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| RE | Restricted to a group specified by the consortium (including the Commission Services) | |
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1 Introduction to ACORN project

The sea is a very aggressive environment that has significant adverse effects on most structures and materials exposed to it. Corrosion and biofouling are major problems for structures and materials in marine environments. For this reason, ocean energy devices and other offshore structures as platforms, buoys, docks and wind tower foundations, need to be protected because periodic dry docking is often impossible and in-situ maintenance can be difficult and costly. Conventional solutions such as paint and cathodic protection already offer a solution but with limited efficacy against corrosion and biofouling in the long term. Developing coatings that are resistant to both corrosion and biofouling with a 25+ years design lifetime can reduce maintenance costs and increase device lifetime.

The objective of Advanced Coatings for Offshore Renewable eNergy (ACORN) project is to develop a new, potentially patentable and long-lasting solution to the problem of corrosion and barnacle biofouling, offering specific advantages for offshore structures such as wind turbine towers and ocean energy generators. By developing such a coating, the Levelized Cost Of Energy (LCOE) for wave and tidal energy converters can be lowered. ACORN project will take advantage of the proven long-term corrosion protection of Thermally Sprayed Aluminium (TSA) for steel substrates. TSA provides both a barrier between seawater and steel, as well as providing sacrificial protection in damaged regions. Using the TSA as a matrix coating, the active antifouling substance will be embedded in the coating in very tiny concentrations. The antifouling mechanism prevents barnacle cyprids from settling on the surface when they come into contact with the substance. Barnacles are one of the most harmful fouling organisms and found throughout the world's oceans. Significant barnacle settlement can destroy protective paints, alter local water flow behaviour and provide an environment that promotes further biofouling.

In addition to this long-lasting solution to corrosion and biofouling, the project will also develop and prove a corrosion and cavitation resistant coating with a 10+ year design life, suitable for tidal energy generators. Cavitation damage is also relevant in this type of generators because it is highly likely that tidal turbines will be subjected to the effects of cavitation. The movement of the turbine blades can change pressures of the fluid and form vapour bubbles that collapse and damage the generators.

2 Objective of Deliverable D5.1

The aim of this report is to prove that at least one coating, of the ones that were selected previously in Work Package (WP) 3 by the ACORN research team, has been successfully demonstrated in a marine environment and has exhibited fouling and seawater corrosion resistance over one summer season.

3 Coatings selected

ACORN project selected five different long-lasting solution to corrosion and biofouling in WP3. The coatings take advantage of the proven long-term corrosion protection of TSA for steel substrates (see Figure 1) and implement 5 different strategies to combat the problem of biofouling, especially to avoid barnacle cyprids to settle on the surface. For a 25+ years design lifetime, ACORN research team estimated that a coating thickness of 350µm was necessary. More detailed information about the coatings is not included due to confidentiality.

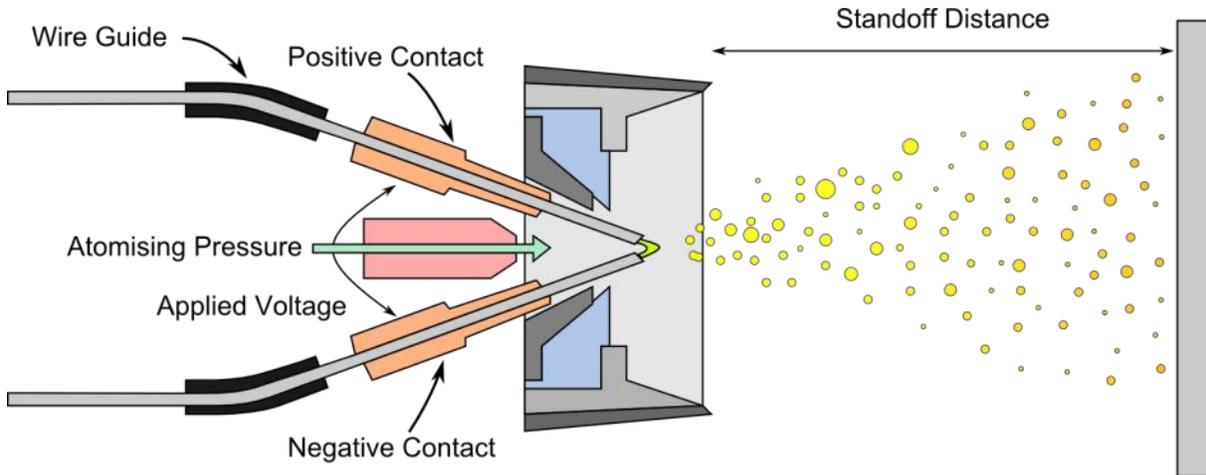


Figure 1: Schematic diagram of TSA application

4 Test Site

To demonstrate that at least one of the five coatings has exhibited fouling and seawater corrosion resistance over one summer season in a marine environment, the coatings were exposed in the Marine Corrosion Test Site (MCTS) EI Bocal [1]. It is located at the shoreline of the Cantabria coast, few kilometers away from Santander city, and it is placed in open water so specimens tested there are subjected to real marine environment. For this reason, the corrosion and biofouling conditions are quite similar to the ones a typical offshore structure faces along its life cycle, which is the main requirement of this part of ACORN project.

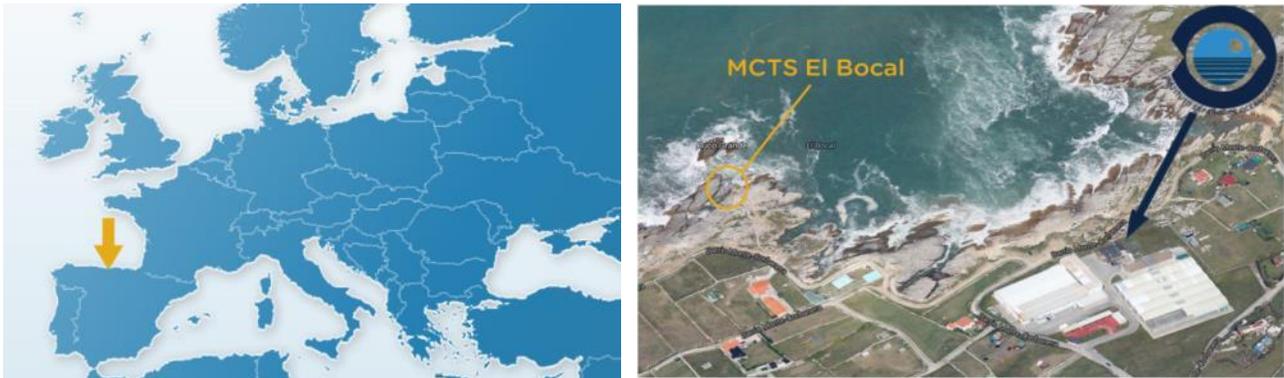


Figure 2: MCTS EI Bocal location

The setup of MCTS EI Bocal allows to cover a wide range of corrosion and biofouling marine environments (see Figure 3). ACORN project wanted to assess marine effects on the five coatings in the splash, tidal and submerged environments, so several identical samples were tested in these zones.

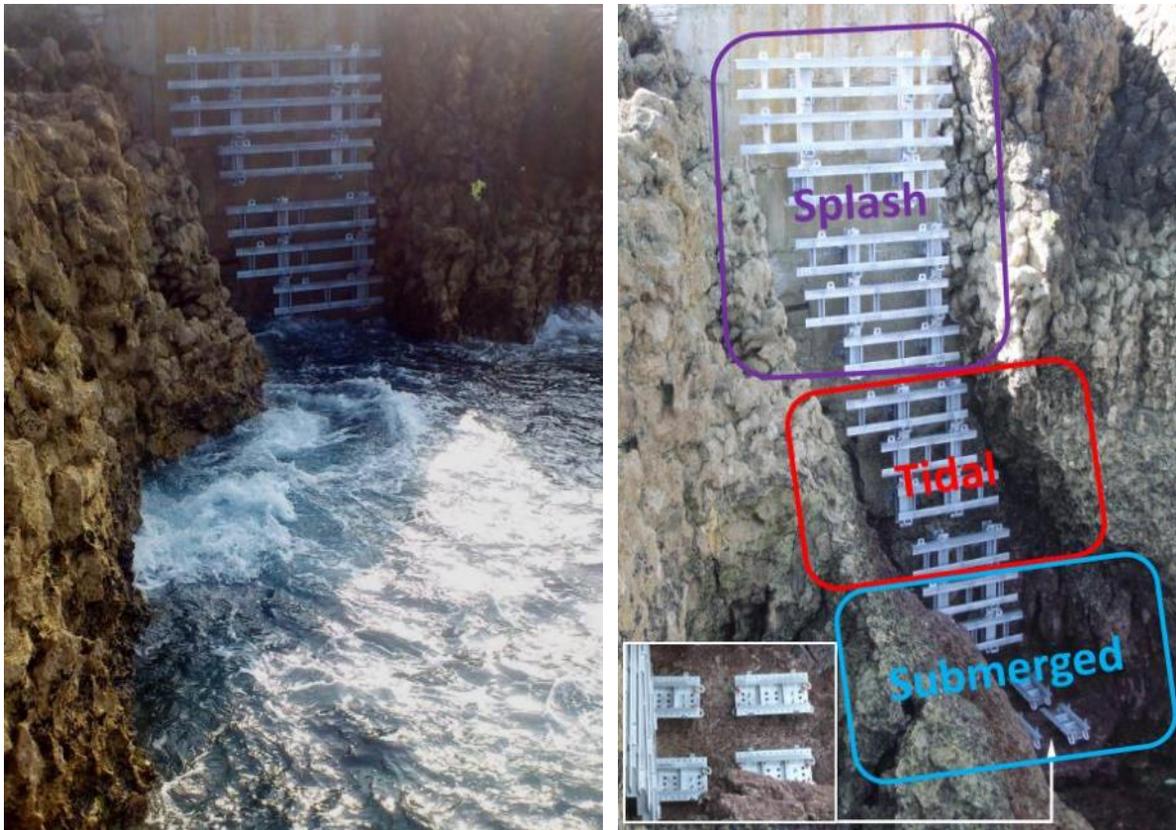


Figure 3: High tide (left) and low tide with exposure zones (right) at MCTS EI Bocal

MCTS EI Bocal was selected for the marine trials because it was considered an ideal test site for corrosion and fouling studies. Figure 4 is one example of the presence of fouling while the marine trials were carried out. It shows some limpets attached to the rocks around the metallic structure used to fix the samples tested.



Figure 4: Limpets settled to rocks around the structure where samples were tested

5 Samples tested

The selected coatings by the ACORN partners were applied to 45 samples made of steel. 36 of the 45 samples were flat rectangular panels and the rest of them, nine, were fabricated with a welded handle (see Figure 5) . The handle was added to demonstrate that these coatings are not affected by crevice corrosion.

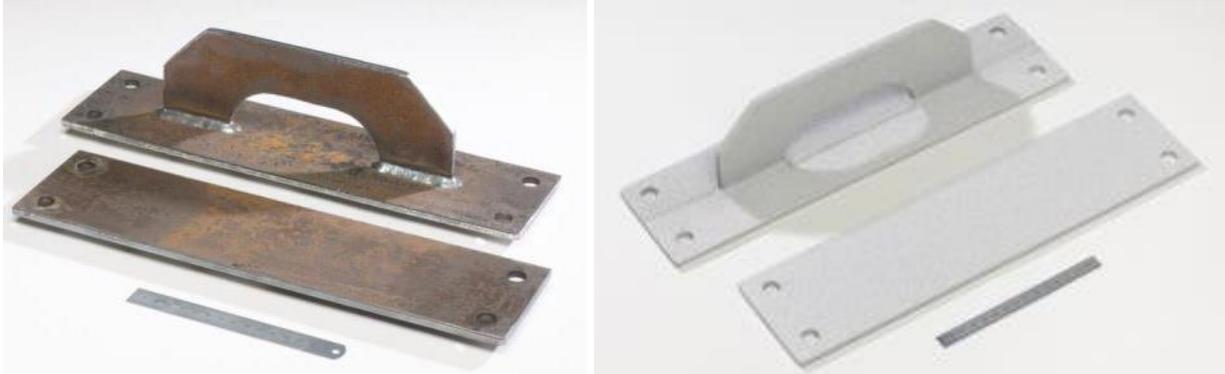


Figure 5: Samples before (left) and after (right) TSA has been applied

As the 45 samples were exposed in the three environments mentioned previously, 15 were tested in the splash zone, 15 in the tidal and 15 in the submerged. In each zone there were 2 panels coated with each coating (10 panels in total), one panel coated only with TSA, one sample without any type of coating (bare steel) and three welded samples (a sample with one coating, another one with a different coating and the remaining one only with TSA) for a total of 15.

The coatings were applied only to the front face of the samples, and their thickness was $350\mu\text{m}$ and the concentration of antifouling substances varied along the sample. Figure 6 shows the three zones with different concentration where the lightest zone had no antifouling effect, the darkest zone had the highest antifouling effect and the middle zone had an intermediate antifouling effect.

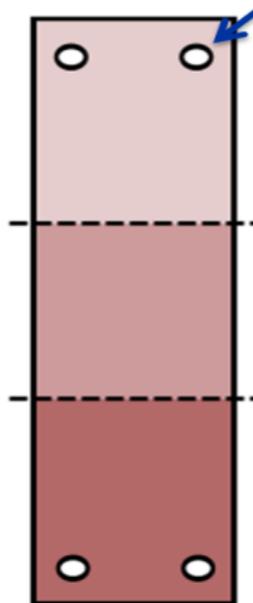


Figure 6: Distribution of antifouling substances along the sample

6 Evolution of the marine trials

The length of the tests has been divided into periods of four weeks for easier inspection and assessment. The installation of the samples was carried out the 19th and the 20th of March 2015 and they were decommissioned the 28th and the 29th of October 2015. Figure 7 shows the schedule with the installation and decommissioning dates of the samples (orange) and the four-week periods considered for inspection. The beginning of these periods is marked in red with an “M” and the number of the period.



Figure 7: Schedule of the marine trials

6.1 Installation on 19&20/03/2015

15 samples were tested in each exposure zone: splash, tidal and submerged (see Figure 8). Coupons in the splash zone are numbered, with a label in the upper right hole, from 1 to 15. The first one on the left is C1 and they are numbered in order to C15, the first one on the right. The same for the tidal zone, from C16 to C30, and submerged zone, from C31 to C45. From the moment they are in contact with sea water, the coupons without TSA (bare steel) are rusted. Rest of coupons are in good conditions for the marine trials, there were no problems during the installation of the samples.

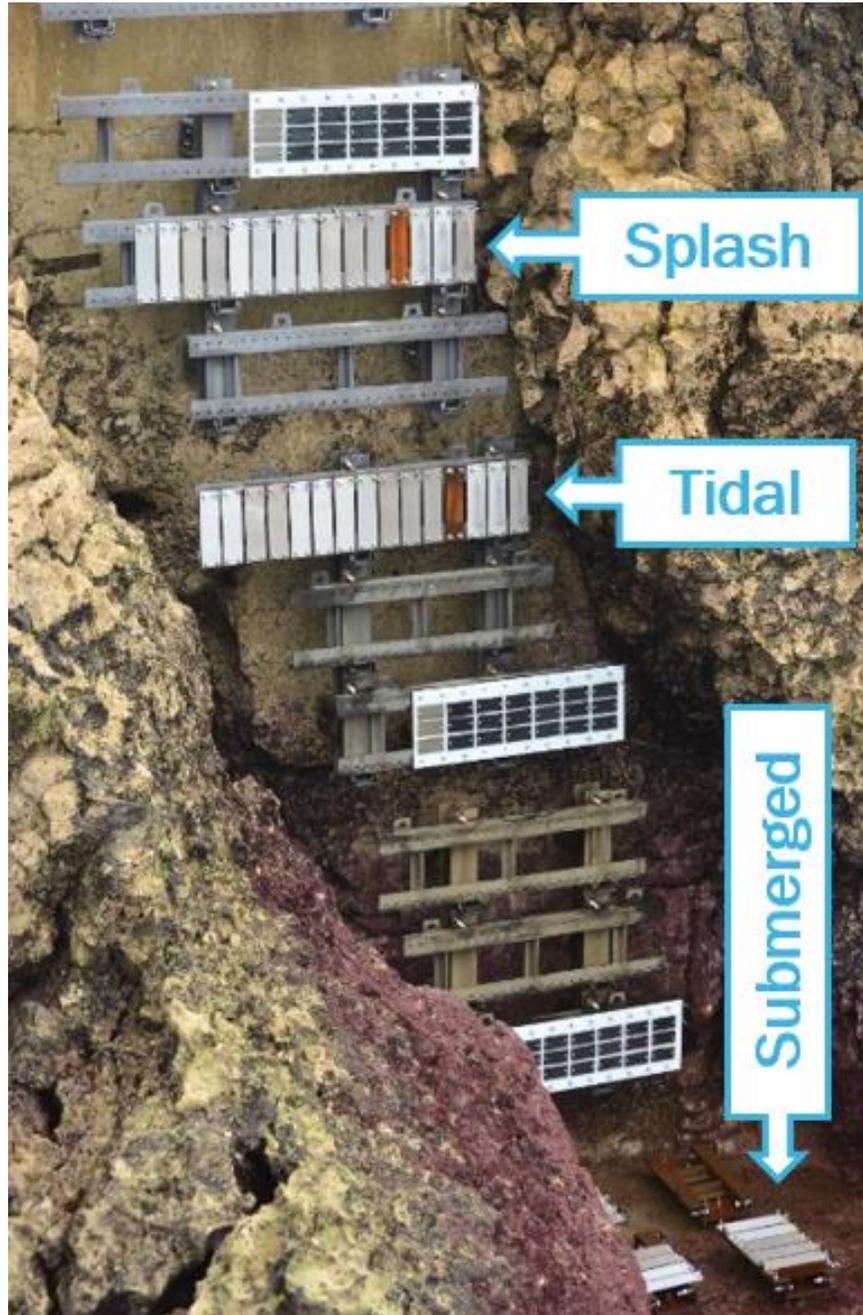


Figure 8: General overview of the distribution of ACORN project samples at MCTS El Bocal



Figure 9: Samples the day of the installation: splash (up), tidal (middle) and submerged (bottom)

6.2 Month 1 (from 20/03/2015 to 19/04/2015)

Splash: all the specimens have the same visual aspect than they had in the installation except the one without TSA (see Figure 10). It is observed that coupon 15 (C15) (the first specimen on the right) has been discolored at one side of the welded part.



Figure 10: Samples in splash zone 18 days after installation

Tidal: Figure 11 shows the presence of rust in the upper screw of C25, which was the sixth coupon from the right, probably dropped from C12 (coupon without TSA in the splash zone just over C25). This rust had possibly activated the presence of algae in the coupon as it is showed in Figure 12. Figure 11 shows the first rust traces and Figure 12, taken ten days later, shows more rust and a larger presence of algae.



Figure 11: Samples in the tidal zone 18 days after installation

In addition to it, algae were appearing at the bottom of the following coupons: C18 and C19 (same coating system) and C20 and C21 (same coating system) (see Figure 12).

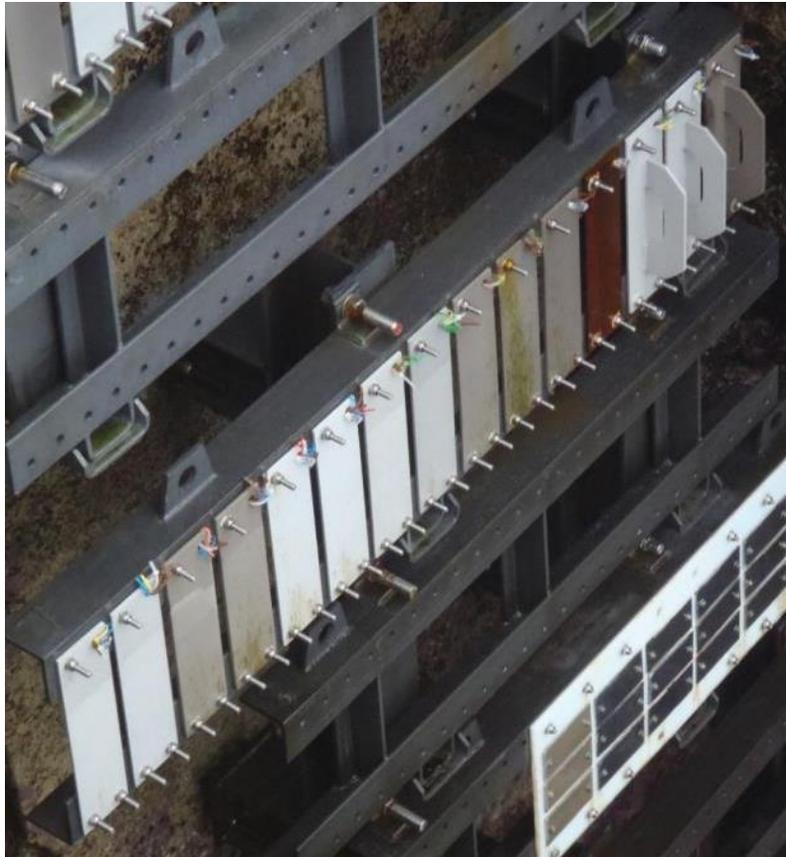


Figure 12: Samples in the tidal zone 10 days after Figure 11 was taken

Submerged: Figure 14 shows a substance similar to mud covering all the specimens. No green algae were present on these coupons. The quality of the image is not so good due to the weather conditions



Figure 13: Samples in submerged zone 18 days after installation



Figure 14: Samples in submerged zone 10 days after Figure 13 was taken

6.3 Month 2 (from 20/04/2015 to 17/05/2015)

Splash: all specimens had the same visual aspect than they had in Month1 (M1). Figure 15 shows an important difference of color between C3 and C4 (third and fourth sample from the left) which were protected with the same coating system.

Traces of algae were observed in the lower part of C3 (see Figure 16). C15 continued being discolored at one side (right side) of the welded handle. There was also algae stuck behind C1 (see Figure 17).



Figure 15: Samples in the splash zone in M2



Figure 16: Traces of algae in lower zone of C3 (sample on the right)



Figure 17: Algae stuck behind C1 (first sample on the left)

Tidal: there were more coupons with algae than in the previous month of exposure, M1. C16 and C17 were the only flat samples that did not have algae in their surface. The three welded coupons had algae although C30 was the one most influenced by this phenomenon. Figure 18 shows how the presence of algae began below the upper screw (C20 and C26). It might be because water drops fell from the screw once the wave has gone.

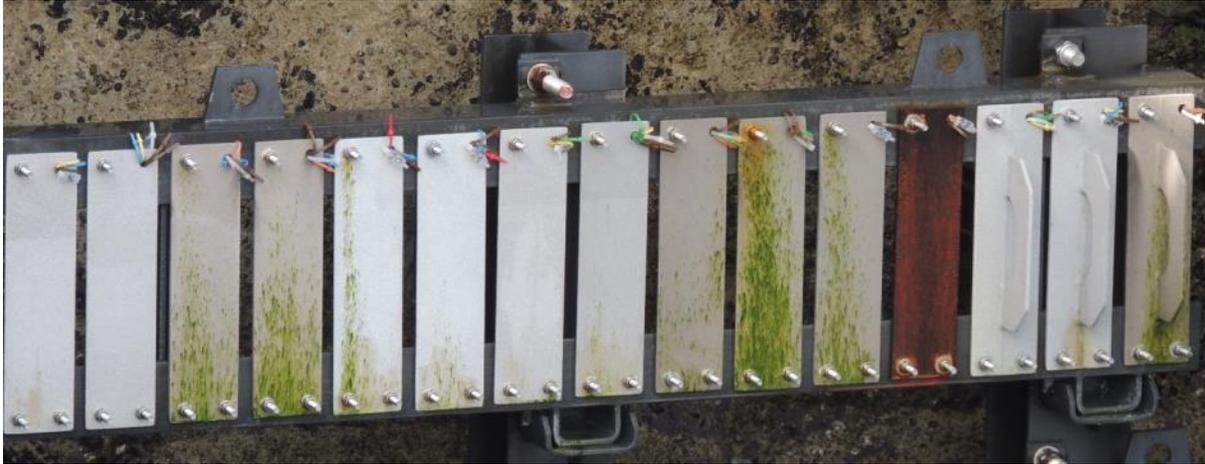


Figure 18: Samples in the tidal zone in M2

Figure 19 shows a limpet on the lower part of C24 and the significant presence of algae in C25. Figure 20 shows the way a limpet followed to feed itself (lack of algae in the sample).



Figure 19: A limpet next to the screw on C24 (second sample from the left)



Figure 20: Path followed by a limpet to feed itself in C24 (first on the right)

Figure 21 was taken only 8 days after Figure 18 and a difference on the quantity of algae on coupons was noted, it had been increased in this short period of time. For example C28 and C29 (welded coupons) did not have algae previously and now they do.

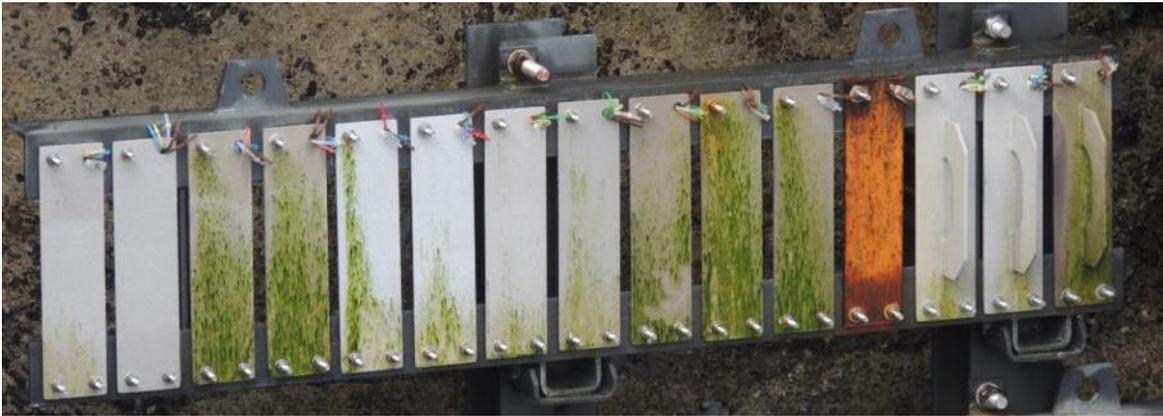


Figure 21: Samples in the tidal zone 8 days after Figure 18 was taken

Submerged: Figure 22 shows a limpet on C39. The limpet cannot be distinguished because there was algae on it. This image also shows the possible way the limpet followed for feeding itself. It indicates that the brown substance on coupons and frames had a vegetal origin and it was not rust as it could be thought the first time this substance appeared.



Figure 22: Detail of a limpet on C39

Figure 23 shows brown algae on the coupons and on the frame. It is noted that the quantity of algae on submerged coupons had been increased considerably in 26 days, the time between when Figure 22 and Figure 23 were taken. It can be a normal phenomenon because the temperature of water and the light time had been increased from previous months.



Figure 23: Samples in the submerged zone covered by brown algae

Figure 24 shows a limpet next to the screw on C32 (left side). In this case there was no evidence of lack of brown algae on the sample which could indicate a way followed by the limpet.



Figure 24: Detail of a limpet on C32

6.4 Month 3 (from 18/05/2015 to 14/06/2015)

Splash: more quantity of algae were observed in the lower part of C3 and some traces of it were observed in C1 and C2 (see Figure 25) and C6 (Figure 26).



Figure 25: Samples C1, C2 and C3 (from left to right respectively)

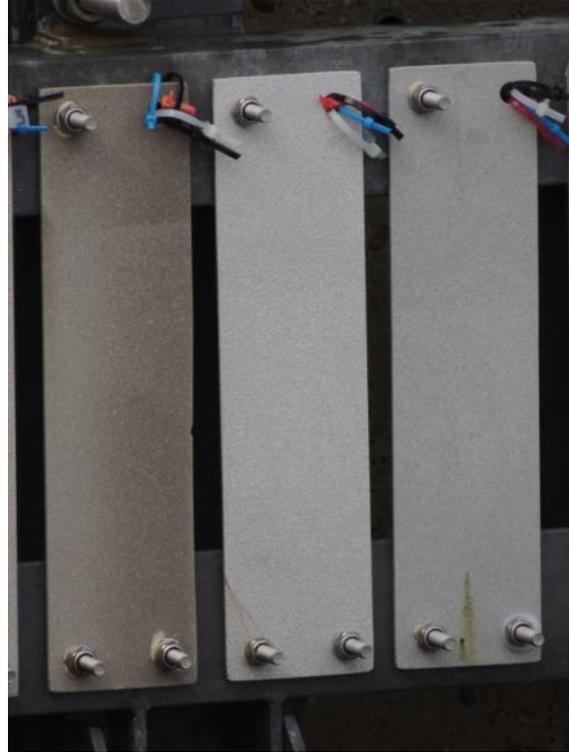


Figure 26: Traces of algae in C6 (first on the right)

Figure 27 shows an important difference of color between C3 and C4, having their coatings the same composition, and C15 continued being discolored at one side of the welded part (right side).



Figure 27: Samples in the splash zone in M3

Tidal: Figure 28 shows how C17 was the only coupon that did not have algae on its surface. The three welded coupons had algae although C30 was the most influenced by this phenomenon. It was also noted how the presence of algae began below the upper screw. It might be, as it has been mentioned previously, because the water drops fell from the screw once the wave had gone.

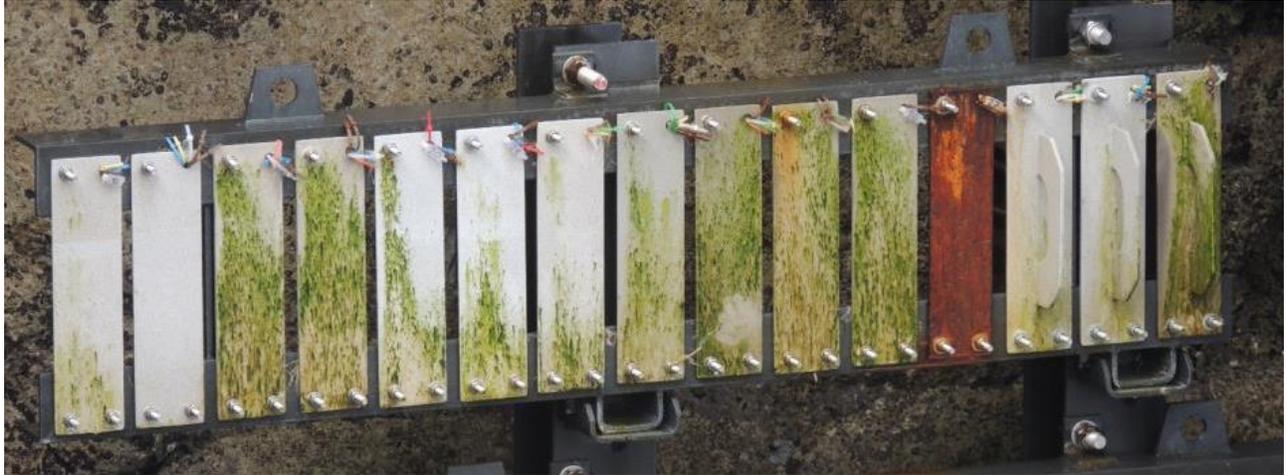


Figure 28: Samples in the tidal zone in M3

Submerged: Figure 29 and Figure 30 show a big difference in the presence of algae compared to the previous month (M2). There were a lot of seaweed in all coupons except in the ones which were more hidden from the sun. Not only brown algae appeared attached to the samples as before, images taken in M3 showed green algae too for the first time.



Figure 29: Samples in the submerged zone in M3



Figure 30: Detailed view of the samples in the submerged zone

6.5 Month 4 (from 15/06/2015 to 12/07/2015)

Splash: there was no a big variation from M3 in the coupons of this exposure zone: algae observed in C1, C2 and C3. Some spots were observed in C13 coming probably from contamination from the rust in C12 (bare steel). Figure 31 shows a general view of all the specimens in the splash zone and Figure 32 shows in detail the samples mentioned before.



Figure 31: Samples in the splash zone in M4

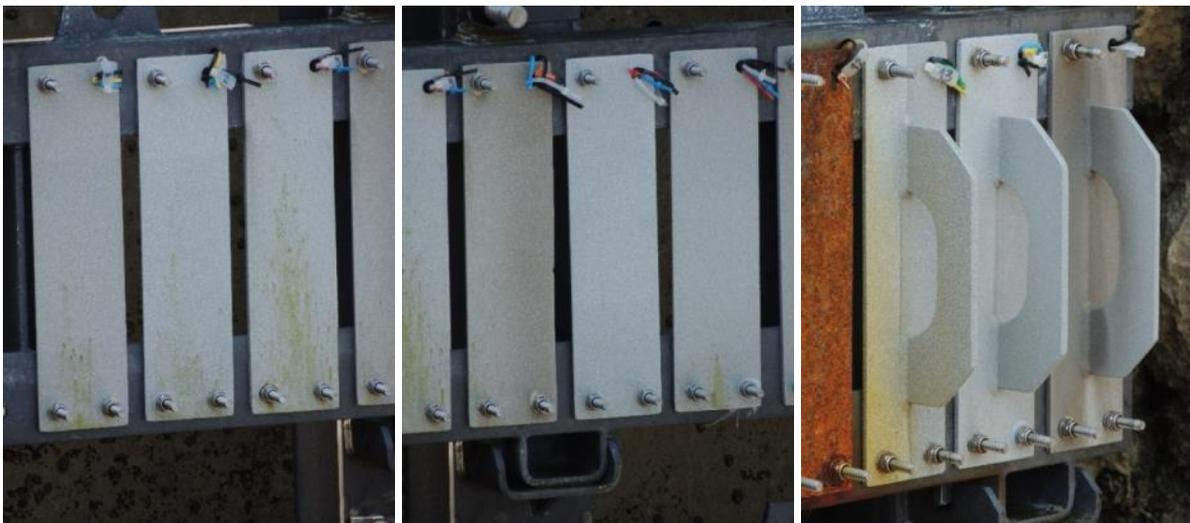


Figure 32: Detailed view of the samples in the splash zone

Tidal: Figure 33 shows that C17 was the only coupon that did not have algae on its surface. The three welded coupons had algae although C30 was the sample which had more spots on the handle (see Figure 34). C24 and C25 had rust spots (see Figure 35) coming from C12. C12 was completely oxidized and was just over them as it can be observed in Figure 36.



Figure 33: Samples in the tidal zone in M4

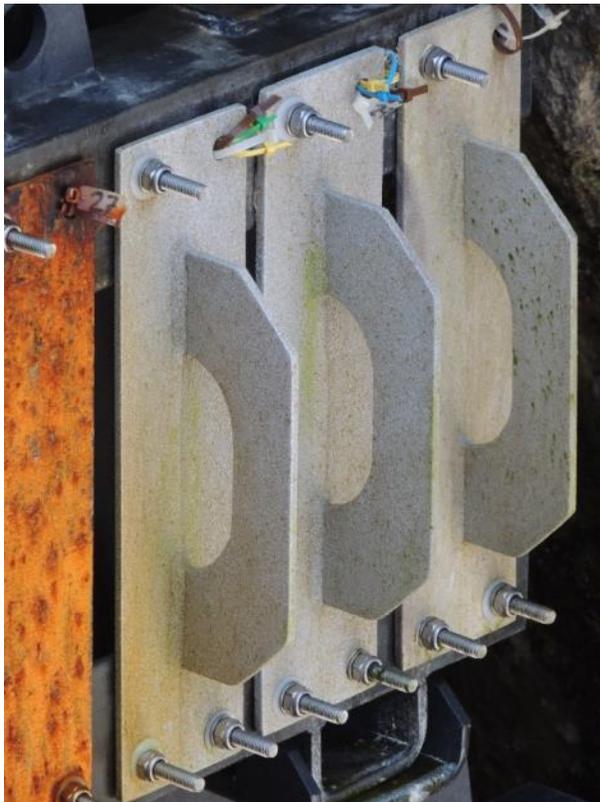


Figure 34: Three welded coupons in tidal zone



Figure 35: Rust spots on C24 and C25

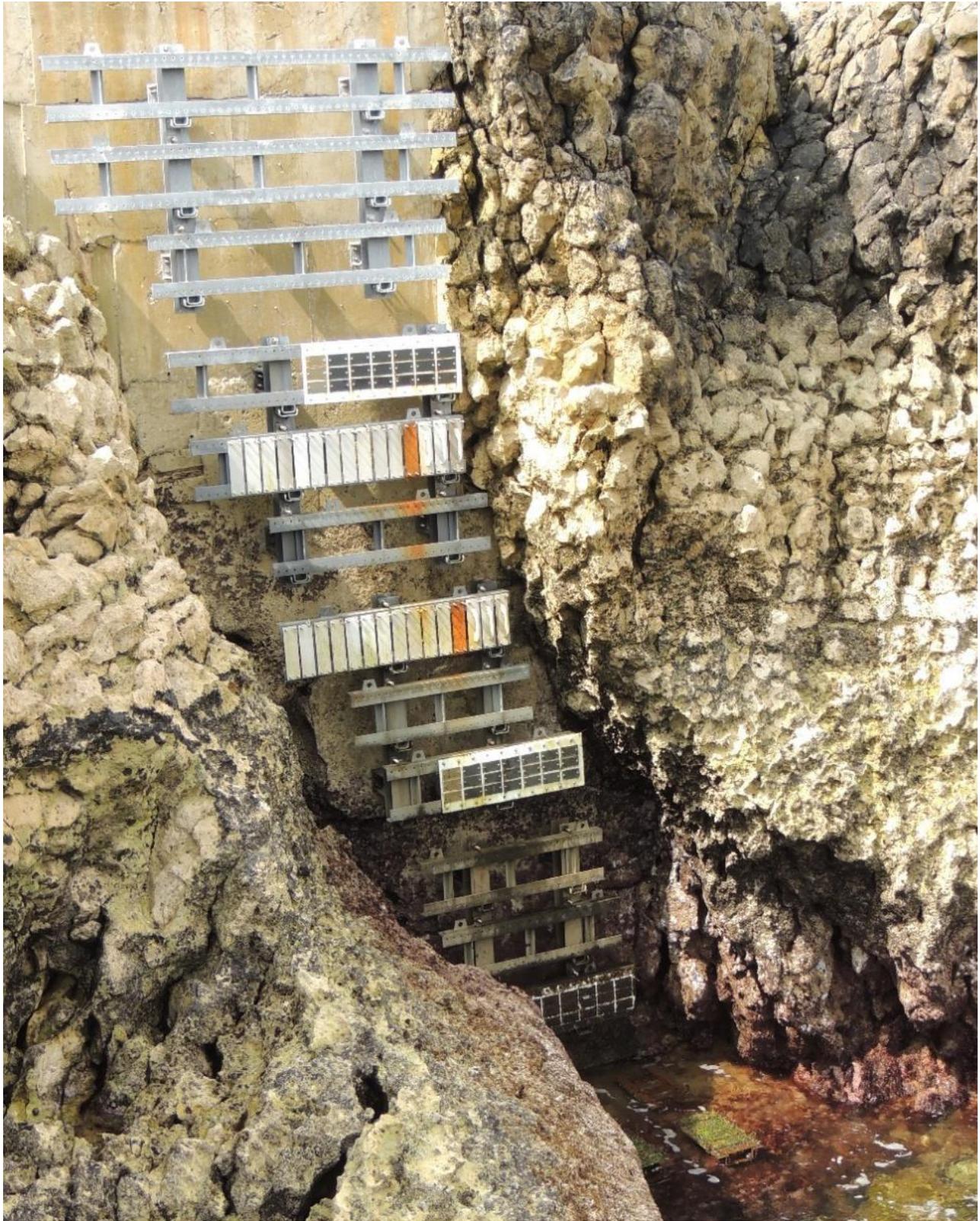


Figure 36: General overview of the samples in M4

Submerged: Figure 37 shows lots more sea lettuces in this exposure zone than in M3. There was an important increase of the quantity of algae in these coupons. Even in this period of time this growth was noted. Figure 38 shows the difference in the state of the samples in a period of 17 days.



Figure 37: Samples in submerged zone in M4



Figure 38: Evolution in 17 days time

6.6 Month 5 (from 13/07/2015 to 09/08/2015)

Splash: Figure 39 shows that there was not a big variation of the state of the coupons from M4 in this exposure zone. Very little traces of algae were observed in C1, C2, C3 and C6. Some spots of rust were observed in C13 which probably have their origin in the rust originated in C12.



Figure 39: Samples in the splash zone in M5

Tidal: Figure 40 shows that C17 was the only coupon that did not have algae in its surface. The three welded coupons had algae in all their surfaces. C24 and C25 had rust coming from C12. C12 is completely oxidized and is just over them. At this point, C12 was moved to the left of C1 to avoid more contamination. Of this way the rust spreaded by C12 would not fall over any coupon.



Figure 40: Samples in the tidal zone in M5

Submerged: Figure 41 shows that the quantity of sea lettuce was similar than in M4. There was no evolution of the quantity of algae in these coupons during this month.



Figure 41: Samples in the submerged zone in M5

6.7 Month 6 (from 10/08/2015 to 06/09/2015)

Splash: The presence of very little traces of algae are showed in Figure 42 (C1, C2, C3 and C6) although they were progressively disappearing. The reason of that could be the increase of temperature of the last weeks.



Figure 42: Samples in the splash zone in M6

Tidal: Figure 43 shows a significant increase of the presence of algae in the coupons in this exposure zone respect to M5. C18 and C19 were the coupons that had more algae and C17 continued being the one less affected by algae.

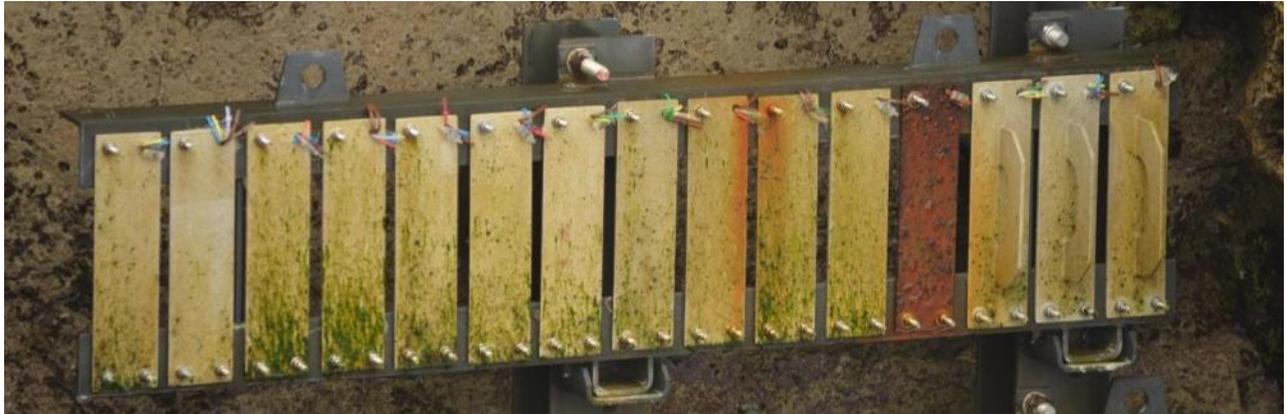


Figure 43: Samples in the tidal zone in M6

Submerged: Figure 44 shows that the quantity of green algae in the coupons during this month was similar to the previous month (M5). There was an important difference of seaweed between the samples closer to wall of the MCTS El Bocal (Figure 44 left) and the two closer to the sea and further to the wall (Figure 44 middle and right). This difference in the seaweed growth may be due to the amount of time they were exposed to the sun was not the same. The ones closer to the wall, even being really close to the other ones, were in a gloomier area.



Figure 44: Samples in the submerged zone in M6

6.8 Month 7 (from 07/09/2015 to 04/10/2015)

Splash: Figure 45 shows the presence of some traces of algae although they were progressively disappearing, probably because of the increase of temperature during the previous weeks or due to less wet time. C12 was removed from where it was fixed and it was set to the left side of the frame to ensure samples below it were not contaminated further.



Figure 45: Samples in splash zone in M7

Tidal: Figure 46 shows a significant increase of the presence of algae in the coupons in this exposure zone respect to M6. Most coupons were covered almost entirely by algae C17 was the sample that continued being least affected by algae.



Figure 46: Samples in the tidal zone in M7

Submerged: Figure 47 shows that the quantity of sea lettuce in the coupons during this month was similar to the previous month (M6). As in the previous month, there was an important difference of seaweed between the samples closer to wall of the MCTS El Bocal and the two closer to the sea and further to the wall.



Figure 47: Samples in the submerged zone in M7

6.9 Month 8 (from 05/10/2015 to 27/10/2015)

Splash: The state of the coupons in this exposure zone was the same as in the previous month (see Figure 48).



Figure 48: Samples in the splash zone in M8

Tidal: Figure 49 shows a significant increase of the presence of algae in the coupons in this exposure zone with respect to M7. Besides algae, it was noted that some coupons, as C16, C18, C19, C22, C23, C24 and C25, had other organisms fixed to them (see Figure 50 for a detailed view).



Figure 49: Samples in the tidal zone in M8



Figure 50: Detailed view of coupons 16, 17, 18 (left) and 22, 23, 24

Submerged: Figure 51 shows that, in addition to the green algae that were already set in the samples in M7, some brown algae were identified. The amount of brown algae was higher in the samples closer to wall of the MCTS EI Bocal (image on the middle) than in the others.



Figure 51: Evolution in 26-10-2015

6.10 Decommissioning on 28&29/10/2015

The 28th and the 29th of October the decommissioning of the tested samples at the MCTS EI Bocal was carried out. Two days were necessary to accomplish the works due to two low tides were necessary to pull out all the samples. The next figures show the state of the samples the day of the decommissioning.



Figure 52: Samples C33, C34, C35 and C36 the day of the decommissioning



Figure 53: Samples C37, C38, C39, C40, C41 and C42 the day of the decommissioning



Figure 54: Samples C31, C32, C43, C44 and C45 the day of the decommissioning

7 Assessment of the marine trials

After the marine trials were carried out, the samples were moved to the Technological Centre of Components laboratory to assess the corrosion and fouling performance of all the coatings.

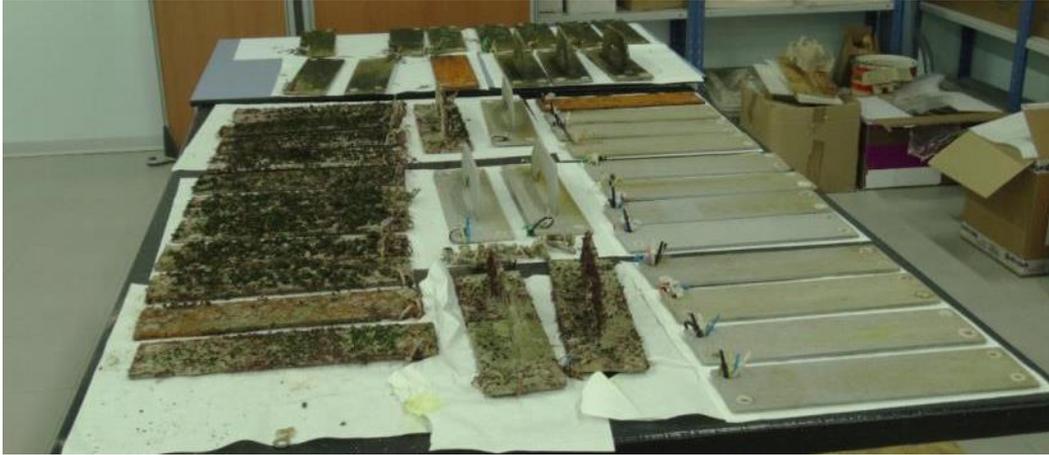


Figure 55: Samples in the laboratory after the marine trials

7.1 Corrosion performance

All coatings showed good behavior against corrosion, none of the samples were affected by this surface degradation effect. Some of them had rust spots but this rust was coming from bare steel coupons situated vertically above them. The corrosion rate was less than $3\mu\text{m}/\text{yr}$ for any coupon. This value of corrosion rate is very low compared with the rate of the bare steel coupons. Figure 56 shows the corrosion rate of the bare steel sample exposed in the splash zone during the tests performed at the MCTS EI Bocal.



Figure 56: Corrosion rate of the bare steel sample tested in the splash zone

7.2 Fouling performance

The fouling assessment revealed that there were no barnacles in any of the faces of the samples coated with ACORN coatings (only front faces had ACORN coating as mentioned before). For the samples tested in the splash zone the presence of no barnacles was evident with a fast review of the samples. A more exhaustive review of samples exposed, after algae removing, in tidal and submerged zones was needed because barnacles could be hidden among the algae.

The back faces of the samples were not protected with ACORN coatings, they were coated with TSA. The samples exposed in the submerged zone presented some juvenile barnacles attached to these faces. Also bryozoan were fixed to these faces. Two examples of these facts are Figure 57 and Figure 58, where both faces of two submerged samples are shown.

ACORN coatings were not conceived to avoid algae settlement. As it was indicated in the pictures taken during the development of the marine trials, there was algae in all the samples in the tidal and submerged zone. Algae were only in the front face of the samples, which were the faces exposed to sunlight.

Taking into account that ACORN coatings were designed to avoid barnacles settlement on the surfaces of the specimens, it can be concluded that their goal was achieved.

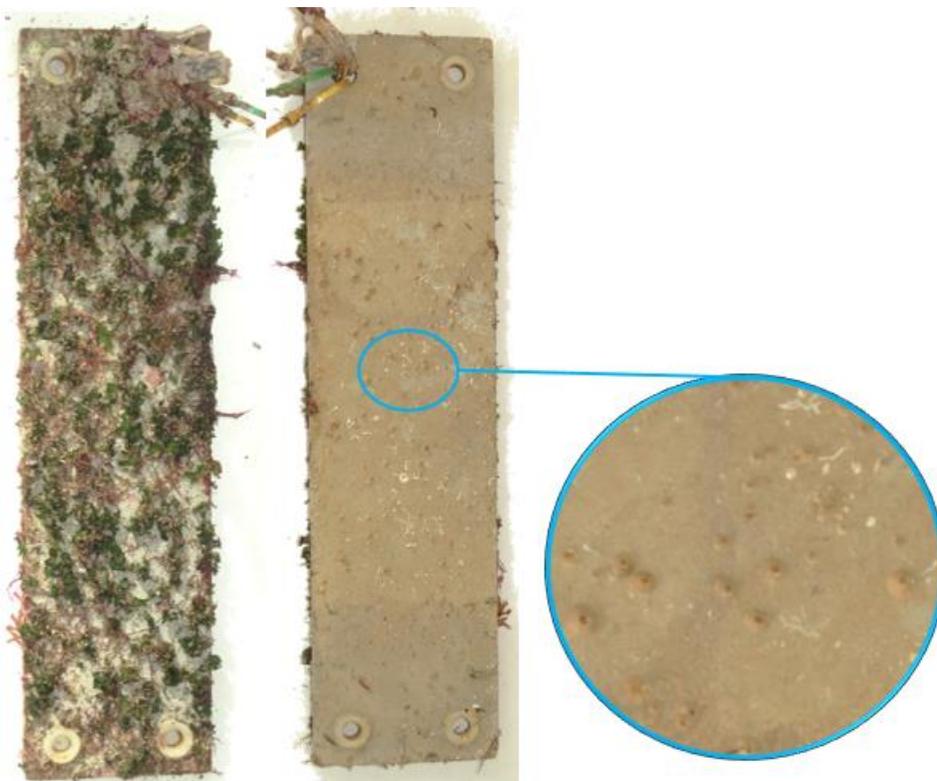


Figure 57: Upper face (left) and bottom face (right) of C38 after marine trials

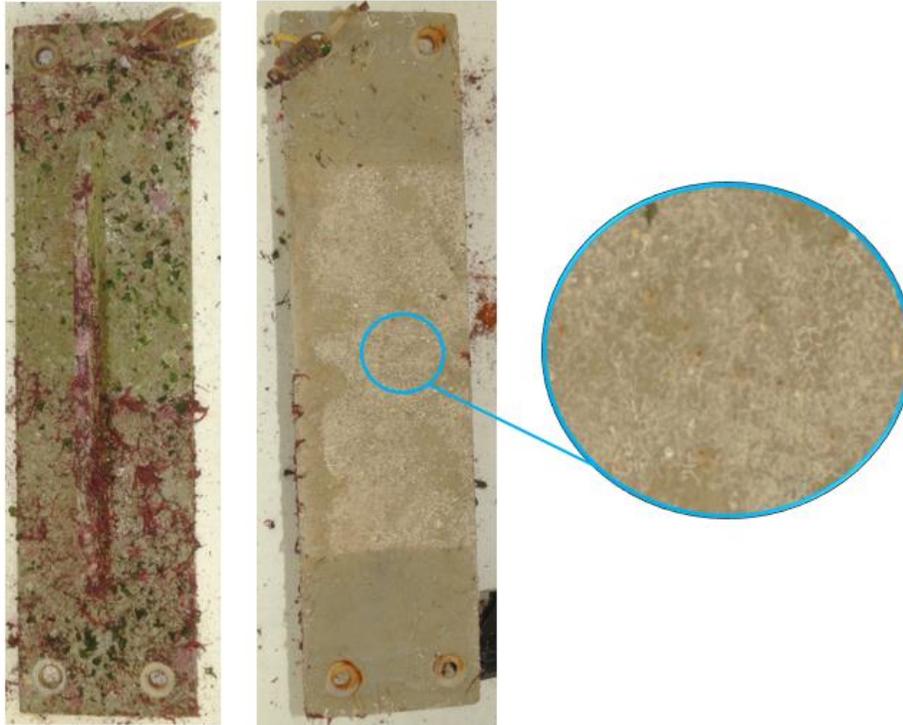


Figure 58: Upper face (left) and bottom face (right) of C43 after marine trials

7.3 Adhesion tests

Adhesion tests were carried out on the next three samples: C11 (splash), C26 (tidal) and C41 (submerged). To assess the adhesion of the coatings, pull-off testing was carried out following the standard ASTM 4541 [2]. Figure 59 shows the preparation of the sample and the dollies to run the tests. TSA adhesion greater than 6.89MPa is required by NACE 12 [3] for thermal spray coatings. For example, the typical adhesion for paint is around 3MPa.



Figure 59: Dollies glued to run an adhesion test

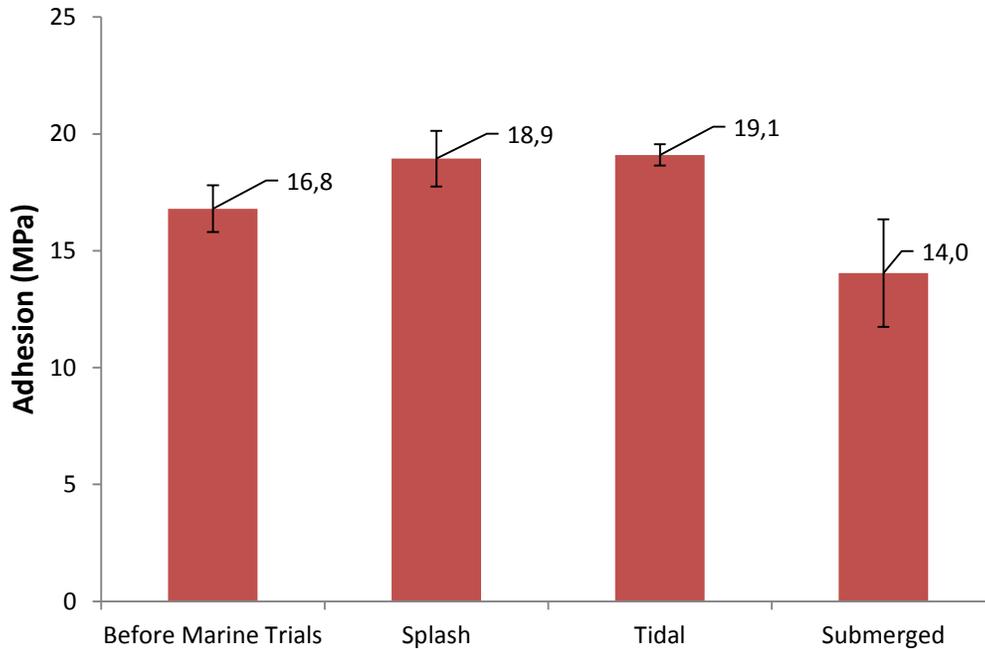


Figure 60: Adhesion tests before and after marine trials

Several tests were carried out in each sample to obtain an average adhesion value. The results of these tests are shown in Figure 60. The performance of the tests is explained as follows:

- Splash: all tests mainly failed at glue-coating interface which represents a lower bound of the coating-substrate bond strength
- Tidal: all tests had an adhesive failure in the glue
- Submerged: a lower average value obtained likely due to bond pull testing pulling off corrosion products from surface of coating rather than pulling coating from substrate

7.4 Roughness tests

Roughness tests were carried out for the three exposure zones after the marine trials were performance. Six samples were tested for each exposure zone:

- Splash: C1, C3, C5, C7, C9 and C11
- Tidal: C16, C18, C20, C22, C24 and C26
- Submerged: C 31, C33, C35, C37, C39 and C41

To run the roughness tests a focus variation microscopy was used to generate a 3D scan of the surface (Figure 61). The average roughness of the samples before the marine trials is $\sim 50\mu\text{m}$, a higher value than a regular TSA coating. The results of the tests are shown in Figure 62.

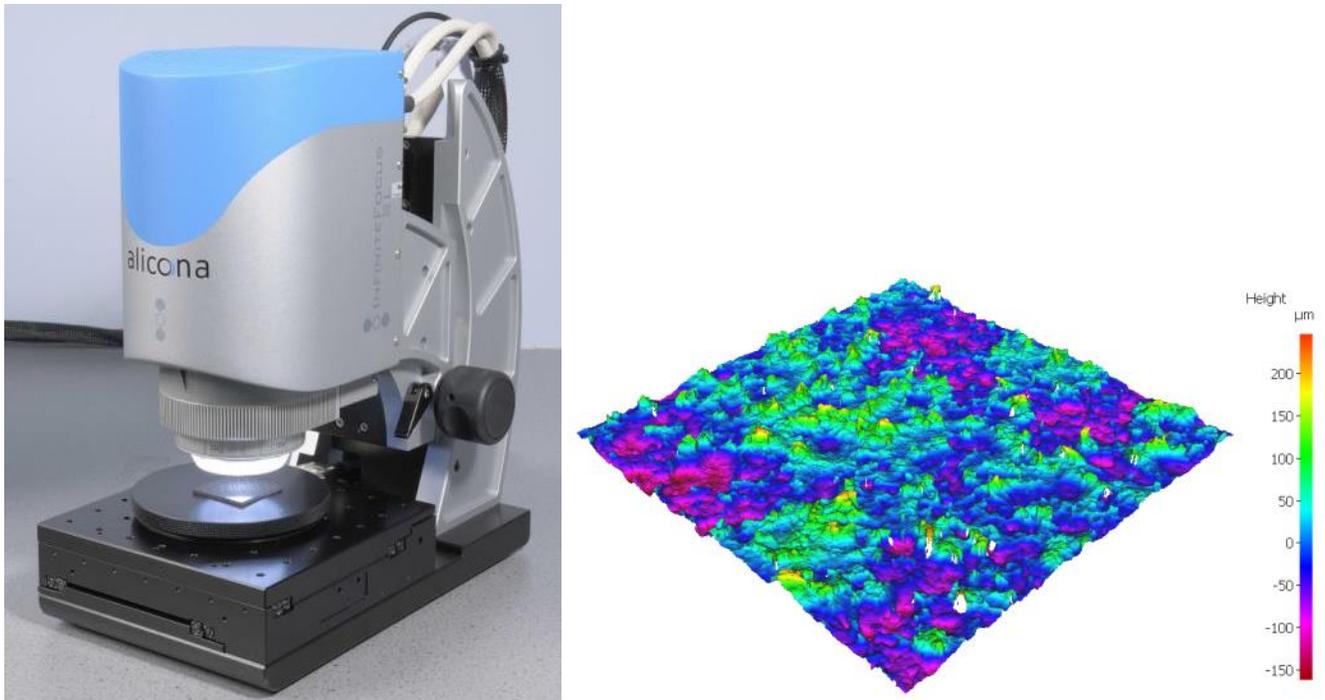


Figure 61: Focus variation microscopy and 3D scan of the surface

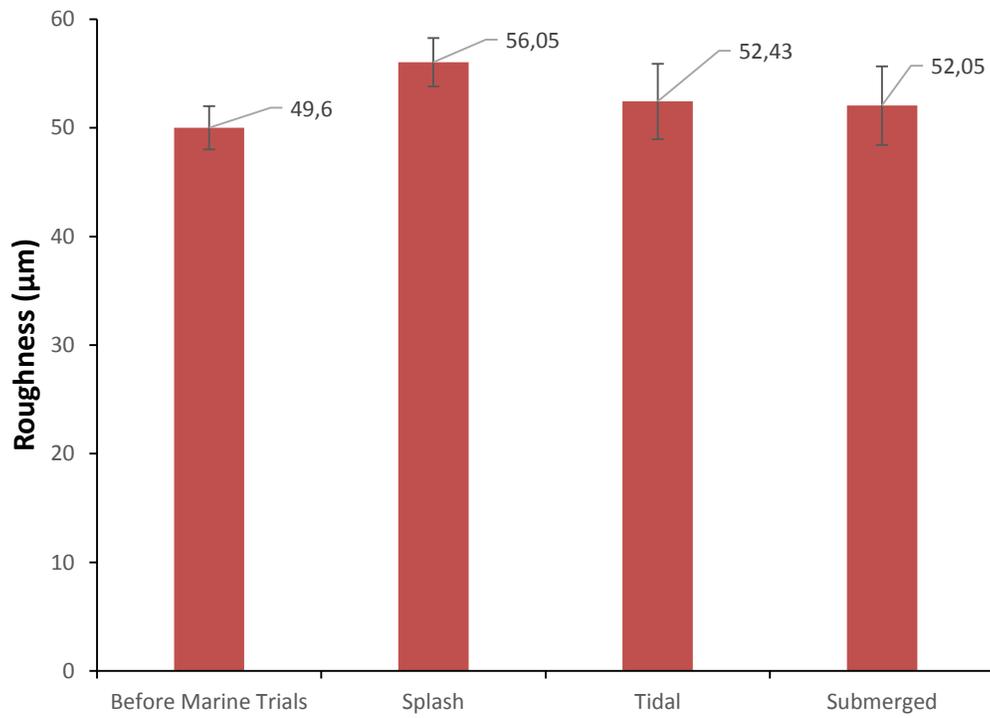


Figure 62: Roughness tests before and after marine trials

8 Conclusions

The following conclusions have been obtained along WP5.

- Extremely good protection against corrosion was achieved. After marine trials there was a nearly insignificant weight loss.
- No barnacles were detected in the faces of the samples with ACORN coatings.
- Adhesion value after marine trials was not altered for splash and tidal zone. For submerged zone the value decreased but it was still good.
- Acceptable roughness value of the samples after the marine trials.
- Longer test periods will be required to fully assess the efficacy of the ACORN coatings in preventing barnacle colonisation.

9 References

- [1] <http://ctcomponentes.es/en/mcts-marine-laboratory-el-bocal-2/>
- [2] ASTM D4541 “Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers”
- [3] Nace No. 12, SSPC-CS “Specification for the Application of Thermal Spray Coatings (Metallizing) of Aluminum, Zinc and their alloys and Composites for the Corrosion Protection of Steel”