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## Hvad er chloridtærskelværdien?

Præsenteret af:

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## OUTLINE

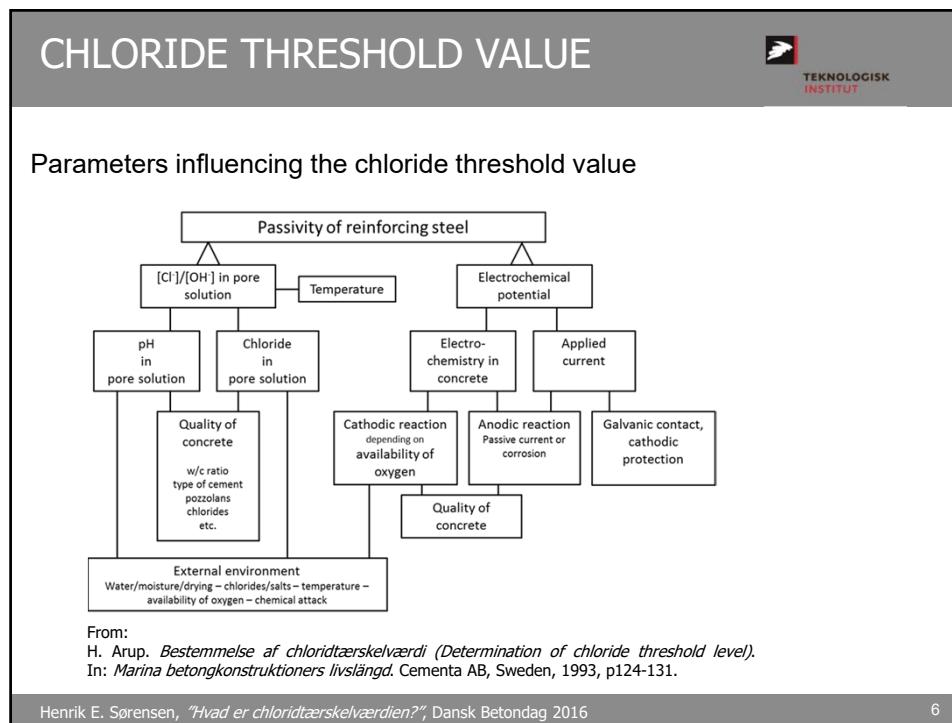
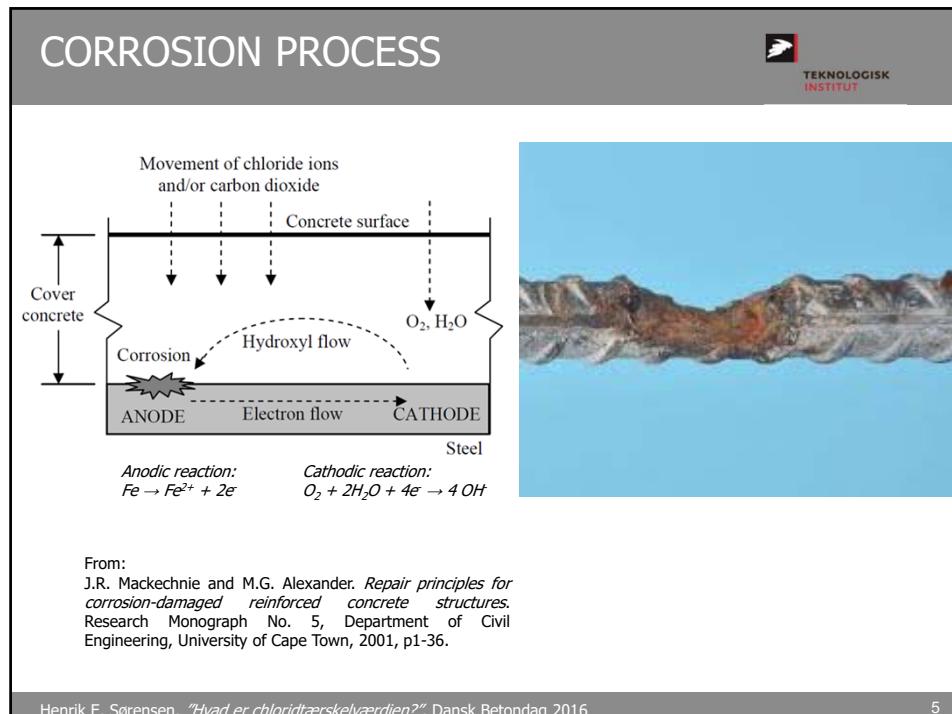


- Introduction
- Corrosion process
- Chloride threshold value
- RILEM TC 235-CTC findings
- Femern field exposure site in Rødbyhavn
- Data from corrosion monitoring and chloride analyses
- Preliminary chloride threshold values after 5 years exposure
- Some conclusions

## INTRODUCTION



- Chloride induced reinforcement corrosion is typically the main concern for durability of marine structures
- Service life modeling of marine structures are based on estimates of the chloride penetration and the chloride threshold concentration (CTC) for corrosion initiation
- A standard test method for determination of CTC-values are not established (RILEM TC 235-CTC were not successful on that)
- Anode ladders for corrosion monitoring have been installed in many structures, but in many cases the evaluation of data from HCP-values has been difficult



## CHLORIDE THRESHOLD VALUE

**Estimation of service life by fib Model Code [fib Bulletin No. 34, 2006]**  
 – data from Träslövsläge and Fehmarn exposure sites  
 Influence of chloride threshold value ( $C_{crit}$ )

Input parameter	Concrete
Binder	(75% PC + 25% FA)
$C_{crit}$ [wt%/binder]	0.6 (0.5-2.2)
$C_0$ [wt%/binder]	0.001
$C_{s,Ax}$ [wt%/binder]	5.2
a [mm] (cover)	75
$\Delta x$ [mm]	0
$k_e$ [-]	1.25
$b_e$ [K]	4800
$T_{ref}$ [K]	293.15
$T_{real}$ [K]	293.15
$D_{RCM,0}$ [mm <sup>2</sup> /år]	867
$k_t$ [-]	1
n [-] (ageing factor)	0.6
$t_0$ [yr]	0.0877

Calculated service life (years)

$C_{crit}$  (wt% of binder)

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## CHLORIDE THRESHOLD VALUE

**Estimation of service life by fib Model Code – TBM tunnel elements**  
 Influence of chloride threshold value ( $C_{crit}$ )

Symbol	Value	Unit	Explanation
$C_{crit}$	1.3	[wt%/binder]	Critical chloride content for corrosion initiation
$C_0$	0.019	[wt%/binder]	Initial chloride content in concrete
$C_s$	5.0	[wt%/binder]	Chloride content at the concrete surface
A	50	[mm]	Concrete cover
$\Delta x$	0	[mm]	Depth of the convection zone
$b_e$	4800	[K]	Regression variable
$T_{ref}$	293.15	[K]	Standard test temperature
$T_{real}$	291.15	[K]	Temperature of the structural element
$D_{RCM,0}$	131	[mm <sup>2</sup> /year]	Chloride migration coefficient
$k_t$	1	-	Transfer parameter
N	0.386	-	Ageing exponent, $0.0 \leq n \leq 1.0$
$t_0$	0.0932	[years]	Maturity age when $D_{RCM,0}$ is measured

Input parameters			Predicted service life [years]
$C_{crit}$ [wt% of binder]	n	$C_s$ [wt% of binder]	
1.30	0.386	5.0	141
1.06	0.386	5.0	102
1.54	0.386	5.0	195

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## RILEM TC 235-CTC (2009-2015)

**Round Robin Test**

- New proposed standard test
- 10 laboratories participated
- No corrosion initiation in 5 labs

As-received      Cleaned      Pre-rusted

Reference zinc elektrode

Epoxy coated concrete specimen

Exposure tank

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## RILEM TC 235-CTC (2009-2015)

**Test on as-received reinforcing steel**

- Cyclic voltammetry with varying Cl/OH-ratios
- ETHZ in Zürich performed the testing on rebars from 10 different countries
- Very large variations in chloride threshold levels

Designation	Country
A	Switzerland
B	Denmark
C	Germany
D	France
E	Spain
F	The Netherlands
G	Sweden
H	China
I	Sweden
J	Norway

Chloride threshold ( $\text{Cl}'/\text{OH}^-$ )

Designation: A, B, C, D, E, F, G, H, I, J

Chloride threshold ( $\text{Cl}'/\text{OH}^-$ )

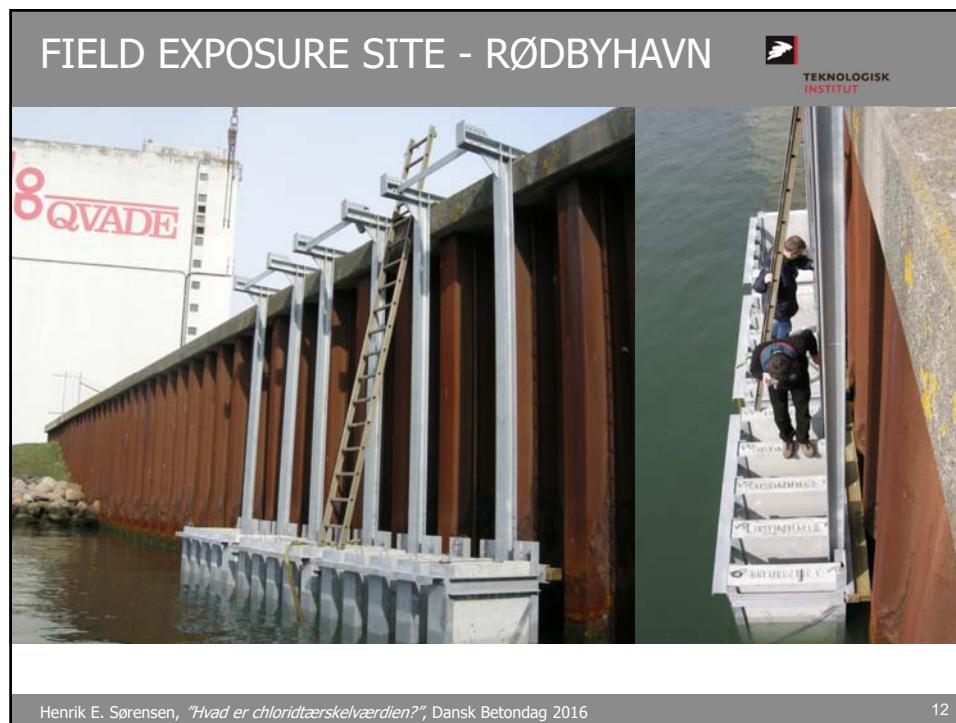
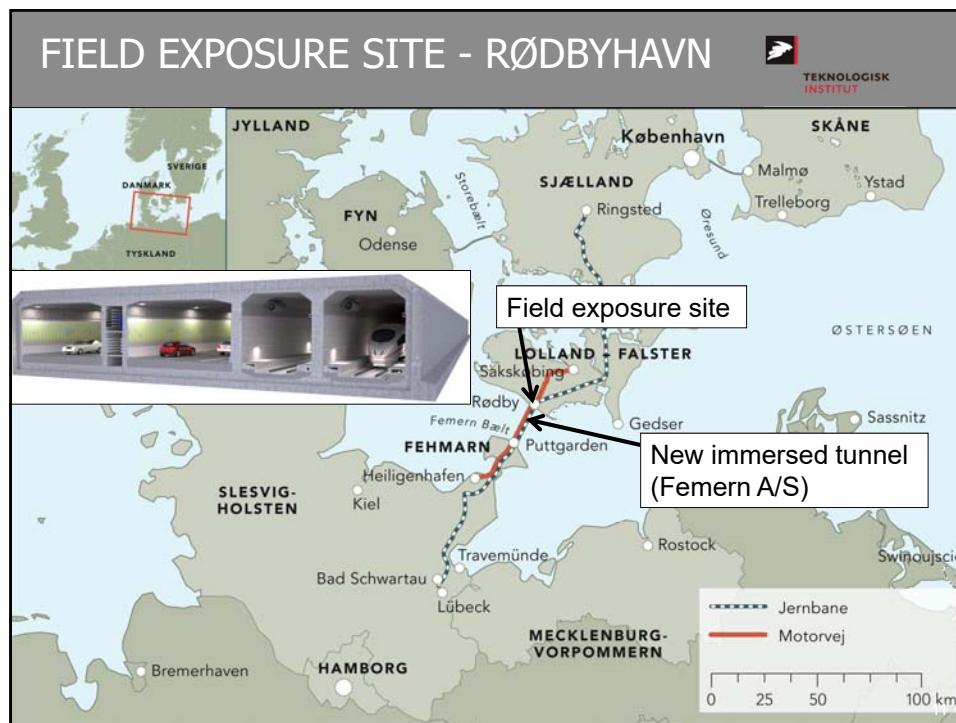
Series: C and F

Martensite      Ferrite-Pearlite

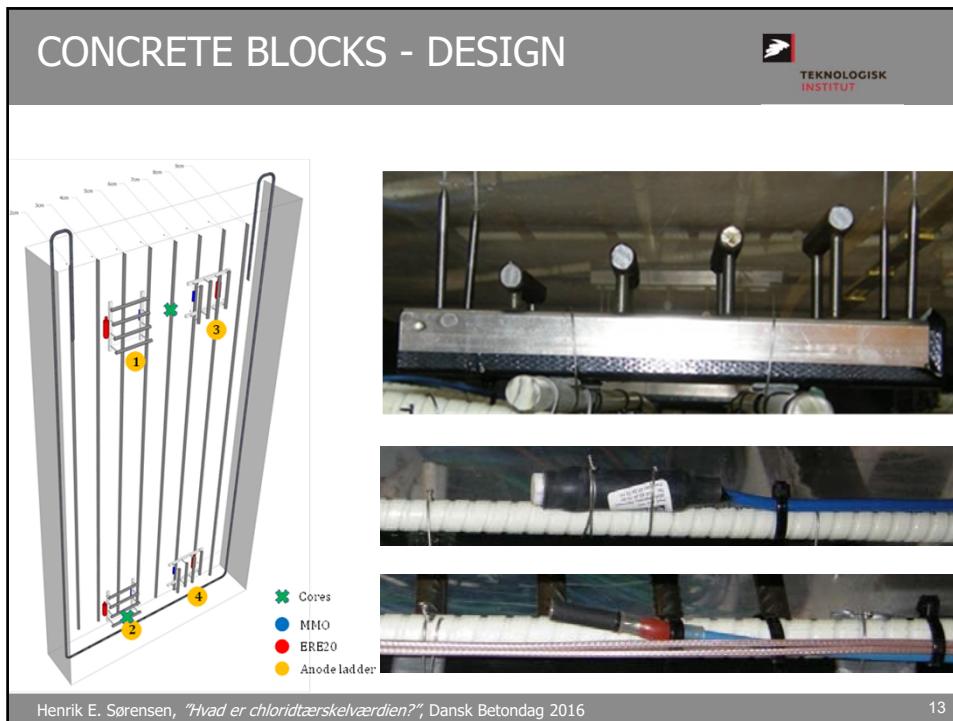
From:  
U.M. Angst and B. Elsener. Forecasting chloride-induced reinforcement corrosion in concrete – effect of realistic reinforcement steel surface conditions, Proceedings of the ICCRRR conference, Leipzig, October 2015

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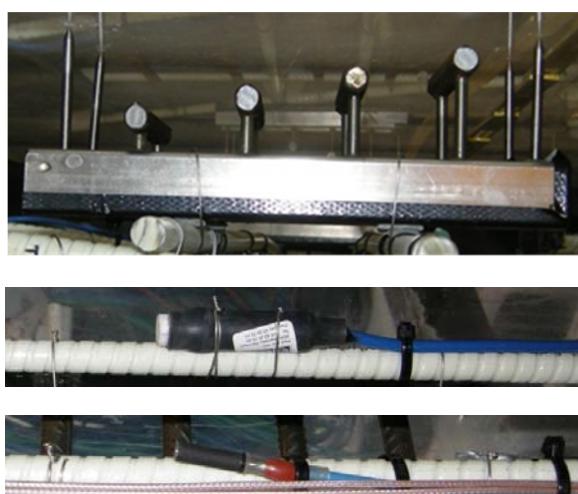
## CONCRETE BLOCKS - DESIGN



The diagram illustrates a cross-section of a concrete block with various internal components labeled:

- Cores (green asterisk)
- MNO (blue circle)
- BRE20 (red circle)
- Anode ladder (yellow circle)

Dimensions shown on the left side of the diagram are: 30cm, 40cm, 50cm, 60cm, 70cm, 80cm, 90cm, and 100cm.



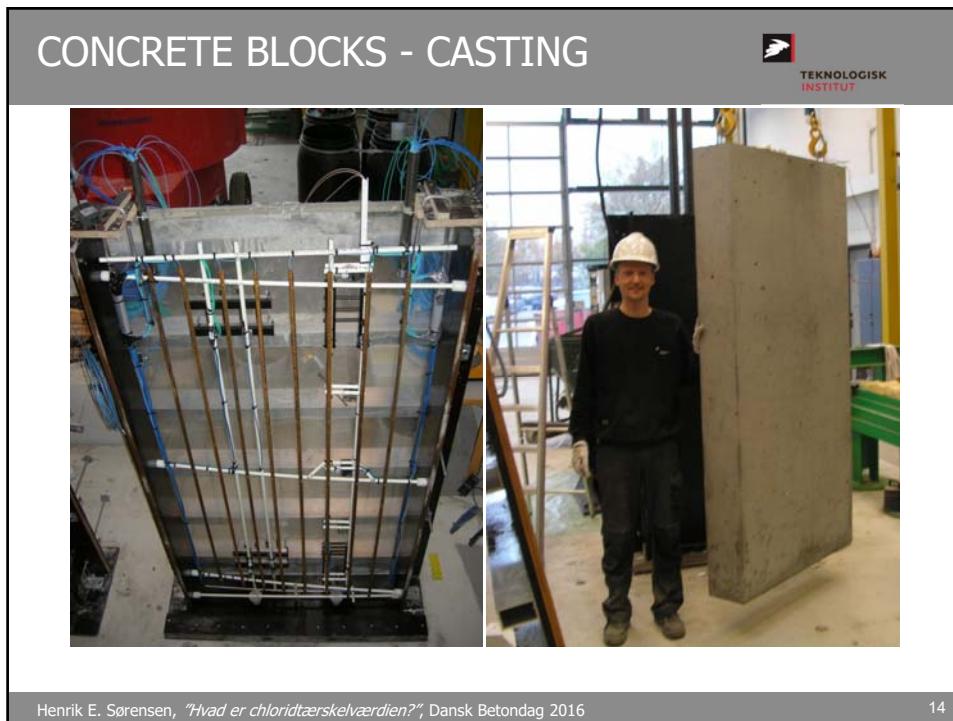
Three photographs showing different parts of the concrete block casting machinery:

- A top view of a metal frame with several vertical rods and a central support structure.
- A close-up view of a horizontal metal plate with various attachments and a small label.
- A view of a conveyor belt or transport system with some components.

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## CONCRETE BLOCKS - CASTING



Two photographs showing the concrete block casting process:

- A large metal frame containing multiple vertical rods, likely part of the casting apparatus.
- A man standing next to a large, rectangular concrete block in a workshop setting.

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## CONCRETE MIX DESIGNS



ID	Three instrumented concrete blocks
Mix A (Portland cement)	Low-alkali SR Portland cement CEM I 42,5 N (HS/EA/ $\leq$ 2)
Mix F (3-powder mixed cement)	84% low-alkali SR Portland cement 12% fly ash 4% silica fume
Mix K (Slag cement)	Slag cement CEM III/B 42,5 N
w/b ratio	0.40
Anode cover depth	Approx. 10, 20, 30 and 40 mm

Details regarding cement composition and concrete mix designs are presented in the full paper on the conference CD-rom

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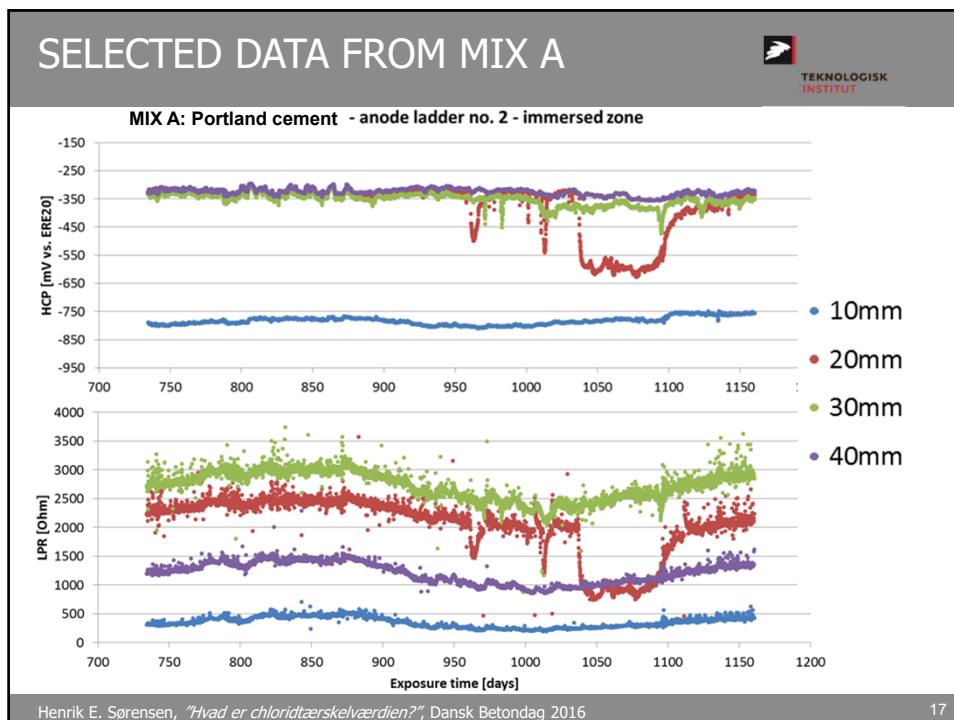
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## FIELD EXPOSURE



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### CORROSION INITIATION

Observations of anodes with of possible corrosion initiation:

Mix/Ladder/Anode depth	Date/exposure time	mV drop	Remarks
Mix A/No. 1/10 mm	17-07-2014/1357 days	181 mV	46 days until repassivation
Mix A/No. 1/10 mm	23-09-2015/1790 days	172 mV	Corrosion until sampling after 1832 exp. day
Mix A/No. 2/10 mm	05-10-2011/342 days	447 mV	Corrosion continues
Mix A/No. 2/22 mm	30-08-2013/1037 days	287 mV	78 days until repassivation
Mix A/No. 2/22 mm	03-09-2015/1770 days	320 mV	Corrosion continues
Mix A/No. 3/8 mm	23-10-2015/1821 days	192 mV	Manual measurement
Mix A/No. 4/6 mm	18-02-2014/1208 days	286 mV	106 days until repassivation
Mix A/No. 4/6 mm	07-05-2015/1652 days	280 mV	38 days until repassivation
Mix A/No. 4/16 mm	22-05-2015/1667 days	343 mV	Corrosion until sampling after 1832 exp. day
Mix F/No. 2/7 mm	13-12-2010/46 days	286 mV	Corrosion continues
Mix F/No. 3/8 mm	At first exposure	271 mV	Initial corrosion continues
Mix F/No. 4/7 mm	25-03-2011/148 days	263 mV	Corrosion continues
Mix F/No. 4/17 mm	14-07-2015/1720 days	273 mV	Corrosion until sampling after 1832 exp. day

Corrosion initiation is defined by a potential drop of min. 150mV for at least 30 days

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## CORROSION INITIATION



Typical values for half-cell potential and linear polarisation resistance on passive anodes:

Exposure conditions	Immersed zone			Splash zone		
Concrete composition	Mix A	Mix F	Mix K	Mix A	Mix F	Mix K
HCP (mV vs. ERE20)	-300	-400	-600	-200	-300	-300
LPR (kOhm)	1-3	1-5	1-5	1-3	1-3	1-5

HCP-values are measured against the ERE20 reference electrode ( $Mn/MnO_2$ ). Correction to CSE reference electrode ( $Cu/CuSO_4$ ) is done by adding 100 mV.

Observations on corroding anodes show that the half-cell potential (HCP) with time drops to values below -800 mV vs. ERE20 and the linear polarisation resistance (LPR) drops to values in the range 100-400 Ohm.

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## CORE DRILLING



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## POSITION OF CORES – 532 DAYS

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- Two cores were drilled from similar positions in all three blocks
- Top cores were placed between the two corrosion ladders
- Bottom cores were placed directly over the outmost horizontal anode

**After core drilling**

**After repair**

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## INSPECTION OF ANODES

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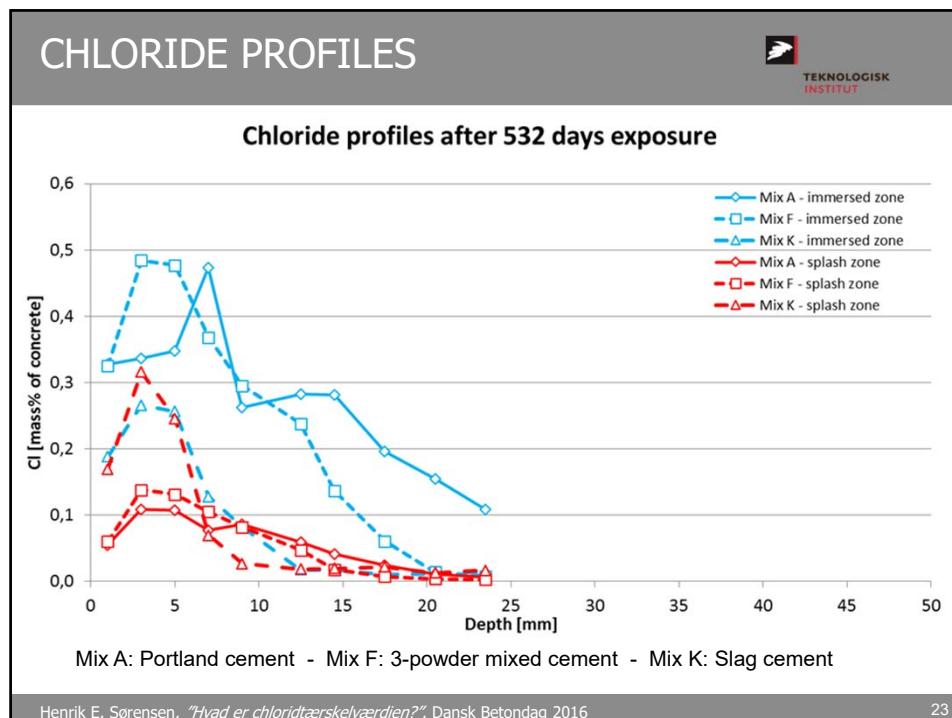
Example:

**3-powder mixed cement:**  
Three rusting spots is seen on the electrode and also in the concrete interface (arrows).

These three spots were dark just after breaking the sample, but became brown before the photo was taken.

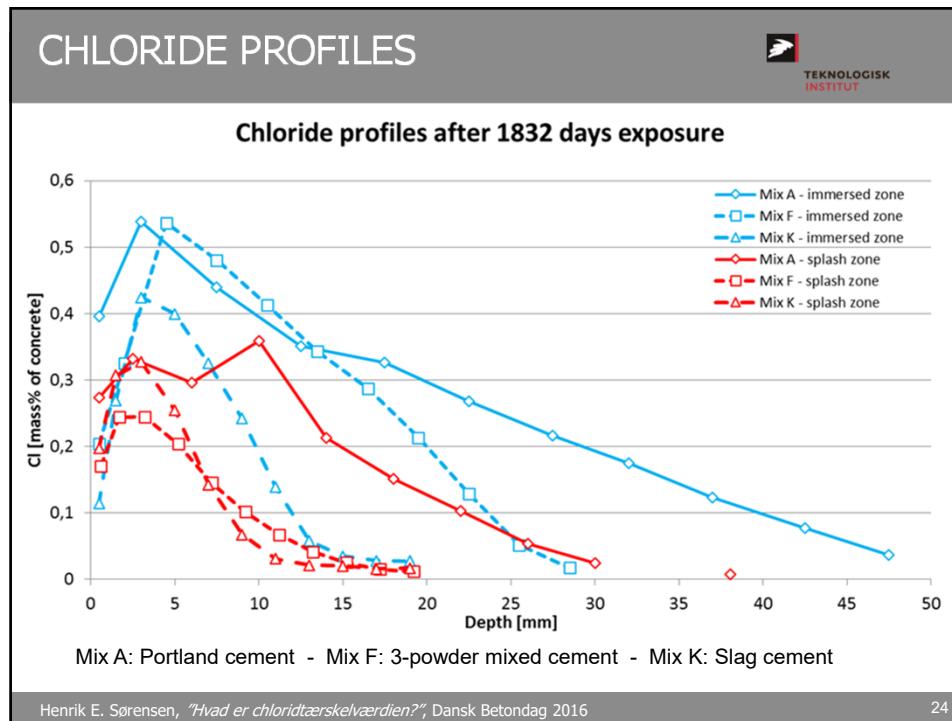
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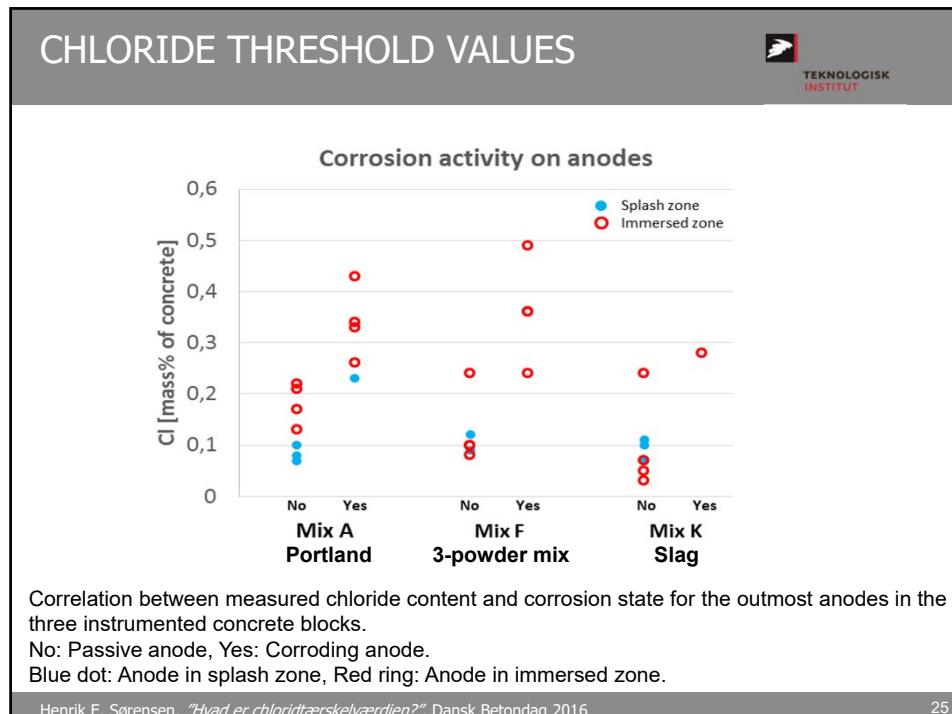
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## CHLORIDE THRESHOLD VALUES

Preliminary chloride threshold values from marine exposure for 5 years

Mix/Exposure zone	Corrosion activity	Chloride threshold value	
		[%Cl by mass of concrete]	[%Cl by mass of binder]
Mix A / Splash zone Mix A / Immersed zone	Corrosion on 1st anodes Corrosion on 1st and 2nd anodes	>0.14 and <0.23 >0.22 and <0.26	>0.9 and <1.5 >1.4 and <1.7
Mix F / Splash zone Mix F / Immersed zone	No corrosion on anodes Corrosion on 1st and 2nd anodes	>0.12 Approx. 0.24	>0.8 Approx. 1.6
Mix K / Splash zone Mix K / Immersed zone	No corrosion on anodes Corrosion on 1st anode	>0.11 >0.24 and <0.28	>0.7 >1.6 and <1.8

**Mix A:** Portland cement - **Mix F:** 3-powder mixed cement - **Mix K:** Slag cement

The chloride content at the depth of the anodes has been calculated from the curve fitted parameters at 532 days and 1832 days of marine exposure

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## CONCLUSIONS



- Chloride threshold values can be estimated from in-situ HCP measurements on anode ladders combined with chloride analyses. A monitoring system with frequent measurements is required to produce reliable data on the corrosion initiation.
- LPR measurements can be used as an alternative or supplementary method to HCP measurements. So far, however, it seems as the more complex LPR measurements does not give any additional information on corrosion initiation compared to HCP measurements.
- In the present investigation with 5 years marine exposure of anode ladders in different concrete types with eqv. w/b ratio of 0.40 corrosion initiation has been detected on anodes with concrete cover up to approx. 20 mm.
- The corresponding values of chloride content indicate that the chloride threshold values are at least 0.10 %Cl by mass of concrete (0.7 %Cl by mass of binder) in the splash zone and at least 0.20 %Cl by mass of concrete (1.4 %Cl by mass of binder) in the immersed zone for all three concrete mix designs.
- Furthermore, the observations indicate that the chloride threshold values for the two concrete types with Portland cement (Mix A) and 3-powder blended cement (Mix F) are not more than 0.24 %Cl by mass of concrete (1.6 %Cl by mass of binder) in the immersed zone. More observations are needed to extent the estimations of chloride threshold values.

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*The Concrete Expert Centre is a cooperation between the Danish Technological Institute and the Danish Technological University*

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# PAPER KAN HENTES PÅ TI-STANDEN



## CHLORIDE THRESHOLD VALUES FROM CONCRETE BLOCKS EXPOSED AT RØDBYHAVN MARINE FIELD EXPOSURE SITE

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### ABSTRACT

The threshold value for chloride-initiated reinforcement corrosion is of major importance for the outcome of concrete structures in marine life models. Unfortunately, a generally accepted standard test method for determination of this parameter does not exist. The durability of the coming European-life link between Denmark and Germany is highly depending on the choice of a correct design value for chloride penetration parameters and chloride threshold values. This resulted in start-up of a Danish marine field exposure site in Rødbyhavn harbour in 2010.

This paper presents details on the concrete composition, the layout of concrete blocks, the test set-up, and the marine exposure for the ongoing reinforcement corrosion tests in Rødbyhavn marine field exposure site. Chloride threshold data from continuous measurements during the first 5 years exposure are presented, and chloride threshold values are estimated.

**Keywords:** Chloride threshold value, Reinforcement corrosion, Field exposure, Marine environment, Monitoring.

### 1. Introduction

The threshold value for chloride-initiated reinforcement corrosion is of major importance for the outcome of concrete structures in marine life models. Unfortunately, a generally accepted standard test method for concrete structures subjected to chloride exposure does not exist. In the period 2009–2010 the RILEM Technical Committee 253-TCI (RILEM, 2010) worked on the development of a commonly accepted test method for determining chloride threshold values. However, no agreement was reached and no common test method was performed. However, the results were not satisfactory, so the RILEM TC 253-TCI activities did not succeed in developing a standard laboratory test method for determination of chloride threshold values.

The durability of the coming European-life link between Denmark and Germany in 2010 is highly depending on the choice of correct design values for chloride penetration parameters and chloride threshold values. This resulted in start-up of a marine field exposure site in Rødbyhavn harbour in 2010 where the field exposure conditions are more severe than the European-life test conditions. Therefore, in order to take the lack of reliable test methods for determination of chloride threshold values, it was decided not only to test chloride ingress into different concrete mix designs, but also to include reinforcement corrosion tests on uninstrumented concrete blocks. This paper presents the first results of the marine chloride threshold values on exposed concrete with relevant reinforcement type, concrete composition, and exposure conditions.

### 2. Design and production of instrumented concrete blocks

The instrumented concrete blocks were designed in a co-operation between Fersus A/S and Danish Technological Institute. Based on experience from former field exposure tests in Sweden (Gönnberg, 1998) and Denmark (Sørensen, 2009) it was decided that instrumented concrete blocks with rebars and anode ladders should be used. The blocks have a height of 75 cm and a width of 150 cm. The blocks are cast in two stages before interaction from the opposite exposed face needs to be taken into consideration. Furthermore, the large exposed area allows many samples to be extracted from a concrete specimen, that is still having significant size and weight. Each concrete block has a ring reinforcement of stainless steel 316L and also

from two opposite sides of the block (Fig. 1). The stainless steel ring reinforcement used in all blocks is made from Ø12 mm ribbed (sleeve grade 1.4362 duplex). Detailed information regarding the design is given in the following subsections.

### 2.1 Reinforcing bar diameters and detailing

The concrete blocks have 8 nos. of vertical Ø12x180 mm ribbed rebars facing the front with concrete cover from 2 cm to 9 cm (Fig. 1). Four anode ladders are placed on the backside. The two upper anode ladders are located in the splash zone and the two lower anode ladders are located in the submerged zone, when the concrete blocks are exposed to sea water. One of the two upper anode ladders has 4 nos. of vertical rebars and the other ladder has 4 nos. of horizontal rebars. The two lower anode ladders are positioned in the submerged zone. Each anode ladder contains one negative reference electrode and a separate working electrode made of stainless steel grade 1.4362 electrode head on manganese dioxide. The working electrode is a mixed metal oxide (MMO) electrode head on manganese dioxide.

All the ordinary steel rebars and the anode ladders used in the instrumented blocks were made from Ø12 mm ribbed rebar type 1K350. All the rebars had a total length of approximately 180 cm and bars were removed from the cut faces. The steel was protected by outside epoxy coating, but not fully to simulate a real situation.

All the anode ladders were custom made for this project. The 2.5–11 cm long anode ladders were made from the same material as the steel rebars. The four ladders have a nominal cover of 10, 12, 14 and 16 cm, respectively, for levels 1, 2, 3 and 4 respectively. All anodes were pretreated by natural exposure before installation. The anodes were connected to the concrete blocks via the concrete surface by four titanium rods mounted on the base bars of the anode ladder. An insulating sleeve was placed around each anode through a cable eye mounted in the base bar on the bottom of each ladder. Two titanium rods holding the anodes. The base bars consist of stainless steel grade 1.4401, is electrically isolated from the anodes. The base bar is filled with epoxy.

Fig. 1. Principle of the design of the concrete blocks. Only steel reinforcement, electrodes and sensors are shown. View from back side.

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