North Sea small scale mineral deposition tests

Lucia, Margheritini; Simonsen, Morten Enggrob; Bjørgård, Trine Larsen; Goreau, Thomas

Publication date:
2019

Document Version
Publisher's PDF, also known as Version of record

DEPARTMENT OF CIVIL ENGINEERING
AALBORG UNIVERSITY

North Sea small scale mineral deposition tests

Lucia Margheritini
Morten Enggrob Simonsen
Trine Larsen Bjørgård
Thomas Goreau

ISSN 1901-726X
DCE Technical Report No 272.

Aalborg University
Department of Civil Engineering
Water and Environment

DCE Technical Report No 272.

North Sea small scale mineral deposition tests

by

Lucia Margheritini
Morten Enggrob Simonsen
Trine Larsen Bjørgård
Thomas Goreau

December 2019

Published 2019 by
Aalborg University
Department of Civil Engineering
Thomas Manns Vej 23
DK-9220 Aalborg Ø, Denmark

Printed in Aalborg at Aalborg University

ISSN 1901-726X
DCE Technical Report No 272.

Preface

This report has been prepared by Lucia Margheritini under the investigations financed by the EUDP project " New material for wave energy substructures" (https://www.civil.aau.dk/Project+websites/newmatrialwes/?page=1).

The version 0.1 contains the reporting of tests and results with correction on power consumption

Version	Date	Comment
0.0	November 2019	Lucia Margheritini (LM)
0.1	December 2019	LM corrected Amps in Hantholm from 0.02 to 0.2 and 0.3

Contents

1. Introduction

Electrodeposited calcium carbonate ($CaCO_3$) on steel templates could be an alternative building material for subsea structures. Deposition of $CaCO_3$ from seawater can be induced by an electrochemical method. The electrochemical system consists of two electrodes, an anode and a cathode immersed in seawater, connected to a power supply. An electrochemical reduction of the water in close vicinity to the cathode surface causes a local increase in pH according to $2H_2O + 4e^- \rightarrow H_2 + 2OH^-$.

$$2H_2O + 4e^- \rightarrow H_2 + 2OH^-$$

Equation 1 Reduction of water at cathode

As the pH close to the cathode increases, the hydrogen carbonate equilibrium is displaced towards carbonate according to Equation 2.

$$CO_2(g) \leftrightarrow CO_2(aq) \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$$

Equation 2 Carbonate equilibrium

The transition from bicarbonate to carbonate is shown in Equation 3.

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

Equation 3

When carbonate ions are formed close to the cathode, it can bind to calcium ions present in the seawater. The precipitation of calcium carbonate form according to Equation 4.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

Equation 4 Deposition of calcium carbonate

At higher applied voltage magnesium ions from the sweater can bind directly to hydroxide ions that increases to higher concentrations at the surface of the cathode and magnesium hydroxide ($Mg(OH)_2$) is deposited rather than $CaCO_3$. Magnesium hydroxide and calcium carbonate are two very distinct materials with very different characteristics: briefly, $Mg(OH)_2$ is more porous compared to $CaCO_3$, making $CaCO_3$ a more suitable construction material, and for our purposes the competing reaction depositing $Mg(OH)_2$ should be avoided.

Deposition of $CaCO_3$ is common in the field of cathodic protection (CP) of steel and has therefore been widely investigated. Electrochemical deposition of $CaCO_3$ has also been suggested as a solution for prevention of scaling in cooling systems. It is also used for restoration of coral reefs by professor Thomas Goreau. Therefore many factors that affects the kinetics of electrodeposition of $CaCO_3$ have been previously evaluated. What has not been investigated is how to optimize the deposition of $CaCO_3$ (especially in cold water) and use it as a construction material. The idea was described by Professor *Wolf* Hilbertz and was visionary but was never completed.

The tests described in this section are the first of a kind in cold water is real sea environment. The tests stood behind systematic laboratory tests under controlled conditions (DCE Technical Reports 268 and 271, Aalborg University).

2. Objectives

The general objectives of the monitoring campaign can be summarized in the following points:

- To realize the first real sea cold water installation for Electrodeposited calcium carbonate.
- To assemble a portable, easy to handle system for testing electrochemical mineral deposition in cold waters.
- To collect data on the main parameters affecting the process (temperature, salinity, potential).
- To report on testing conditions.
- To analyze the collected material in terms of mineral composition and deposition rate and compare it to laboratory results.
- To quantify the deposited material and give a preliminary evaluation of the cost.

3. Locations and tests duration

The Real sea cold water investigations were thought to be performed in two different locations: Hantholm Harbour (in kind donation) and Nissum Bredning, under a contract with DanWEC (Fig. 1)

The two systems were designed with data logging equipment and minimal need of intervention, so to be able to stay several weeks undisturbed.

The water in the two locations previously analyzed with ICP (Inductively Coupled Plasma). Results are shown in Table 1

Tabel 1. ICP water analysis results

ICP elements	Hanstholm [mg/l]	Nissum Bredning[mg/l]	% Change
Ca	481,4	395,8	18%
Mg	1269	1070	16%
Na	7252	6260	14%
K*	757,9	720,3	5%
Sr	6,2	5,97	4%

*Potassium is susceptible to bigger uncertainties

Figure 1. The two locations of the Sea Trials.

Ideally the tests would last one year, but North Jutland was hit by record wind storms between 2018 and 2019 and the DanWEC facility was severely damaged only 40 days after the set up was in place (we were

informed only at the beginning of January 2019) and there had been a power short-circuit few hours after we installed

The power cable in Hanstholm was also damaged due to excessive friction against the concrete deck under the action of wave forces. Despite this last accident did not affect power production, it was necessary to remove the set up here to in order to maintain the cable.

Therefore, while the tests in Hanstholm could be considered successful, the ones in DanWEC did not. Aggravating the DanWEC situation, is the fact that after the storm that damaged the access bridge, we received pictures of the installation, from which we deduced no power was flowing (evident rust). We got a warning not to go there as the bridge was hazardous but we did make clear there was no power. Despite this, no one from DanWEC went to re-establish power connections. Once we reached DanWEC on the 07 of March with our own electrician, we could see that there had been a power shortcut at location only few days after installation, as the power consumption measurements where close to zero. Regretfully, despite the promising installation, it resulted in aborted tests and loss of money as we did pay the access but did not received the granted service of electricity supply and also had to pay for decommission, even if the contract stated that in case of failure of the facility, the decommission would be covered by DanWEC.

Table 2 summarizes the milestone for the sea trials.

Table 2. Milestones *for Sea Trials*

24/05/2018	**06/06/2018**	**18/06/2018**	**18/08/2018**	**03/09/2018**	**12/11/2018**	**?/11/2018**	**05/01/2019**	**07/03/2019**
Hanstholm installation	Site inspection	Site inspection	Site inspection	Site inspection	Nissum Bredning installation	Power Shortcut in Nissum Bredning	Notice of major damage to Nissum Bridge	END of sea trials

Total successful test duration and data acquisition in Hantholm Harbour: 287 days

Total unsuccessful*l test duration in Hnatholm Harbour: 0 days

Total successful test duration in Nissum Bredning: 1 day

Total unsuccessful*l test duration in Nissum Bredning, DanWEC: 115 days

(*unsuccessful refers to the inability to perform tests due to malfunctioning of the system)

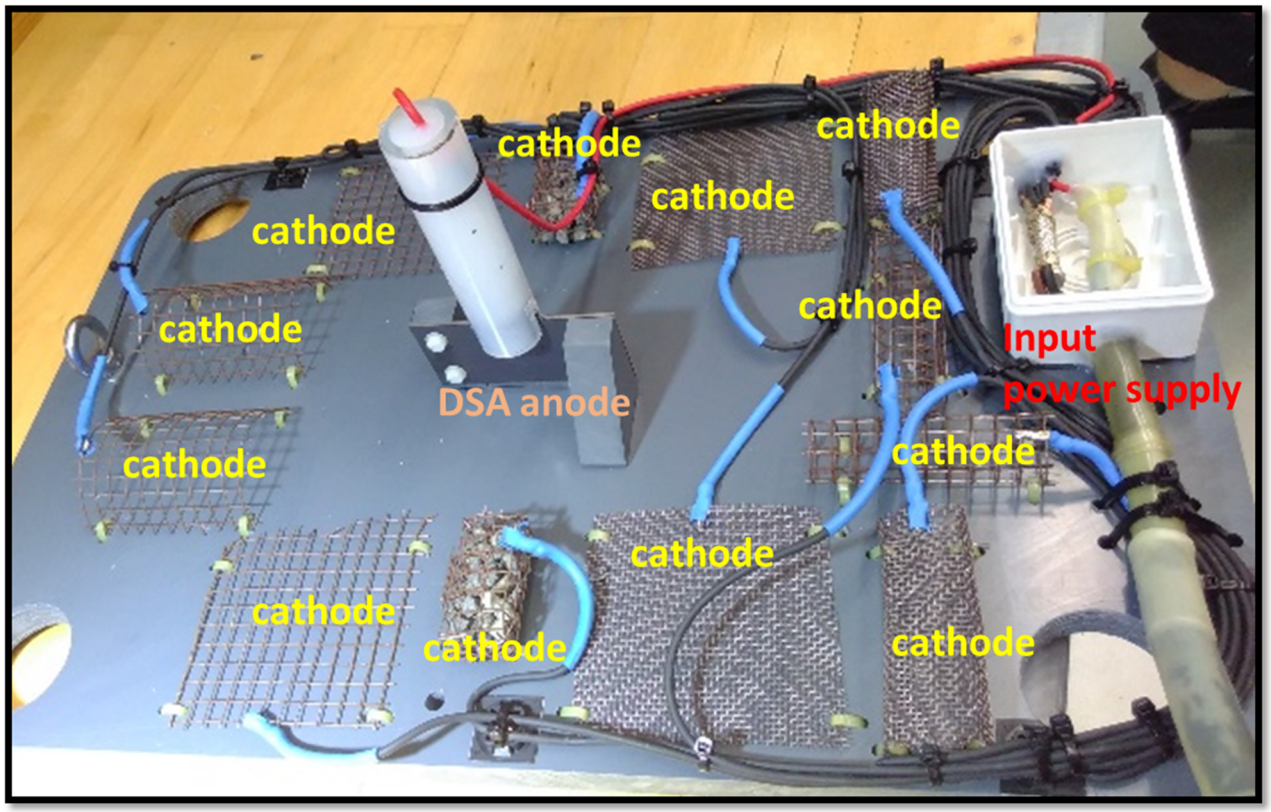
4. Setup

Hanstholm set up

The set up in Hantholm consisted of a self-contained hard plastic box adequately perforated to allow water circulation, containing the 6 sets of cathodes (2 par shape, all weighted), anode, HOBO data logger and secured connections. The entire electrode setup fitted the bottom of the box over an area of circa 0.55x0.38 = 0.21 sqm. The cathodes were placed around the anode at an average distance of circa 16 cm from centroids. All electrical connection were isolated and the anode connection waterproof (silicon) (Fig. 1).

The cathodes are connected to the negative pole and the anode to the positive. A water proof box hosted the split connections.

The day of the installation was the 24/05/2018. Sunny day, no waves.



Figur 1. Setup previous installation.

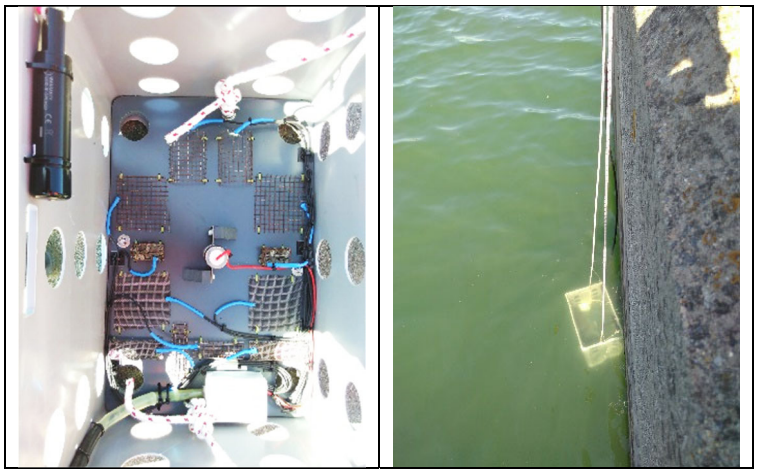
The setup was lowered circa 20 cm above the sea bottom at - 5 m below surface with a rope. The "suspended solution" was chosen in order to try to avoid massive deposition of fine particles over the electrodes, typically occurring in harbours (but unfortunately, it did not serve the purpose), (Fig 2). The lowering was monitored with an underwater camera with led lights. Visibility is generally very poor, almost complete darkness at 5 m depth. Marine life seem to be abundant and identifications of anemones, crabs and fish could be done.

Once in the water, a V pf 5 – 5.5 was applied for few seconds until bubbling, and after the voltage was set to 2.5 V, corresponding to 0. 3 A. The power was sourced from the electrical grid from a pole 100 m away

from the installation (Fig 3). Power consumption was monitored. The test were run at constant 2.5 V. The current was initially 0. 3 A and then shifted to 0.2 A till the end of the tests (Fig. 3).

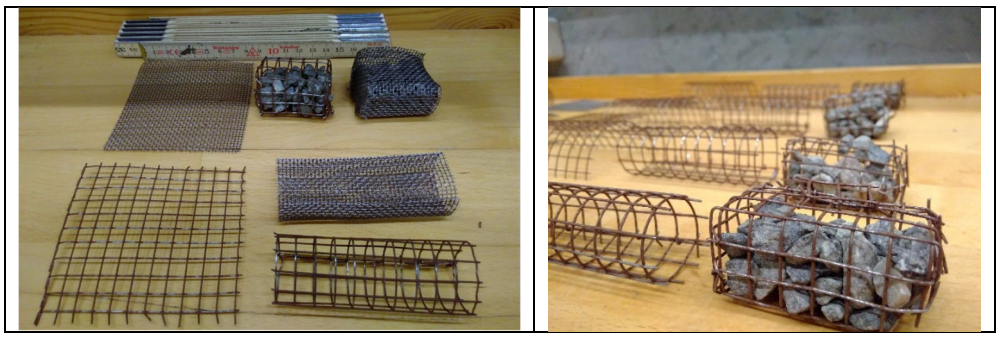
The cathodes were pieces of circa 10x10 cm of metal grid and net shaped by hand into cylinders and blocks (Fig 4). The cathodes materials, untreated steel, have the characteristics in Table 3.

The anode was 9.5 x 4.6 x 0.2 cm DSA provided by Electrocell.



Figur 2. Hanstholm setup at location.

Figur 3. Overview of installation at Hanstholm Harbour.



Figur 4. Cathodes for Hanstholm installation.

Tabel 3

FINE GRID Maske 8,5 mm Tråd 0,8 mm Maske: 8,5 x 8,5 mm Trådtykkelse: 0,8 mm Bredde: 1000 mm Materiale: Ubh stål	*WIDE GRID* Maske 1,6 Tråd 0,5 Maske: 1,6 x 1,6 mm Trådtykkelse: 0,5 x 0,5 mm Mesh: 12 x 12 Åbent areal: 58 Bredde: 1020 Vægt (kg/m2): 1,527 Materiale: Ubh stål

Nissum Bredning setup

The set up in Nissum Bredning consisted of a mesh of circa 1x1 sqm of the small mesh kind in Table 3 as a cathode. The mesh was secured around one of the poles/legs of the bridge. A thick rubber insulation made of a black and white layers of several mm was placed between the cathode and the metal leg of the bridge in order to avoid electrical connections. The anode was 9.5 x 4.6 x 0.2 cm DSA provided by Electrocell, with waterproof connection (silicon) (Fig. 5). The tests were set to run with constant 2.5 V. the current at installation was then 0.449 A.

Figur 5. Electrodes installation at Nissum Bredning

Few meters (4-6) of cables where connecting the electrodes to the power supply inside the protected DanWEC container. Power consumption was monitored. Unfortunately, as mentioned in chapter 3, a shortcut occurred few days after installation and the overall power consumption was only 0.02 kWh (Fig. 6). This also means that the setup was never properly running. Regretfully, even when we indicated to DanWEC that there was no power flowing to the cathode, they did not do anything to reestablish the necessary conditions for the tests. This accident, and the later storm that damaged the bridge making it impossible for us to go there, led to the decision of decommissioning (Fig. 7). Without the protection of the electric current, the cathode rusted as expected (Fig. 8).

Figure 6. The power supply at installation (lf) and on the day of decommission with indication of energy consumption (ce and rt).

Figur 7. Nissum Bredning damaged bridge

Figur 8. Rusted cathode from Nissum Bredning – after 4 months unprotected at sea.

5. Monitoring

Only the monitoring of Hanstholm site is presented.

On the 06/06/2018 a site inspection was made. There was some wind and some ripples/ small waves where at the surface of the sea. Everything was working correctly and a layer of white solid material was covering the cathodes. The setup was covered in circa 0.5 cm of very fine dark sediments.

The conductivity was measured directly with a probe, and the reading was 48.9 ms/cm.

The data from the HOBO instrument was extracted with the Shuttle and salinity at the same time of reading was 34800 µS/cm. The temperature measurement was the same. It must be noticed there may be a small difference (circa 1 m) in the measurement of the HOBO and the punctual probe.

6. Results

Results here presented include only the data coming from Hanstholm Harbour as the set up at DanWec did not receive current and power due to malfunctioning of the facility.

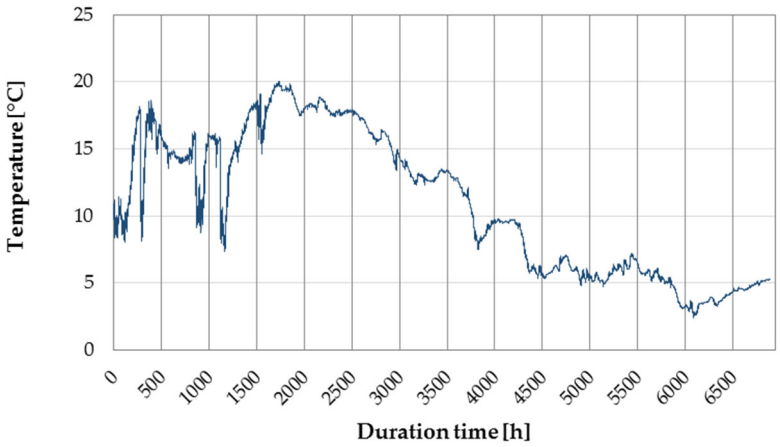
Salinity and water temperature

The data logger for salinity and temperature was installed in the setup. Continuous measurements are therefore available from installation besides malfunctioning of the instrument. The logger recorded the temperatures and conductivity of the water in the exact setup every 30 minutes during installation, for a total of circa 13770 data points each.

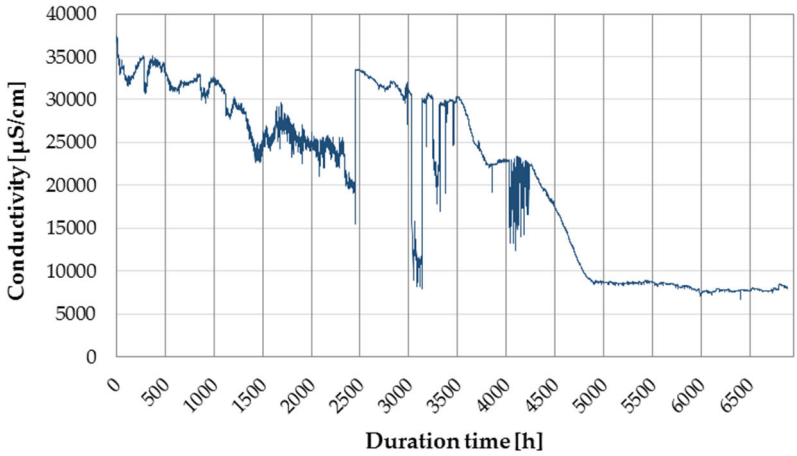
The maximum and minimum temperatures recorder were 20.0 °C and 2.4 °C respectively.

The maximum and minimum conductivities recorded were 37530 and 6666 µS/cm.

The harbor can be considered a small basin of water and rain can influence the salinity. Additionally, bio-fouling might have affected the conductivity measures in the last 3 months of testing.



Figur 9. Water Temperatures from 24th of May 2018, 1:30 PM, to the 7th of March 2019 1:00 PM



Figur 10. Water Temperatures from 24th of May 2018, 1:30 PM, to the 7th of March 2019 1:00 PM

Mineral composition

The deposited material over the cathodes was analyzed after site inspection and decommission. The XRD analysis of the biorock sample showed that the material became stronger in time (% of aragonite increased from 65.9% to 75.8 %), Table 4. As a comparison, a material previously analyzed from a tropical biorock station in Thailand contained 78% of aragonite and 22% of brucite.

The shift toward aragonite in time is reported by other authors and by the same Thomas Goreau:

"Overcharging the cathode with higher electrical current densities greatly increases hydroxyl ion concentrations, which causes precipitation of the mineral brucite, Mg(OH)2 instead of aragonite. Brucite requires very high pH to precipitate, appears to have little or no kinetic barrier to precipitation, and should grow at a rate proportional to the square of the microsite pH next to the cathode. Brucite, a white mineral similar in appearance to limestone, is structurally weak and flakes off. In seawater of normal pH brucite dissolves, the hydroxyl ion raise the pH, and convert bicarbonate ion to carbonate ion, which reacts with calcium ions. Consequently as the material grows and brucite ages it is replaced by aragonite. To optimize strength the Biorock minerals are grown at a low charging rate to produce hard limestone rather than soft brucite. We find experimentally that a growth rate of not more than 1-2 cm/per year provides maximum growth and structural strength, and above that brucite dominate. These results are strongly affected by temperature, because brucite is a normal mineral whose solubility increases with temperature, while calcium carbonate minerals are extremely unusual in having retrograde solubility, being more soluble in cold water than hot water. As a result materials grow faster and harder in warm tropical waters than in cold boreal waters. In addition the electrical conductivity is directly proportional to the salinity, so growth rates are highest in very salty waters and brines, lower in brackish waters, and very small in pure fresh water."

What we have found is that impressing a voltage of 2.5 (minus cable losses) generated the same results, in terms of mineral composition, than in warm waters.

Table 4.

Composition after 2 weeks	Composition after 3 months
Aragonite: 65.9% Brucite: 33.2% Calcite: 0.8%	Aragonite: 75.8% Brucite: 23.3% Calcite: 0.8%

Weight of the mineral deposition

The layer of deposited material was between 2-7 mm depending on location, showing thicker deposition where the mashes on the cathodes intersect. The material was also easily detached from the cathode.

One reason behind the small growth could be the temperature but more likely the sediment deposited on the setup. As noticed by several authors, the interaction between the mineral deposition and organic matter or bacteria is very difficult to define. We consider the conditions close to the bottom of the harbor to be of such a kind. In first place, organic matter is a barrier to the oxygenation of the water and clays have shown to increase deposition time compared to laboratory.

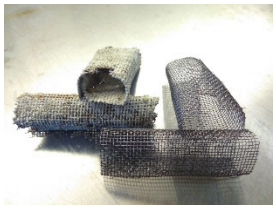
The cathodes were removed for the setup and washed in the laboratory. Suspended material was removed with a soft brush.

The samples after 1 hour in the oven at 100 °C to remove water, have been put in the oven at 550 °C for 4 hours to remove any trace of organic matter.

After this time, the cathodes have been weighted and a comparison with weight before mineral deposition has been made to calculate the weight of the deposited material (Tables 5-7). The results are presented divided by the mesh types.

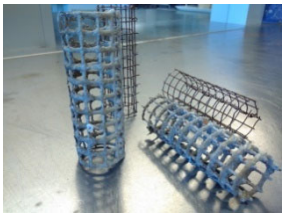
Figur 11.

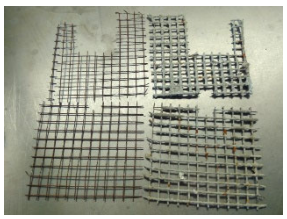
Tabel 5



FINE GRID				
Squared shape, plates				
sides 1 [cm]	**side 2 [cm]**	**weight before [gr]**	**weight after [gr]**	**Gain [gr]**
9,5	10	13,25	27,97	14,72
Squared section, columns				
10		13,5	26,41	12,91

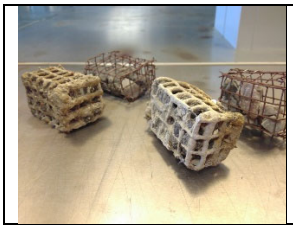
Tabel 6





WIDE GRID				
Squared shape, plates				
sides 1 [cm]	**side 2 [cm]**	**weight before [gr]**	**weight after [gr]**	**Gain [gr]**
9,5	10	9,0	17,3	8,3
Round section, columns				
9,5	3	8,5	20,43	11,93

Tabel 7.



Box with small stones					
sides 1 [cm]	**side 2 [cm]**	**side 3 [cm]**	**weight before [gr]**	**weight after [gr]**	**Gain [gr]**
5,5	2,5	3,5	45,25	59,45	14,2

Calculation power consumption:
I*V=P
0.2*2.5 = 0.5
P*h=Wh
H=24
Total days: 287
→ h=24*287=6888
0.5*6888=3400 Wh = 3,4 kWh
The losses from the cable are negligible:
0.21 Ohm in total = 0.06 kWh

Tabel 8, Summary of results

total produced material
121,0 gr
0,121 kg
Energy consumption
25,5 kwh (from meter – wrong?) 3,4 kWh (by calculation)
TOT El. Cost (2,5 dkr/kWh)
63,75 dkr 8,5 dkr
El. Cost of material produced
527 dkr/kg **70 dkr/kg**
on the total weight
318,06 gr
0,318 kg
27 dkr/kg
Reinforced concrete
15 dkk/kg

7. Discussion and conclusions

The sea trials incurred in a very unpleasant failure in Nissum Bredning, with complete loss of money and no support from DanWEC.

The sea trials in Hanstholm have been successful.

A couple of things must be considered when looking at the material yeald:

1) The salinity of the North Sea is the area is not high compared to the one in tropical waters where usually data from biorock installation are reported. Less ions in the water mean less conductivity and surely a slower process. Additionally, being inside a harbor it is also to be noticed that run off water and discharges may stay trapped temporarily and therefore, as measurements indicated, the salinity in medium low.
2) The set up has been covered several times with very fine sediments. The sediments have not been analyzed but from literature it is reported that suspended sediments can slow down the process.
3) The cathode material (both meshes) presented a smooth surface. It seems that this could have prevented the mineral deposition to stick to the surface (this is also mentioned in some practical experiences in the biorock applications). The best material is still a corrugated, deformed non galvanized metal (such as the one on rebar).

At present we are finishing a second setup to be installed in Hansthlm again, so to correct 2) and 3).

Recent publications in the DCE Technical Report Series

ISSN 1901-726X
DCE Technical Report No 272.