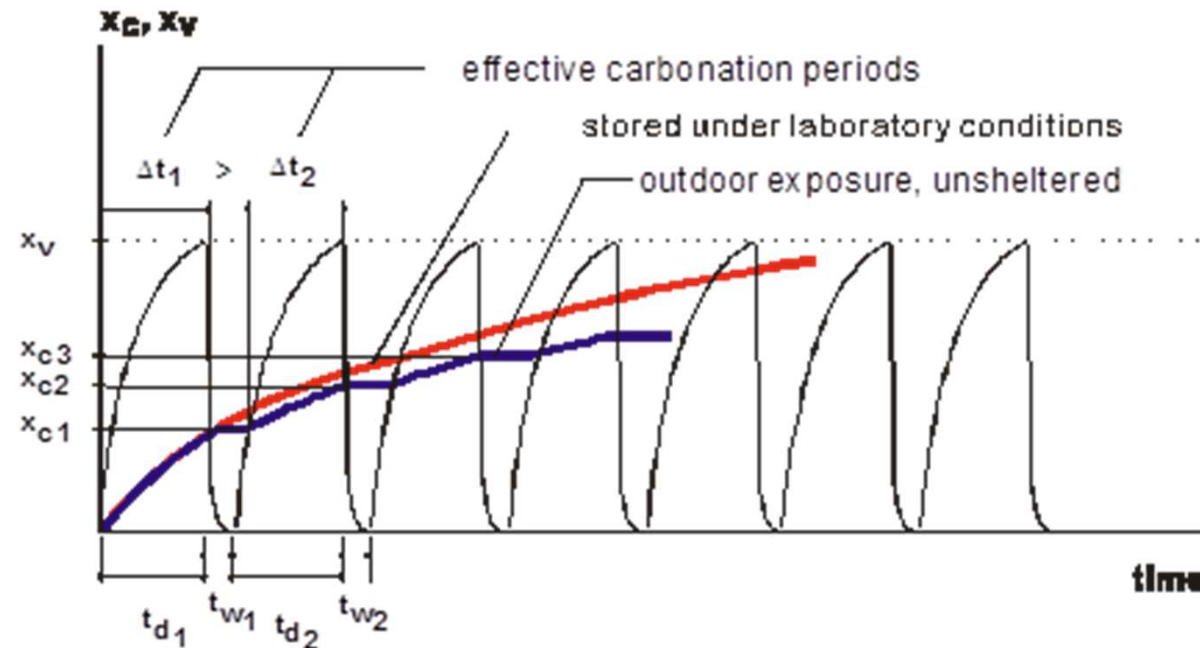


4. Designing for sufficient resistance against carbonation: Service life design

Determine ALL variables in the model

- › Contrary to LAB test, the moisture conditions are not constant class'
- › Introducing weathering function (W) to estimate the effective time of carbonation

$$x_c(t) = W(t) \sqrt{2k_c k_e c_s t / R}$$



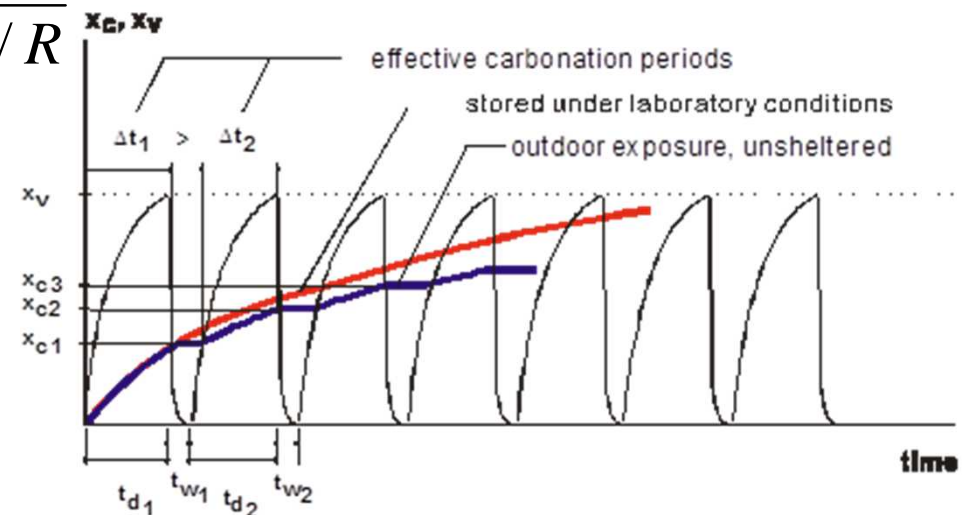


4. Designing for sufficient resistance against carbonation: Service life design

Determine ALL variables in the model

- › The weather function $W(t)$
 - = 1 for sheltered indoor
 - $0 < W < 1$ for unsheltered conditions
 - = 0 for permanent wet surfaces

$$x_c(t) = W(t) \sqrt{2k_c k_e c_s t / R}$$





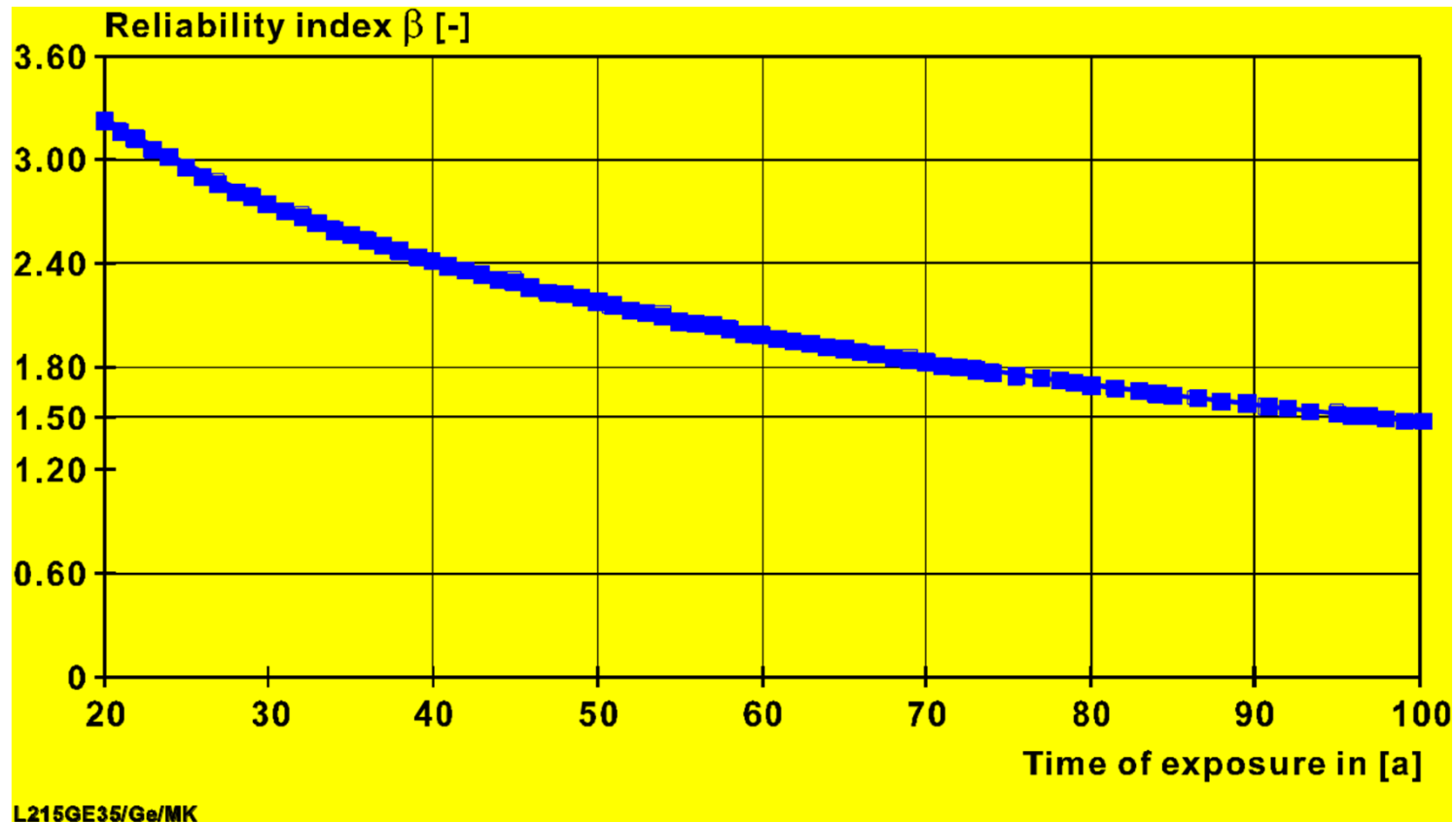
4 . Example: design on durability

variabel no	parameter	dimension	istribution type	u	s	omega
t0	reference time	year	D	0.076712		
t	exposure time	year	D	variable		
tc	curing time	day	D	input		
L	service life	year	D	100		
R	resistance against carbo	mm ² /yr/(kg 2/m ³)	ND	input		
cs	concentration	kg/m ³	ND	0.000688	8.59375E-05	
RH real	relative humidity	%	W	76.3	12.9	100
kc	curing	-	ND	function1		
ke	environment	-	W	function2		
w	weather exponent	-	ND	function3		



4. Designing for sufficient resistance against carbonation: Service life design

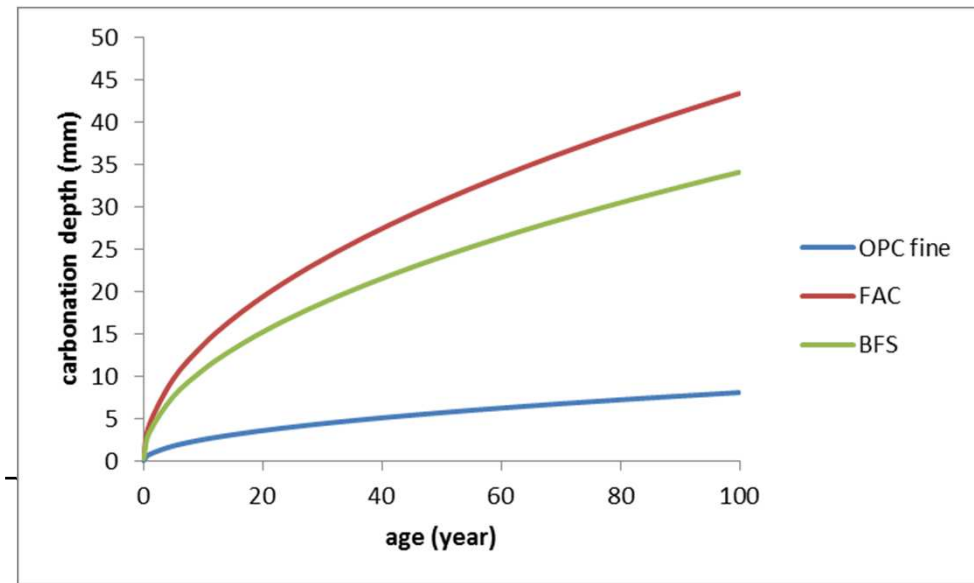
- › Calculate the reliability with age so verify if the design has sufficiently long service life (with defined beta)





4. Designing for sufficient resistance against carbonation: Service life design

- › Methodology is useful to determine design elements like the choice of cements
- › (e.g design by testing)
- › Calculations for:
curing time = 1 day
RH = 75 %



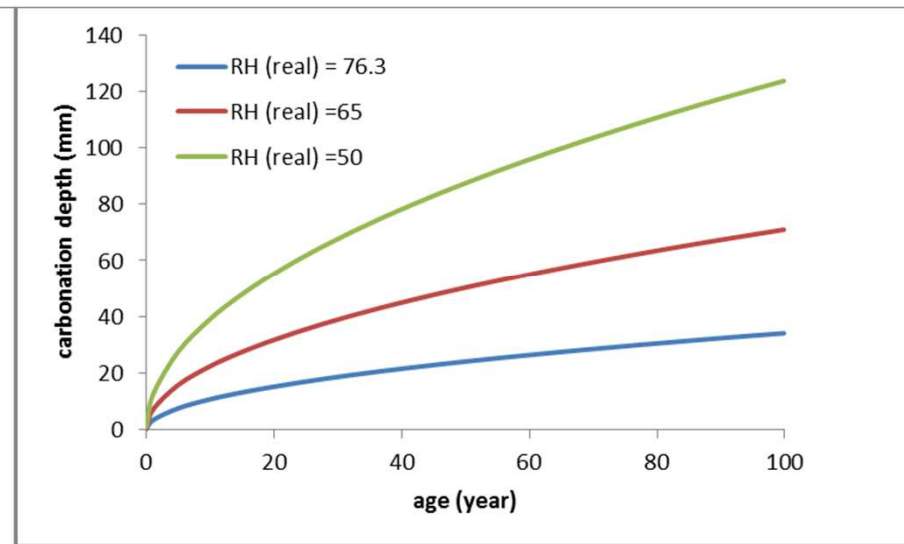
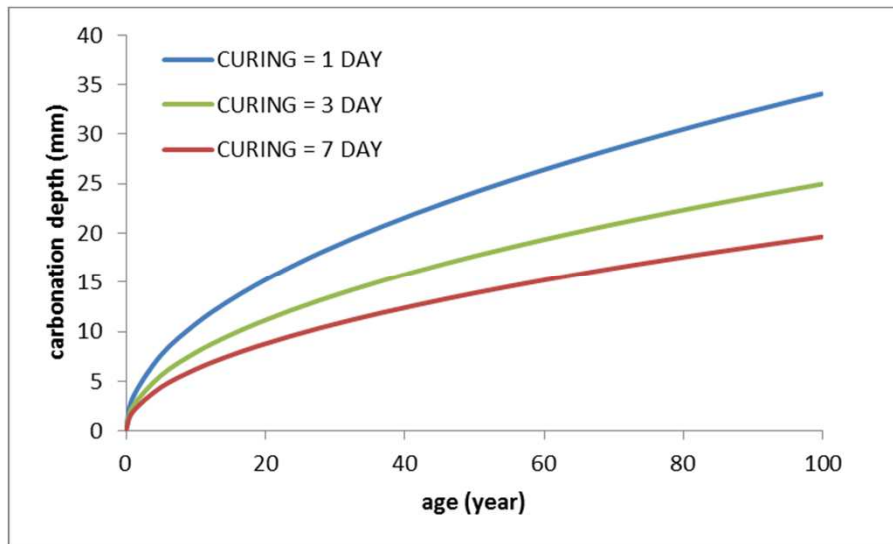
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4. Designing for sufficient resistance against carbonation: Service life design

- › Influence curing
- › (execution steering)
- › (BFS, RH = 75 %)

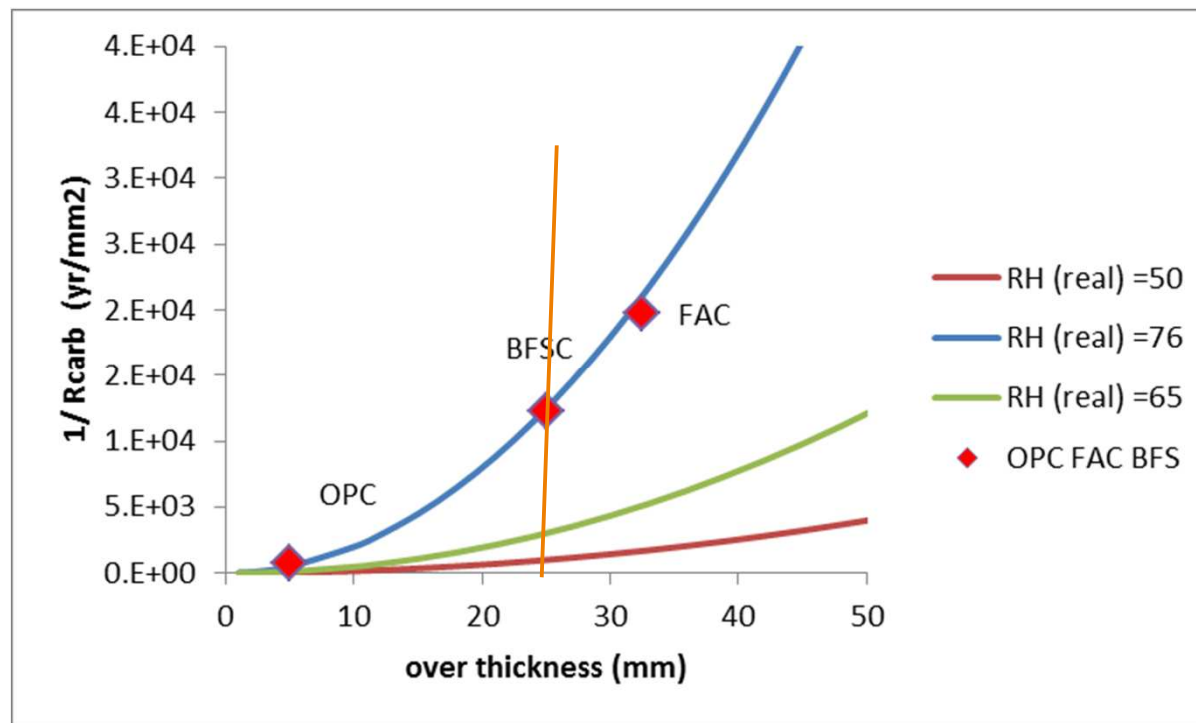
- Influence RH
- (meso-environment)
- (BFS, 1 day curing)





4. Designing for sufficient resistance against carbonation: Service life design

- › Going green? - Trading cover versus cement type
- › From structural design: minimum cover = 25 mm



- › Notice: (1) these are examples for illustration only
- › (2) more performance demands may play a role



Ins & outs of carbonation of concrete

Contents:

1. Introduction: what is carbonation and why should we worry about it?
2. The carbonation mechanism
3. Testing the resistance against carbonation of concrete
4. Designing for sufficient resistance against carbonation:
5. **Conclusions**





5. Conclusions

- › Carbonation of concrete **changes the concrete** itself (e.g. porosity, pH reduction)
 - › pH reduction may introduce **corrosion**, leading to damage;
 - › **more than 50 % of the damage** in Europe is due to carbo-initiated
little insights in the effects of repairs on the performance

- › Carbonation is an **acidifying reaction** that start by diffusion of CO_2 into the pore space
 - › Its front will not move deeper until the buffering OH^- from the cement stone has been depleted
 - › This is easy to model by Fick's law of transport (& can be accelerated in c_s accordingly)
 - › **Take care for a change in transport (water membrane mechanism)**



5. Conclusions

- › Service life modelling has been developed for carbonation
 - › Progress carbonation front with age can be predicted
 - › Resistance of concrete (type of cement!) and curing is included
 - › Influence of RH and rainfall are taken into account
 - › **Probability of corrosion due to carbonation with service life can be calculated!**

- › Optimization of cover thickness, type of cement and curing length can now be made with an efficient and economical design with respect to carbonation