Final report

1. Project details

Project title	New materials for wave energy substructures
File no.	5052-0010
Name of the funding scheme	EUDP
Project managing company / institution	Aalborg University
CVR number (central business register)	DK 29102384
Project partners	Electro Cell, Biorock Technology, Wave Piston, Resen Waves
Submission date	31 August 2021

2. Summary

Danish summary

Formålet med projektet var at udvikle en metode til beskyttelse af offshore undervandsstrukturer mod korrosion og skur. Metoden involverer opbygning af et beskyttende lag ”Seacrete” på undervandsstrukturer, som dannes ved elektrokemisk udfældning på overfladen af stålkonstruktionen. Et af målene med projektet var at undersøge dannelsen af Seacrete i laboratoriet og efterfølgende demonstrere teknologien under virkelige forhold. Seacrete består hovedsageligt af mineralerne aragonit ($CaCO_3$) og brucit ($Mg(OH)_2$) og fordelingen af mineralerne har stor betydning for materialeegenskaberne. I projektet blev der udviklet en model, der er i stand til at forudsige sammensætningen og mængden af det elektrokemisk producerede materiale baseret på vandtemperatur og anvendt strømtæthed.

Der er udført Field test ved to lokaliteter i Danmark (Nissum Bredning og Hanstholm) samt en i det nordlige Italien (Isola di Bergeggi), der repræsenterer henholdsvis områder med kold og varmere havtemperaturer. I begge tilfælde blev der udfældet materiale på konstruktionerne, som bestod at en blanding af aragonit og brucit. Forsøgene ved lavere temperatur resulterede i produktion af mindre materiale med en højere andel af aragonit. Styrken af materialet er baseret på andelen af aragonit, hvor Seacrete med et højt indhold af aragonit har sammenlignelige egenskaber med beton, hvilket vil betyde, at det vil kunne anvendes til konstruktioner som et bæredygtigt alternativ til beton.

Et designkoncept blev udviklet baseret på Resenwaves bølgeenergiteknologi koblet med elektrokemisk udfældning på en offshore installation ved Hanstholm havn. Ved brug af 1-2% af den samlede energi

produceret af en 3 kW bølgekonverter forventes det at opnå beskyttelse af undervandskonstruktionen samt at kunne etablering et kunstig rev. Ydermere ville det være muligt at reducere CO_2 emissionen betydeligt ved brug af Secreate i stedet for beton.

English summary

The aim of the project was to develop a method for protection of subsea offshore structures against corrosion and scour. The method involves the production of a protective layer “Seacrete” on subsea steel structures by electrochemical deposition. One of the goals of the project was to investigate the production of Seacrete in the laboratory and subsequent demonstrate the technology under real conditions. Seacrete is mainly composed of the minerals Aragonite ($CaCO_3$) and Brucite ($Mg(OH)_2$) and the ratio between the constituents was found to be highly important for the material properties. In the project a model was developed capable of predicting the composition and amount of material produced based on water temperature and applied current density.

Field tests were conducted at two sites in Denmark (Nissum Bredning and Hanstholm) and one site in the North of Italy (Isola di Bergeggi) representing cold and warmer water regions respectively. In both cold and warm water locations material was deposited on the structures which was composed of a mixture of aragonite and brucite. The cold-water location produced less material with higher aragonite fraction. Material with high fraction of aragonite was found to have similar properties to concrete, and thus may be implemented in some structural applications in constructions as a sustainable alternative to cementitious materials.

A Design Concept was developed featuring Resenwaves wave energy technology coupled with mineral deposition technology for an offshore installation at Hanstholm harbour. Using only 1-2% of the total energy produced for a 3kW wave energy unit, it is expected to be possible to protect the subsea structure and at the same time create an artificial reef. With a preliminary life cycle assessment, we could verify that the potential for CO_2 reduction compared to the use of concrete is significant.

3. Project objectives

The overall objective of the project was the contribution to reduction of fossil fuel usage in the supply chain for marine renewable energies, in order to promote a cleaner environment with possibility of ecosystem enhancement and cost effectiveness of material. Wave energy technologies are slowly reaching full scale and pre-commercial development stages. One of the setbacks that most of the concept’s face is the high cost of the energy produced (CoE). In order to make the device able to withstand the harsh sea and wave conditions, the production materials accounts for a relatively high amount of the costs. This project set out to investigate if a small part of the electricity produced by the wave energy converters could be used to reinforce delicate parts of the device, generate a scour protection and a coating for rust prevention. To do so, we investigated the application of the mineral deposition technology (already successfully used in coral restoration in tropical regions), in cold waters (North Sea and Mediterranean Sea). This was done both in the laboratory and in real sea conditions. The results have allowed the development of a model to predict deposition quantities and mineral composition, and the concept design of a small wave energy farm powering its own scour protection.

Particularly, the objectives had been identified as:

- To produce the Seacrete material in cold waters both in the lab and under real conditions at different test sites (DanWEC area and Nissum Bredning) in varying water salinities, supplied voltage and on different metal frames that will vary in thickness (preferred material: steel)
- To characterize the obtained Seacrete material both chemically and mechanically using different quantitative analytical equipment including ICP, XRD, XRF in order to determine the chemical composition and crystal structure and basic mechanical testing, including tensile, compressive, torsional and fatigue.
- To gain experience on the growth rate of Seacrete material in cold waters in the lab. and under real conditions.
- To make a first economic analysis to assess the energy efficiency of production in cold waters and to determine if the final product can be competitive with other materials.
- To realize the first concept design of a wave energy device that is able to “self-generate” parts of it structure utilizing directly its electricity production.

4. Project implementation

A large part of the project evolves around research activities as well as field testing which both are associated with high risk. The screening experiments in the lab. showed that it was possible to electrochemically deposit mineral in cold water under controlled conditions and based on these experiments the most optimal conditions were selected to be used in the field testing. In the project 3 test locations were selected for testing the mineral deposition technology under real conditions. Two of the test locations were in Denmark (Nissum Bredning and Hanstholm Harbour) characterized as cold-water locations and a third one was installed in Northern Italy (Isola di Bergeggi) in collaboration with University of Campania which serves as a warmer water reference.

In the project the field testing showed to be challenging as outer circumstances made it difficult to obtain the desired test data from the field installations. The first two test installation installed in Nissum bredning and Hanstholm harbour in 2018 was damaged by a storm in 2019. The storm was powerful enough to damage the pier at DanWEC test facility in Nissum bredning relative short time after installation of the test installation to an extent where it was not possible to repair. The installation in Hanstholm had been running for a longer period before it was damaged by the storm, and it was possible to retrieve the setup and get data for the mineral deposition which was used in making the concept design and economic considerations for the technology.

A new test installation was designed and build; however, the installation in Hanstholm was disrupted by several storms in autumn and winter 2019 in addition to Covid 19. After successful installation in summer 2020 the installation was running fine a couple of months until the remote monitoring showed a loss in current for the setup. It turned out that a biofilm has formed on the electrodes preventing flow of current. The biofouling of the test installation has been suggested to be related to the specific weather conditions at Hansthom harbour at the specific time. A third field test installation was deployed in Hanstholm harbour in spring 2021 after the covid 19 restrictions was lifted. After successful installation this test installation provided valuable data for the mineral deposition in cold water. The problems experienced during the field testing was not expected even through it was anticipated that the highest risk in the project was associated with the field testing. The combination of severe storms and covid 19 was not expected. Covid 19 limited in periods access to the labs and field test location.

Generally, the project evolved as planned regarding implementation of the different parts of the project and all, but one milestone was reached on time. The one milestone which was not on time was the decommission of the third test installation in Hanstholm as it was postponed 2 months in order to get data for the mineral deposition in the summer months (June-July) in 2021.

5. Project results

The first and second objective concerning production and characterisation of Seacrete material in cold waters both in lab and under real conditions have been realized. Lab experiments have been conducted in the temperature range between 25 °C and 4 °C, where it was possible to produce Seacrete material. Furthermore, experiments have been conducted under real conditions in Hanstholm Harbour, (and Nissum Bredning) which also resulted in formation of Seacrete material. Additionally, a setup under real conditions has also been set up in Bergeggi, Italy which showed the formation of calcareous deposition in warmer water.

Lab experiments have been conducted in order to observe changes in the calcareous deposition on the cathode with regards to water composition, the voltage and current applied to the system, temperature and anode material. The obtained Seacrete has been characterised chemically with the quantitative analysis techniques ICP, XRD and XRF where the crystal structure was obtained through XRD and the chemical composition was obtained through XRF and ICP. Furthermore, in case of mechanical testing, samples were tested for compression strength (puncture resistance test) and compared to concrete.

The growth rate of the calcareous material was investigated both in the lab through short time highly controlled standardized experiments using a potentiostate and in-situ Raman spectroscopy to monitor the formation of the material and longer experiments having a duration of up to 2 months under similar conditions as used in the field testing.

A concept design for a wave energy device with "self-generating" substructure combined with a first economic analysis of the energy efficiency of electrochemical production of calcareous material in cold waters has been presented.

Electrochemical deposition of calcareous deposition in the lab

The data presented in the published paper in Sustainability ("Development of an Eco-Sustainable Solution for the Second Life of Decommissioned Oil and Gas Platforms: The Mineral Accretion Technology") have been analysed through Analysis of variance (ANOVA) to analyse the significance of the factors influencing the aragonite formation and the mass produced over a set period of 14 days. The factors were anode type (DSA and Pt-Ti), current (0.22 and 0.31 A), temperature (7 and 22°C) and water type (ASTM and Esbjerg water). Analysing the results type of anode and current had a significant influence on the aragonite formation where an increase in current decreased the formation of aragonite and instead promoted the brucite formation. Furthermore, a significant higher production of aragonite was achieved when using the Pt-Ti anode. The other variable which was the mass of calcareous material produced on the cathode after 14 days was also analysed through ANOVA. The analysis showed that the type of anode, temperature and current had a significant influence on the weight of deposit. An increase in temperature and current would lead to an increase in the production of calcareous material. Moreover, the DSA anode produced significantly higher amount of calcareous material compared to the Pt-Ti anode. An interaction was also observed between the anode type and temperature, where an increase in temperature using the DSA anode increased the production of the calcareous material, meanwhile the opposite is not observed for the Pt-Ti anode.

Kinetic investigation of electrochemical deposition of calcareous material

The initial part of the electrochemical deposition process for calcareous material and in particulate the growth of aragonite and brucite crystals is still not fully understood. Therefore, one of our laboratory studies aimed to investigate the initial reaction kinetics of electrochemical deposition of calcareous material ($CaCO_3$ and $Mg(OH)_2$) on carbon steel plates by varying the counter electrode material (Dimensionally stable anode and Platinum covered titanium anode), applied voltage (-1.0 and -1.2 $V_{Ag/Agcl}$), and temperature (7 and 22 °C) using in-situ Raman spectroscopy and potatiostate to control the applied voltage. In-situ Raman laser probe (785 nm) was installed 1 cm above the carbon steel plate for studying the growth of crystal structures over the course of 20 hours of cathodic polarisation. Raman spectroscopy was chosen since it is a well-known non-destructive spectroscopic technique for studying molecular structures. The results obtained through XRD analysis showed that the material produced at low negative potential (-1.0 $V_{Ag/Agcl}$) in both temperatures (7 and 22 °C) is consisted of nearly pure aragonite (>99.2%). The SEM images showed that the aragonite deposit had denser and compact structure. However, the growth rate of aragonite on the steel plate was higher at high temperature (22 °C). Raman spectra showed the peak intensity of aragonite crystals started increasing within an hour of cathodic polarisation at -1.0 $V_{Ag/Agcl}$ in both temperature for platinum cover titanium counter electrode. Conversely, aragonite crystals formation was delayed up to five hours of cathodic polarisation at -1.0 $V_{Ag/Agcl}$ potential and low temperature (7 °C) for dimensionally stable counter electrode, whereas at high temperature (22 °C) the formation started after an hour. Furthermore, the material produced at high negative potential (-1.2 $V_{Ag/Agcl}$) and high temperature (22 °C) was mainly brucite ($Mg(OH)_2$) (>98%), however the Raman spectra showed that the peak intensity of aragonite crystals started increasing after 5 hours of cathodic polarisation. The SEM images also revealed the presence of disc like aragonite crystals on the porous layer of brucite. On the other hand, the Raman spectra and SEM images showed no major growth of aragonite crystals on the brucite layer at high negative potential (-1.2 $V_{Ag/Agcl}$) and low temperature (7 °C). Additionally, it was also obtained through the current density measurements during cathodic polarisation of the steel plates that increasing temperature significantly increased the current density at high negative potential (-1.2 $V_{Ag/Agcl}$) due to acceleration of oxygen and water reductions. It could be further explained that oxygen and OH^- diffusion coefficients increase at high temperature.

Modelling of the electrochemical deposition of calcareous material

A model for prediction of the composition and amount of electrochemical deposition of calcareous material was developed in the project dependent on temperature and current density. A statistical experimental plan was made with two factors being current density and temperature with two levels. This was combined with centre and outer points to produce a response surface design. The response surface methodology (RSM) was applied to optimise the production of calcareous material. The optimisation was performed with the aim of obtaining a desired composition of aragonite and brucite together with information about the mass of the deposit. Based on the conducted experiments two RSM models were generated. One model predicting the amount of calcareous material deposited and the second its composition in the temperature and current density range between 4-25°C and 55-310 $\mu A/cm^2$ respectively. With the two models the aragonite content of the calcareous deposit was observed to decrease with increase in temperature and current density. However, this was not the case for the mass of the calcareous material, where an increase in the temperature and current density would increase the amount of calcareous material. The material produced at the highest current density (310 μA/cm^2) would consist of only 11% aragonite and 89% brucite, however the mass generated over 14 days was ~9g (area of cathode 100 cm^2). This material produced at the higher current density will have a porous structure which would decrease the strength of the material. Looking at the contrary at a low current density and a low temperature (55 μA/cm^2 and 7 °C) a calcareous material of 86% aragonite would be produced.

Scanning electron microscopy (SEM) images of the carbon steel plates with the deposit showed that the material produced at higher current densities are porous, and the XRD analysis of those materials confirmed that the materials consisted of increasing amount of brucite (Figure 1). However, at lower current the formation was more compact (SEM images) with a rise in the amount of aragonite crystal formation (XRD).

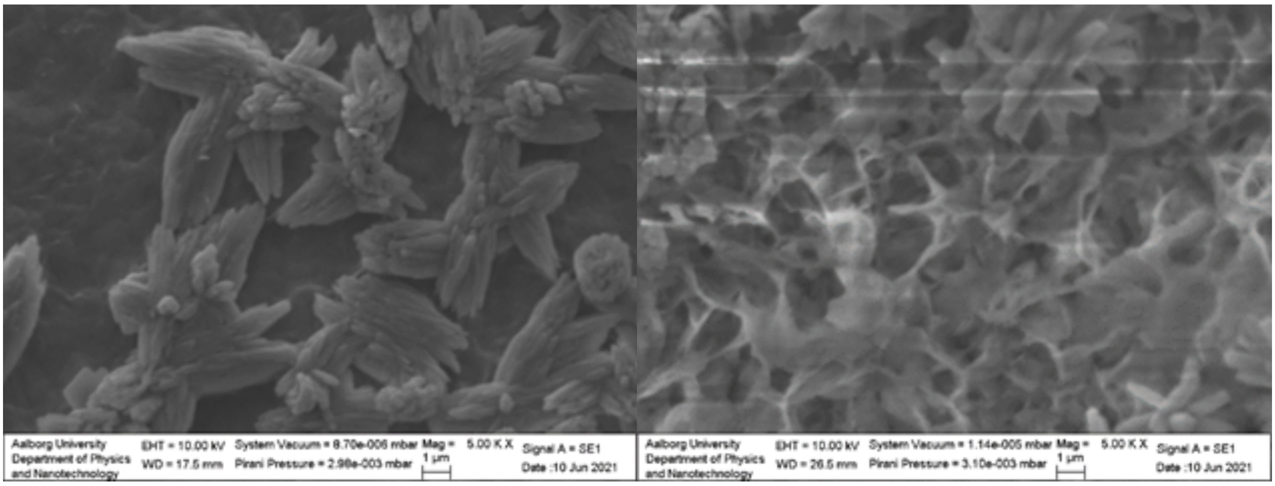

Figure 1 – (Left) The needle like aragonite crystals on top of a porous brucite layer. (Right) Close up on the porous brucite layer.

The material produced would have a greater strength due to the crystal structure of aragonite being very compact as observed by SEM. However, the great strength would come with a price on the production rate, where over the course of 14 days at these conditions only ~1g of the calcareous material would be produced. This is a decrease in the production rate of ~9 times by decreasing the current from 310 to 55 μA/cm^2.

The model showed that the percentage of aragonite in the calcareous deposit tends to decrease with increase in temperature and current density. It could be explained as the generation of OH^- ions increases with increase in current density. Therefore, the alkalinity near electrode surface increases, which favours the formation of brucite instead of aragonite.

Properties of electrochemically produced Seacrete material

In the project measurements of properties such as density, compression strength, puncture resistance, specific heat capacity, thermal diffusivity, thermal conductivity, and water vapour sorption isotherms were performed on low-voltage (LV) and high-voltage (HV) Seacrete material. The LV Seacrete was produced at low voltage (2.5 V) acquired from an installation located in Thailand. It was not possible to test the materials produced from the cold-water field test installations installed in this project due to the small amount of material produced. The HV Seacrete was acquired from Italy where the material was formed around the Italy-Greece submarine power cable by parasitic currents appearing on the latter after the disappearance of the protection sheath. It was estimated that the maximum voltage in this power cable is about 400,000 V. The water depth and temperature for LV installation were 12 m and 25-31°C, whereas for HV were 35 m and 3-24°C. The growth rate of the materials was 0.8 cm/year and 5.5 cm/year with an estimated formation time of 3 months and 12 months for LV and HV, respectively. The XRD results showed that the LV Seacrete consisted of 80.8% aragonite, 18.9% brucite and 0.3% calcite, whereas the HV Seacrete was composed of 46.4% aragonite, 52.3% brucite, and 1.1% calcite. The measured densities of LV and HV samples are 2499.2 kg/m^3 (a 1 σ standard deviation of 17.4 kg/m^3) and 1771.1 kg/m^3 (a 1 σ standard deviation of 17.4 kg/m^3) respectively, whereas normal-weight class concrete sample used for comparison tests has a density of 2122.4 kg/m^3. The result from the compression resistance test showed that HV Seacrete has significantly lower compression resistance than of the concrete, mainly because of the presence of the softer mineral brucite in a higher percentage (52.3%). Additionally, the presence of a higher porosity with more open pores in HV Seacrete resulted in a weaker resistance in its mineral matrix. The result of the puncture resistance test of LV Seacrete was very close to the tested concrete, which was due to the presence of low porous structure composed of the hard mineral aragonite (80.8%). Therefore, it could be reasonably extrapolated that the LV Seacrete has similar compressive strength to the tested concrete with a grade class C20/25. The puncture resistance of the HV Seacrete was significantly lower compared to LV and concrete. The measured specific heat capacities of the LV and HV Seacrete samples were very close to each other with a resemblance to the standard value for concrete material (Eurocode 2 – EN 1992-1-2:2004 (E)).

The LV Seacrete has thermal diffusivity similar to the natural stone and concrete materials ranging from 0.3 to 1.6 mm^2/s, which are commonly used for building construction. Thermal diffusivity of HV Seacrete is significantly lower than the LV Seacrete and standard concrete. Furthermore, thermal conductivity of the Seacrete materials were greatly influenced by the materials' porosity. Thermal conductivity of HV Seacrete was lower than the LV Seacrete due to the presence of higher porosity in the HV samples. The air-filled pores with low thermal conductivity impacted on the overall thermal conductivity of the HV Seacrete. Thermal conductivity of the LV Seacrete at room temperature is within the low range of the thermal conductivity for a standard concrete (Eurocode 2-EN 1992-1-2:2004 (E)). The LV Seacrete material with a similar density to the typical natural stone and concrete materials commonly used for building construction has a thermal conductivity within the range of 0.5 to 3.5 W/mK. Results from the moisture sorption-desorption capacity measurements showed that the LV Seacrete has an isortherm shape, and capacity to exchange and store water vapor similar to concrete. It is due to the similar densities and pore size distribution of the LV Secreate material to the concrete.

Overall, this study provided clear evidence that Seacrete materials has similar properties to concrete, thus can be implemented in some structural and thermodynamic applications in constructions as a sustainable alternative to cementitious materials.

Another study conducted within this project was focusing on the engineering value of the low-voltage mineral deposition (LVMD) technology for artificial reef restoration. Coral Porites exoskeleton (CPE) from Tanzania, LV Seacrete from Thailand and scale produced from high voltage (HV) from the south of Italy were analysed and published in Frontiers in Marine Science ("Innovative Material Can Mimic Coral and Boulder Reefs Properties"). The composition of the three different mineral depositions showed that the coral CPE was made of pure aragonite, whereas the LV and HV Seacretes were consisted of 80.8% and 46.6% aragonite, respectively. The second main mineral composing the LV and HV Seacretes was brucite. This shows that the higher voltage led to the production of Seacrete with a higher amount of brucite while reducing the percentage of aragonite. Regarding the mechanical strength testing, the CPE, LV and

HV Seacretes were compared to a standard 3.5 kN concrete. The strength test of the three mineral deposits showed that the material with higher percentage of aragonite formed a stronger structure. The results obtained from the pore size distribution test showed that LM Seacrete had compact structure in terms of pore volumes being ≤1 μm (microporous) compared to HM Seacrete. The CPE had the highest pore volumes, which are $1.40 \cdot 10^{-2}$ mL/g for micropores (≤1) and $28.5 \cdot 10^{-2}$ mL/g for macropores (>1 μm). The material between macropores of CPE is denser and harder compared to the materials between the fractures and porosities of the HV Seacrete. The pore size distribution of the Seacretes plays a significant role in the mechanical properties of the structures. This study showed that physical-chemical properties of the LV and HV Seacretes were similar to the CPE. However, the LV Seacrete had a compression strength above 3.5 kN, whereas CPE showed a lower resistance to compression than the HV Seacrete having a compression strength just above 1 kN. Overall, following the properties of the LV and HV Seacretes, they can be implemented as the realization of artificial reefs following the guidelines of the 2009 London Convention and Protocol/UNEP regarding the rightness of materials for artificial reefs.

Results of field testing

Based on the screening experiments in the lab the most optimal condition for electrochemical of calcareous material was selected for field tests. Two of the test locations were in Denmark (Nissum Bredning and Hanstholm Harbour) characterized as cold-water locations and a third one was installed in Northern Italy (Isola di Bergeggi) in collaboration with University of Campania which serves as a warmer water reference.

Two identical field test setups were commissioned in Hanstholm in May 2018, which was running for approximately 9 months, but because of a storm which damaged the electric cable to the anode and cathode the setup was taken down. It was possible to retrieve the setup and get data for the mineral deposition. Images showing the cathode before and after deposition of calcareous material is shown in figure 2. The chemical analysis of the material deposited on the cathodes showed that it mainly was composed of aragonite and is comparable with material produced by electrochemical deposition in warmer water (Thailand) (cf. Table 1). Moreover, it was found that the rate of deposition of the material was considerably slower, which could be due to a combination of lower water temperature and sediment/mud on the cathodes caused by the design of the field test setup. The material increase was found to be at a minimum of 100 wt% compared to the weight of the cathode. For more details about the field test and results refer to the DCE Technical Report; Nr. 272, North Sea small scale mineral deposition tests (https://vbn.aau.dk/da/publications/north-sea-small-scale-mineral-deposition-tests).

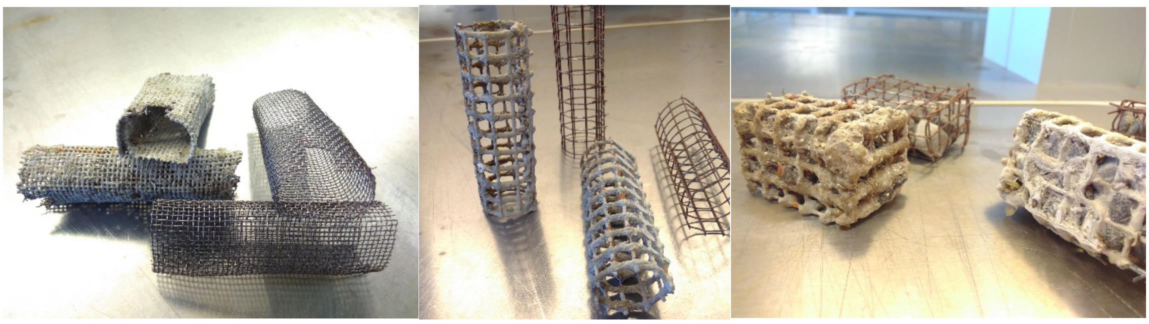

Figure 2 - Cathodes electrified for 9 months and covered in mineral deposition, and cathodes not tested, first Hanstholm Installation.

Table 1 – Result of XRD analysis of material deposited during 1. field test in Hanstholm

Sample	Aragonite	Brucite	Calcite
Hanstholm (2 weeks)	65.9 %	33.2 %	0.8 %
Hanstholm (3 months)	75.8 %	23.3 %	0.8 %
Thailand (reference sample)	78.0%	22.0%	0.0 %

A new test installation was design and build and after a delay commissioned in June 2020 but was taken down three months later due to biofouling accumulating on the cathode surface. Biofouling was fully covering the cathode which resulted in that no calcareous material formation on the cathode, however the setups were still protected against corrosion by cathodic protection. The setups were then cleaned and recommissioned for a third installation in February 2021 and was running until end of the project (end of July 2021). The power supply to one of the setups was malfunctioning relatively soon after installation and thus this setup was used as a reference to observe the corrosion of the metal cathode when not cathodic protected. After decommissioning of the setups, the setup without power connection had corroded extensively (cf. Figure 3). The setup which was connected to the power had no indication of corrosion, which means that it was protected by cathodic polarisation. Samples were taken from the field test, which was cathodic protected (cf. Table 2). The sample after 4 months showed a smaller amount of aragonite in the deposit (33.9%) compared to the results from the 1st field test in Hanstholm, whereas the percentage of calcite was higher (25.9%). The field test was decommissioned after 6 months where the percentage of aragonite had decreased to 4% whereas the percentage of calcite in the deposit increased to 79%. The increase in calcite material, is suggested to be due to biofouling visualized by growth of barnacles on the cathode (cf. Figure 7) as the crystal structure of the exoskeleton was analyzed to be composed on calcite.

Table 2 – Result of XRD analysis of material deposited during 3. field test in Hanstholm

Sample	Aragonite	Brucite	Calcite
Hanstholm (4 months)	33.9%	27.5%	25.9%
Hanstholm (6 months)	4.0%	2.4%	79.0%

Figure 3 – The two setups in Hanstholm, the cathode is the metal construction where the metal plate in the middle of the construction is the anode. (left) The setup disconnected from the power supply showing extensive corrosion. (right) Setup connected to power source with seashells and biofouling growing on the cathode and the PVC structure.

A field test was also installed in Bergeggi, Italy in collaboration with the University of Campaign. The setup consisted of a 1 m cube with extractable bars, half of which electrified and other used as control, was installed in Bergeggi, Liguria at -18 m water depth. The water temperature was varying between 16 and 26 °C, hence the installation served as a warmer water reference.

The calcareous material which was produced for the field test in Italy was made of aragonite and brucite. The setup was running for six months where samples were taken every month. Observing the results, it can be obtained that the material produced after one month was purely aragonite with trace of NaCl, which has crystallized during drying of the sample and could have been removed by washing (cf. Table 3). After the first month the concentration of aragonite in the calcareous material decreased to ~40%, meanwhile the rest of the calcareous material consisted of brucite. This were found to be consistent until the end of the field test.

Table 3 - The samples from Italy

	Aragonite [%]	Brucite [%]	Quartz [%]	NaCl [%]
After 1 month	95.7	0	0	4.3
	95.8	0	0.2	4.1
After 2 months	42.7	57.3	0	0
	46.3	54.7	0	0
After 3 months	44	56	0	0
	37.9	61.4	0.7	0
	44.5	55.5	0	0
After 4 months	43.8	53.6	-	-
	41.9	55.5	-	-
	41.6	56	-	-
After 5 months	39.9	60.1	-	-
	46.1	53.9	-	-
After 6 months	38.5	59.6	1.8	-

Economics and concept design

European targets to reach 40 GW of ocean energy and other emerging technologies by 2050, would benefit from the implementation of innovative solutions promoting sustainable materials and circular economy at sea.

When considering a wave energy or offshore wind energy farm, we envision that part of the electricity generated could be used to power steel frames on the seabed arranged in a carpet. The induced mineral deposition would generate in time a thick and strong calcareous deposit around the metal frame, adding mass, providing habitat for marine life and protecting the seabed from scour. Further, a full system could be engineered, so to use the excess energy from the renewable energy farm, in order to lower the cost of the material and provide relief to the grid when it will reach full capacity.

It is estimated that in 2027 Denmark will end up generating more renewable energy that it can use. When export cables are used at full capacity, excess generation could become a burden on the network. At the same time, marine ecosystems are at stake, as a consequence of overfishing, habitat degradation and loss. With the Design Concept here presented, we therefore propose addressing three issues at once:

- Implementation of a sustainable material for offshore applications
- Marine ecosystem enhancement
- Excess generation from marine renewable energy

ResenWaves developed the Smart Power Buoy, built as a floating mechanical device utilizing the wave movement to activate a generator and produce electric power via the sophisticated carbon spring technology which turns the center drum back and forth with the wave action. The power curve of the machine has been validated in real sea conditions, so it is possible to estimate the energy production at any given location and known sea conditions (cf. Figure 4). Additionally, the device powers a battery pack or docking station on the seabed through the mooring line and therefore they both need to be protected from scour. We propose that part of the energy generated by the machine is used to power a steel net material, arranged like a carpet on the seabed, so that in time it will grow a hard calcareous deposit that will increase ballast, while providing shelter to marine life.

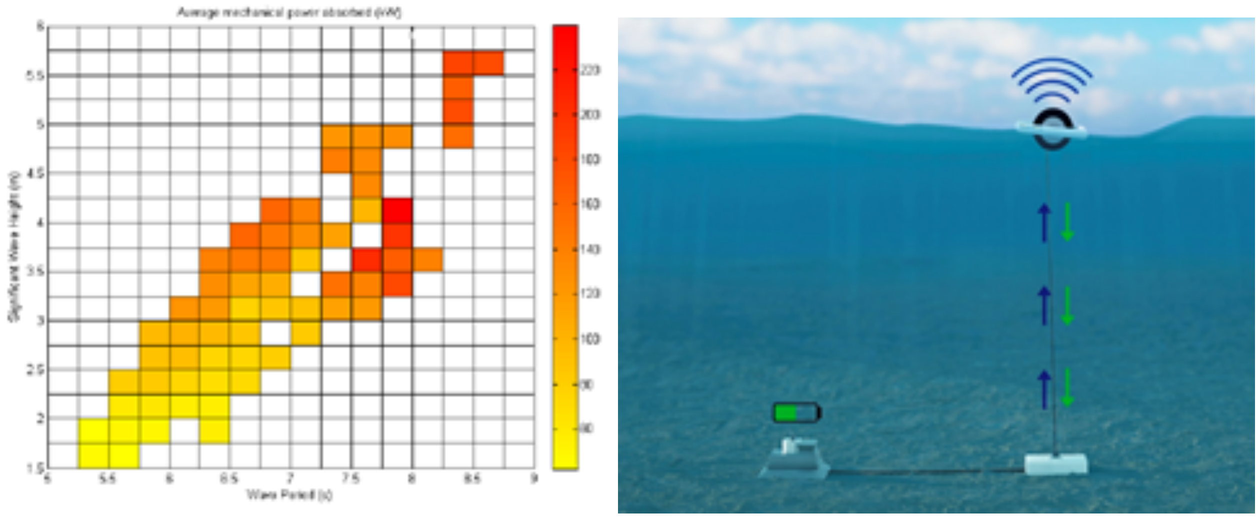

Figure 4 – ResenWaves power curve validated in real sea environment (lf). Resenwaves device with subsea hub (rg) * *https://www.resenwaves.com/wave-energy-data-communications/#tech_and_testing*.

The Design Concept (cf. Figure 5) foresees a wave energy farm offshore from Hantholm harbor, where a number of devices will produce pollution free energy to the grid and use a small fraction of it to grow the seabed protection using the induced mineral deposition technology. The calcareous material will provide habitat for different marine life. For each device installed, 50 kg of steel in form of rebars are placed on the bottom of the sea over the foundations and seabed hub. The steel will be electrified with direct very low current, for a total energy consumption of 215 kWh/y, corresponding to 1-2% of the total energy produced (cf. Figure 6 and Table 4).

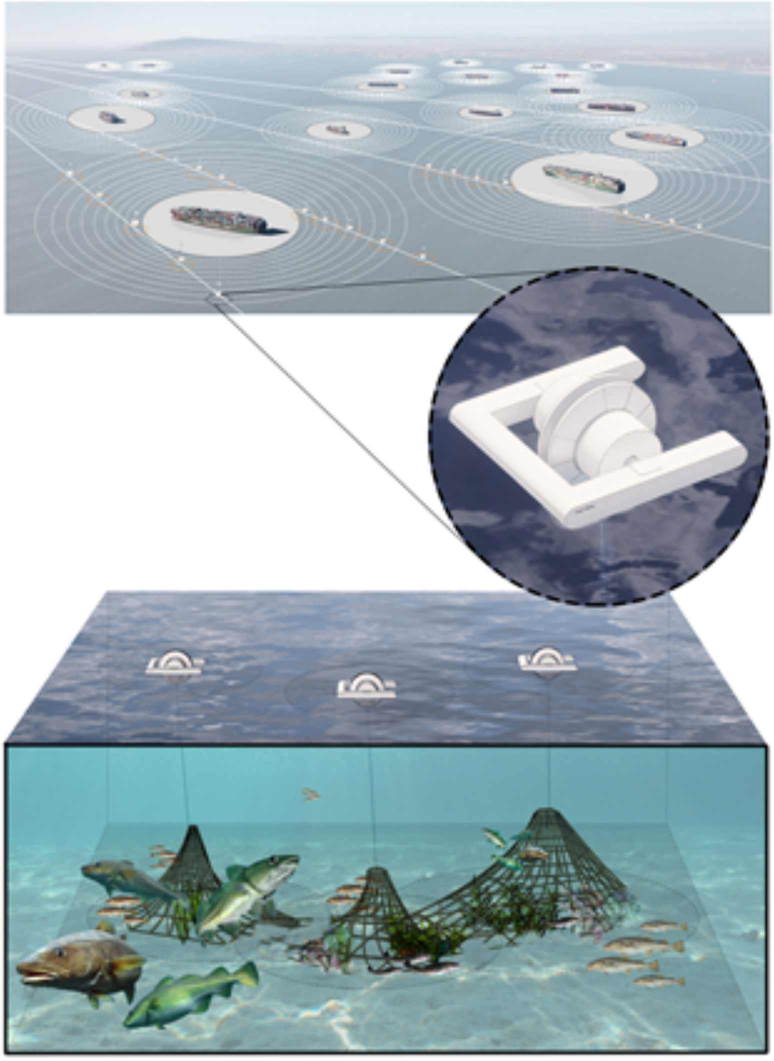

Figure 5 – Design Concept of a wave farm with induced mineral deposition technology.

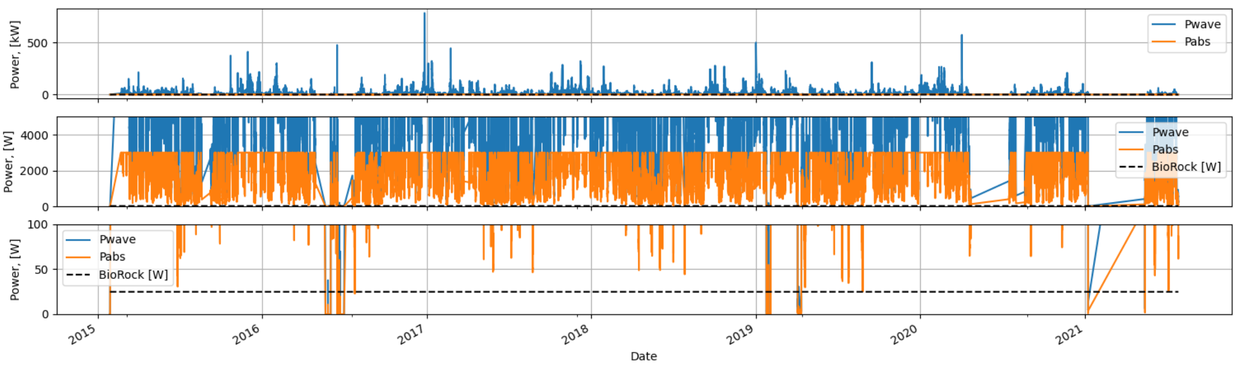

Figure 6 – Wave Power in Hanstholm from 2015 to 2021 (blue). Expected power production of one 3kW Resenwaves device at location (orange). Power consumption of one induced mineral deposition installation made of rebar steel for a total of 50 kg.

Table 4 – System specifications: No. 1 wave energy device + induced mineral deposition technology - offshore from Hanstholm Harbour.

Installed wave energy capacity, dimensions
3 kW, 5mx5mx1m
Average wave climate (Hanstholm location)
9.6 kW/m
Average power production
1.8 kW
Cathode Total steel (rebar)
50 kg rebar steel, circa 280 m in total length
Anode
0,5 sqm DSA
Output current
0.2 A
Output Voltage
1.2 - 2.5 V
% of kWh produced used for the induced mineral deposition technology
1-2%
Density of the calcareous material
1.6 – 2.0 g/cm3
Mineral composition
50% brucite, 44% Aragonite, 6% Calcite
Compression strength of the calcareous deposit
2-4kN

The energy cost from wave energy production is estimated to be 0,4 Euro/kWh, circa 10 times more than offshore wind. We expect to produce circa 7 kg of calcareous material each year of operation. Additionally, a considerable part of the added ballast will come from the colonization of the material by biofouling and marine life. The cost of the generated material is directly dependent on the renewable energy source used for its generation. By considering the results we obtained from this project, we can estimate that the cost of the calcareous deposit is between 1 to 12 Euro/kg (cf. Table 5). Of course, concrete costs between 80-100 euro per cubic meter, circa 0.04 euro per kg. But the comparison can´t be done directly. Indeed, while with the mineral deposition we obtain a material that grows without use of labor after installation, the concrete sold at those prices needs to be casted and transported. There are therefore more detailed calculations and considerations to make that are beyond the scope of the present project, but that would deserve careful consideration and in depth analysis. As a start, during the course of the project we investigated the Life Cycle Assessment of a damaged column refurbished with mineral deposition technology and a generic column realized with concrete, both for marine applications. Despite the many uncertainties and inability to comment of the real technological viability of such a new solution, it was interesting to find out that 328 kg of CO_2 equivalent emissions occurs from business as usual, while only 80.8 kg of CO_2 equivalent emission occurs when using mineral deposition approach. This project supports the idea that the viability of this technology is dependent on the recognition of the added value in terms of CO_2 emissions reductions, improvement of ecosystem and contribution to circular economy (particularly with the possibility of dumping excess generation from renewable energy).

Table 5 – Economic analysis data.

Cost of electricity from wave energy
400 EUR/MWh
Cost of electricity from offshore wind
45 EUR/MWh
Quantity of the calcareous material deposited per year
0,4 cm/y
Weight of the calcareous material deposited per year
Circa 7,2 kg/y + biofouling
Estimated cost of the calcareous material
1-12 euros/kg
Estimated CO_2 mission reduction compared to the use of concrete
75%

The target group for the technology is companies working within design, production, and maintenance of offshore substructures for wave energy devices, wind energy substructures and oil and gas platforms for protection of sub-sea structures from erosion and corrosion. Furthermore, the technology can be used for restoration or creation of artificial reefs. Another solution could be the decommissioning of oil wells, where the electrochemical reactions creating the calcareous material could close the oil well with or without the addition of cement. The produced models can be used to predict the composition together with the weight of the deposit, which can be of interest for building material production.

Dissemination of project results

The project results have been disseminated through peer reviewed scientific journal publications, technical reports, poster presentation (summer school), students projects at AAU, project web page and seminar (Seminar on the Mineral Deposition Technology – North Hemisphere).

The first phase of the project has been published in a technical report regarding laboratory tests on mineral deposition under sea water electrolysis. The field test experiment together with lab experiments have been published in a paper ("Development of an Eco-Sustainable Solution for the Second Life of Decommissioned Oil and Gas Platforms: The Mineral Accretion Technology"). Furthermore, two papers are submitted where one contains a detailed discussion about the Response Surface model for prediction of the mineral composition as previously mentioned in this section and the other one contains the in-situ Raman spectroscopy analysis of the electrodeposited calcareous material.

Table 6 – Dissemination activities.

Activity	Title	Place	Year
peer reviewed scientific journal papers	Innovative Material can mimic Coral and Boulder Reefs Properties	Frontiers in Marine Science	2021
	Thermal, moisture and mechanical properties of Seacrete: A sustainable seg-grown building material	Construction and Building Materials	2021
	Development of an eco-sustainable solution for the second life of decommissioned oil and gas platforms: The mineral accretion technology	Sustainability	2020
	Optimisation of Electrochemical Deposition of Calcareous Material by Implementing Response surface Methodology	Submitted	2021
	In-situ Raman investigation of the electro deposition of calcareous material	In preparation	2021
Technical reports	Laboratory tests on mineral deposition under sea water electrolysis	DCE Technical Reports; Nr. 268	2019
	North sea small scale mineral deposition tests	DCE Technical Reports; Nr. 272	2019
	Report on field testing - FINAL	DCE Contract Report; Nr.18	2021
Poster presentations	Development of new material for sea water substructures by sea water electrolysis	Energiens Folkemøde, Esbjerg	2018
	Development of new material for sea water substructures by sea water electrolysis	8th European summer school on electrochemical engineering, France	2018
Project seminar	Seminar on the Mineral Deposition Technology – North Hemisphere	AAU Aalborg/online 23. Aug.	2021
Student projects at AAU	Investigation of the possibility of electrochemical precipitation of solid material	7th Semester student project	2016
	Undersøgelse af krystalliske strukturer til beskyttelse af offshore elementer dannet via elektrolyse af havvand	3th Semester student project	2017
	Biorock: first tries in cold water	3th Semester student project	2015
	Development of an aragonite-brucite composite as a protective coating for offshore substructures	4th Semester student project	2017
	The production and application of magnesium oxide binder	7th Semester student project	2018
Web page	New Materials for wave energy substructures	https://www.en.build.aau.dk/project-sites/newmatrial-wes/?page=1	
Invitation to speak at Cluster meeting	Mineral deposition technology	https://www.assert.construction/2020/10/21/infrasweden-2030-projektkonferens/	2019
Brochure	Design Concept for wave energy and mineral deposition technology		2021
Poster presentation	"Mineral Deposition technology for offshore applications" - IDRA2020, 14th-16th June 2021	Italian PhD Student	2021
Master thesis	A comparative LCA study on the refurbishment of quays with induced mineral deposition technology	Master Student	2020

6. Utilisation of project results

The results from this project will be utilized by the **offshore energy sector**, the **construction sector**, but also by stakeholders interested in marine **biological restoration** practices and **Public Authorities** (Port and Coastal). The technology could work as corrosion protection and provide increased strength to sub-sea steel structures, support to reinforced concrete structures in maritime environment, protecting them from rust and adding ballast. It could be used as scour protection and as dumping system for surplus energy produced by marine renewable energies. Finally, it could be used to build submerged sustainable artificial reefs to improve fisheries and marine ecosystems.

The precipitated limestone material, in this context called Seacrete, demonstrated to be interesting also for the onshore construction sector. In this case, the design of an industrialization processes should be thought through carefully in terms of economical viability, and also from a life cycle assessment point of view, and leaves space for disrupting solutions.

While these applications are suitable for cold and warms waters, it must be noticed that the project demonstrated that the deposition rates are slower in cold waters and low salinity waters, therefore when added ballast and fast results are needed, the choice of this technology should be carefully evaluated. For this purpose, the project has developed a modelling tool that can predict the quantities and quality of the deposition in different conditions. The modelling tool could be expanded with further calibrations to be able to include many different sea environmental conditions and hence reduce implementation risks.

Different companies working on offshore renewable energy such as wave and wind energy, engineering companies such as COWI in projects such as Vindø for offshore energy islands could use the technology and commercialize it for specific applications. The creation of a start-up seems also a valuable solution to create a product and advertise it.

While this project did not increased turnover yet, it steered interest of the oil&gas sector that commissioned an investigation under the DHRTC program to determine the potential of the technology in well abandonment, of the Swedish Sustainable Company WSP for renovations of quays and DTU Aqua for artificial reefs. It is also relevant to notice that the technology of mineral deposition, being in need of a metal cathode, could benefit immensely of a specifically designed or 3D printed cathode, to obtain the desired shape and complexity. For this, contact with the Teknologisk Institut in Arhus was taken, and expression of interest for collaboration by Lasse Haahr-Lillevang to work on improving metal 3D printing was shown.

The results of the project are still at a low TRL to be immediately commercialized; nevertheless, we believe that this project greatly increased the opportunities for implementation and has the potential to boost advancement in many sectors.

Particularly, in relation to artificial reefs and protection of the foundations of offshore structures, the competition consisted for several years of natural boulder and stones being dumped at location to protect foundations from scour or to create shelter for marine life improving ecosystems. Displacement of boulder and rock reefs for construction purposes has been recently identified as an environmental problem: to remove natural submerged reefs to use the materials for construction purposes elsewhere, is destroying healthy ecosystems. Additionally, we are starting to face shortage of these materials. Companies such as Nordnes (https://www.nordnes.nl/rockinstallation.php) or German NAUE GmbH & Co. KG (https://www.naue.com/naue-geosynthetics/sand-container-secutex-soft-rock/) take care of installation and/or production of scour protection units. Their model includes a start point on land and few days of operation at sea, transporting all the load in vessels.

Due to the use of natural stones fished at sea and consequent removal of natural habitats, artificial reefs are being developed with different materials: concrete, recycled construction materials, geotextiles… etc. In order to restore the lost ecosystems. Unfortunately, in very few cases, the solution demonstrated to be fully compatible to marine life and suitable to develop a complex ecosystem. This technology has shown to produce a material almost identical to biological calcareous structures and therefore easily colonized by marine life (cf. Figure 7). Companies such as the Dutch ReefDesignLab (https://www.reefdesign-lab.com) could be competitors for this technology and a comparison with their products should be initiated when more data on installation and maintenance will be ready for us.

Figure 7 - Control structure rusting away, from latest sea trials in Hanstholm harbor. Rg: electrified structure with mineral deposition highly colonized by marine organisms.

The entry barriers consist of lack of case studies that can be showcased as success stories. The efforts so far have been proving the technology. The price of the material produced is still in the order of 5-10 times more expensive than concrete. Nevertheless, the results conducted in life cycle assessment demonstrate that the impact on the ecosystems and the CO_2 emission are also 80 times lower that regular business as usual. Therefore, it is reasonable to think that economical feasibility is intrinsically linked to savings in relation to the cost of the emissions. In this respect, the project results quantify the savings in terms of CO_2 emissions and proof the technological feasibility of a solution that can contribute to decar-bonization.

The project results have been utilized in the education of chemical engineers at AAU. In both the BSc. In Chemistry and Biotechnology and MSc. in Chemical Engineering educations at AAU the project aim/con-tent and results were used in the framing of 5 semester projects on 3rd to 7th semester. Moreover, the results of the project have been presented for master student in the forum Friday morning science at AAU campus Esbjerg. A list of the dissemination activities is shown in Table 6 including journal papers, tech-nical reports, posters, and oral presentations.

7. Project conclusion and perspective

The project has concluded that the mineral deposition presented in the main literature, corresponding to 2 – 2,5 cm year of deposition in tropical areas, are unachievable in the existing temperatures in the North Sea and the Mediterranean location (Bergeggi, -18 m water depth). This technology can be implemented to provide protection against rust and scour; however, the deposition rate is governed by the water temperature. Nevertheless, the technology is still interesting for protecting and strengthening foundations of offshore renewable energies, especially if associate to the possibility to dump excess power and restore marine ecosystem with artificial reefs.

For further development of this technology, involvement of different areas such as power electronics, offshore/coastal engineering, electrochemists and marine biologists along with the renewable energy sector is required.

Parallel projects demonstrating applications to offshore foundations and artificial reefs should be investigated. Additionally, further model calibration to decrease risks of future implementations should be carried on. Given the cost of marine operations, the search for funding opportunities, that need to be adequate, is the bottleneck for the continuation of activities. In this entire process, the involvement of relevant companies and creation of a start-up for commercialization is complimentary. The efforts should aim at the creation of a turnkey product and engage in communication with policy makers for possible mechanisms to facilitate market penetration.

The project increased confidence on the mineral deposition technology. Thanks to the involvement of different industrial partners and the project results, we can foresee a future where offshore wind parks will use part of the produced energy (possibly surplus energy) to electrify metal nets around the foundations to create artificial reefs, protect cables and substations from rust and scour. This will of course require formation of specialized staff and workers, for installation and maintenance. Also interesting is the possibility to generate a solution for surplus power, which is an issue, especially when renewable energies will have a bigger share in the energy mix, as it is stated by the energy targets.

8. Appendices

Link to project home page:
https://www.en.build.aau.dk/project-sites/newmatrialwes/?page=1

Link to publications:
DCE Technical Reports; Nr. 268, 2019
Laboratory tests on mineral deposition under sea water electrolysis
https://vbn.aau.dk/da/publications/laboratory-tests-on-mineral-deposition-under-sea-water-electrolys

DCE Technical Reports; Nr. 272, 2019
North sea small scale mineral deposition tests
https://vbn.aau.dk/da/publications/north-sea-small-scale-mineral-deposition-tests

Journal paper: Frontiers in Marine Science, 2021
Thermal, moisture and mechanical properties of Seacrete: A sustainable seg-grown building material
https://vbn.aau.dk/da/publications/innovative-material-can-mimic-coral-and-boulder-reefs-properties

Journal paper: Construction and Building Materials, 2021
Thermal, moisture and mechanical properties of Seacrete: A sustainable seg-grown building material
https://vbn.aau.dk/da/publications/thermal-moisture-and-mechanical-properties-of-seacrete-a-sustaina

Journal paper: Sustainability, 2020
Development of an eco-sustainable solution for the second life of decommissioned oil and gas platforms: The mineral accretion technology
https://vbn.aau.dk/da/publications/development-of-an-eco-sustainable-solution-for-the-second-life-of