WATERBORNE BIOFOULING AND CORROSION RESISTANT FOR SEAWATER HEAT EXCHANGERS AND OFF-SHORE EQUIPMENT (OIL & GAS, WIND AND SHIPPING).

Application fields:

- Steam condensation in coastal Power Plants
- Natural Gas cooling in off-shore, subsea
- Wind offshore: Nacelle hub & machinery (gear boxes, main frames, etc.)
- Structural parts (tubes, steel long profiles, etc.), Towers, Sheet Piles, Jackets, Foundation, Cast iron parts

Corrosion and fouling are the main problems especially acute for seawater heat exchangers and any other structure as well. (Figure 1)

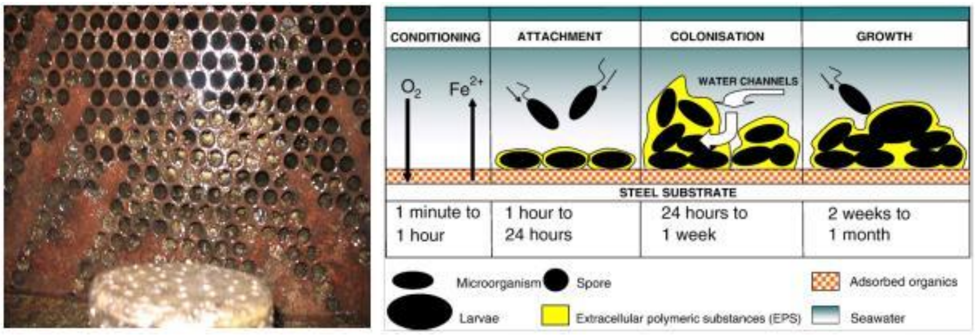


Figure 1. Corrosion in a heat exchanger and the Mechanism of growing fouling (Reference: Chambers et al.,2006)

Kera-Coat has a new solution with different ceramic coatings tested in tidal environment. First plate is the "Uncoated" one in carbon steel. Rust in the rest comes from the holding hole drilled after coating.

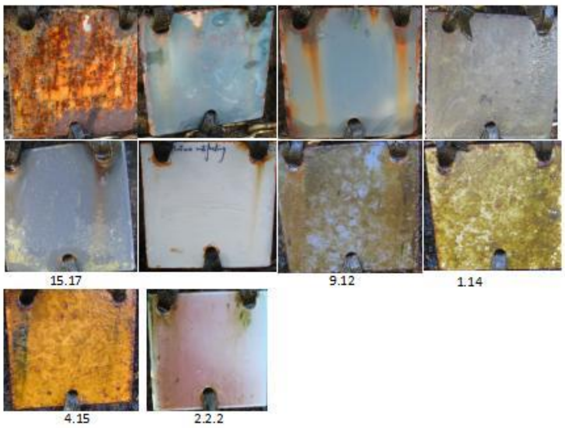


Figure 2. Ceramic coating tested in tidal environment

Figure 3. Test rig for antifouling tests (samples attached to the splash / tidal part) developed by Kera-Coat/IK4-Cidetec).

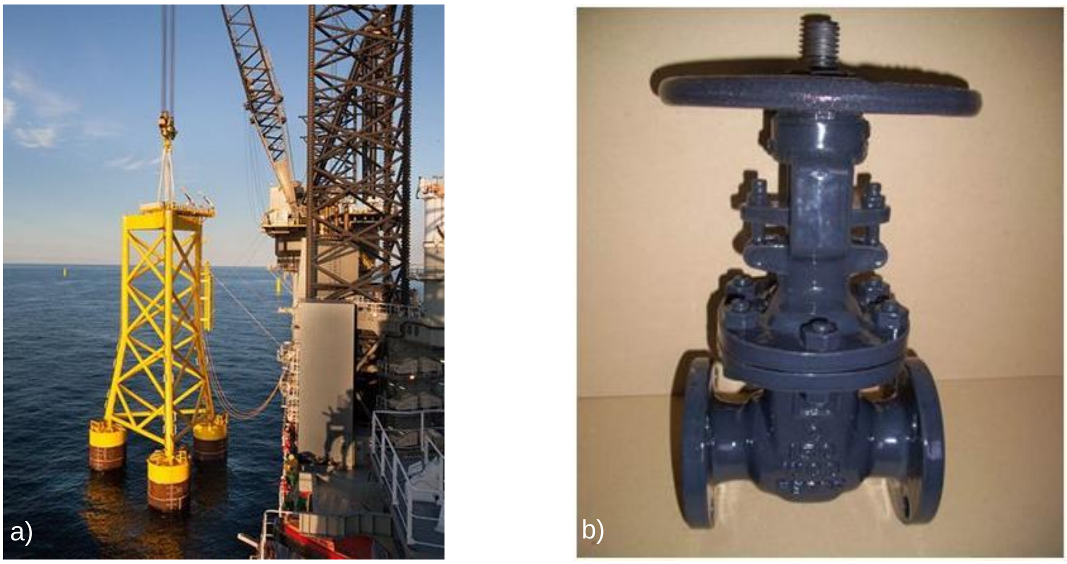


Figure 4.
a) Jacket Foundation for off-shore wind
b) Complete valve with high anticorrosion ceramic coating

The samples are continuing the sea trials on the whole on 2015 and 2016

1 - WIND OFF SHORE

Cast iron parts : Nacelle & Hub components (Figure 5)

Some of the heaviest and critical parts (Hub and main frame) of the wind generator are made on machined Nodular Iron Castings

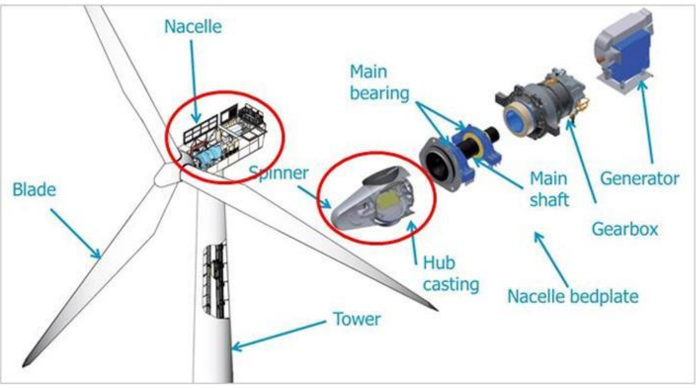


Figure 5 – Nacelle and Hub

In offshore applications and due to the sea conditions, the anticorrosion protection and low maintenance are of paramount importance to reduce the OPEX. As per today, the industry is employing coatings with polymeric-organic binders in several layers and curing steps. These coatings are applied *"after machining"* due to the fact that the metallic chips at high temperature and the machine tool clamps would spoil the coating if previously made. This process involves a lot of hand **labour** to mask all the **machined** parts, which increases the CAPEX. The polymeric-organic coatings are relatively soft and for this reason the coated parts must be carefully handled during transport and assembly.

The corrosion resistance of such machined castings is still a question mark in the long-term operation, especially in the sharp edges and borders with the machined areas (i.e.: crevice corrosion) that are not well protected.

At this point, The Research Centre IK4-CIDETEC and his industrial spin-off KERACOAT have developed a ceramic coating, based on advanced ceramic coatings, chemically bonded to the cast nodular iron that may help to solve the above-mentioned problems. The aqueous ceramic formulation is applied before machining, using spray technology, as cast, just after sand blasting and without any further pre-treatment, avoiding all the masking work to protect machined areas that are common in other types of protective coatings. The ceramic is applied in 2 layers, ground and cover coat, with total thickness around 300 microns. The ground coat gives a chemical bonding to the substrate by the formation of a metal/ceramic interface after a first sintering process (800ºC - 1472ºF). Finally, the cover coat, applied in the same way that the first one (thermal heating over 820ºC (1508ºF) provides all the chemical and mechanical properties needed in offshore conditions.

One of the main differences with organic coatings concerns to the chemical bonding to the metal substrate formed after heating treatment, with a continuous interface of about 5 microns avoiding any corrosion between ceramic and iron, because there is no “room” between them, so any corrosion in a machined surface will not expand to the coated areas. Therefore machining can be made on already coated parts.

The finishing of ceramic coating shows a smooth vitreous surface with hardness of around 60 HRc, with a thermal resistance up to 500ºC (932ºF) (so no harm from hot chips, as opposed to organic coatings applied nowadays) and the roughness value (Ra) is already 0’10 microns, thus preventing corrosion particles adherence to the Nacelle structure. Comparing with organic-polymeric coating it provides a higher resistance to scratches but lacks the plastic deformation under big impacts, destroying locally the coating, (No cracks - No delamination)but it can be repaired by the application of the same cover formulation with a localized heating. The high corrosion resistance of advanced ceramic coating, tested in different aggressive media, resists perfectly seawater even in splash and tidal zones.
In this way it aims to obtain a coating technology capable of protecting the nacelle castings and other metallic parts, making extensible to other components in off-shore wind generation such as splash zone’s metallic elements, tower sections & rings, etc. in order to reduce drastically OPEX

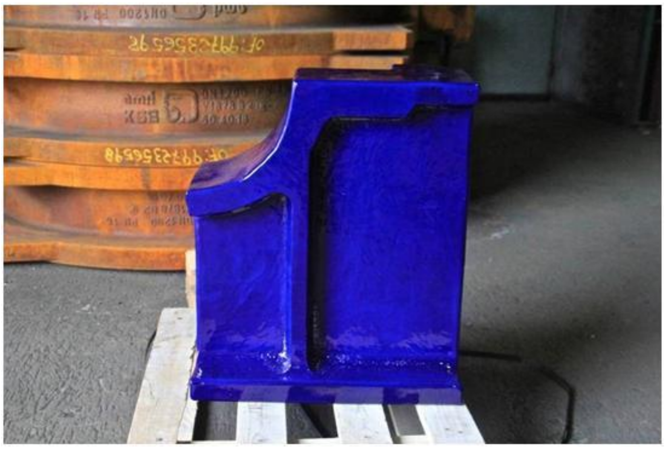


Figure 6. Nodular iron casting (gearbox part) coated before machining

Figure 7. Coated valve part with high chemical resistance for desalation Sour Service.

Wind Off-Shore Towers.

Due to the huge weights and dimensions of these components, a radically different approach is being developed, especially for the sintering phase on which the ceramic and the immediate steel surface have to be over 800ºC for some minutes

This is being engineered to became a laser sintering made by robots

COLABORATIONS

We are also cooperating with the Biofouling unit of the University of Cantabria:

http://biofouling.unican.es/laboratorios/laboratorios.html

for accelerated lab tests in different areas.

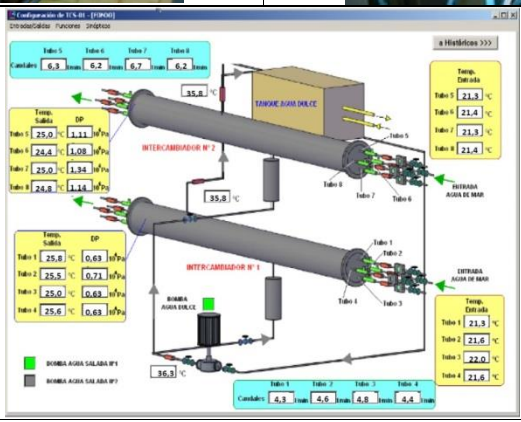


Figure 8; University of Cantabria facilities

2 - CORROSION UNDER SEA WATER CONDITIONS

We have tested our ceramic coatings in different sea water environments:

Plentzia's Marina (*Image 1*).

Image 1– Plentzia's Marina

The samples were:

Coated two faces, without any protection at the edges and holes.

Dipped in seawater at the Marina, one meter below the water surface, with a minimal tide effect.

Cleaned by hand and water after 9 month in sea water. Actually they continue submerged in sea water.

In these conditions the results were (*Images 2*):

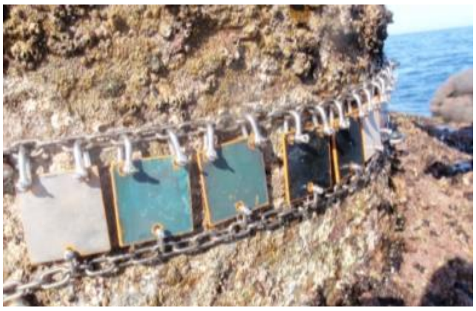
COATED CARBON STEEL		
Before	**Time elapsed**	**After (cleaned by hand and water)**
	9 Months **24h / day**	
	9 Months **24h / day**	

Images 2

The color difference between Before and After images, should be produced by the light (Before – Laboratory photos // After – Marina photos).

Pasajes Off Shore (Image 3)

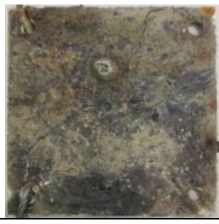
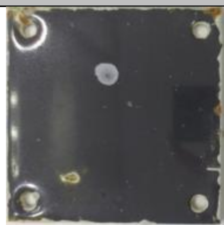
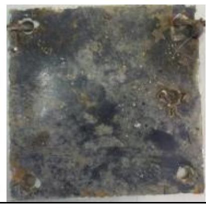
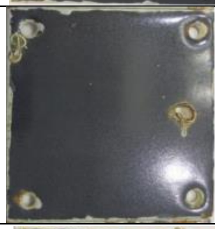
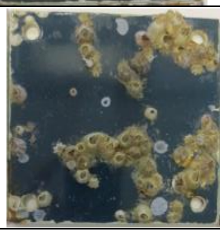
The samples were placed in Splash Zone and affected by tides, as you can see in the below images (*Images 3*).

Images 3 – Pasajes Off Shore

The samples in the third image (Images 3) are not corresponding the below test.

The back and edges of coated sampled were protected with a protective paint. The results were:

COATED CARBON STEEL			
Before	**Time elapsed**	**After** **Before cleaning // Cleaned by hand and water**	
	7 Months **(24h / day)**		
	7 Months **(24h / day)**		
	7 Months **(24h / day)**		

The white points in the middle of the some pieces corresponding cirripedes and limescale (not protective paint).

CONCLUSION

As you can see in all the images, there is Biofouling's growth, very easy to clean (low adherence), **but NOT a single** corrosion or delamination on the ceramic coating.

Corrosion and fouling in offshore

Overview

Offshore components and devices have serious technical and economic problems as a result of aggressive phenomena of fouling and corrosion.

The traditional solutions to avoid:

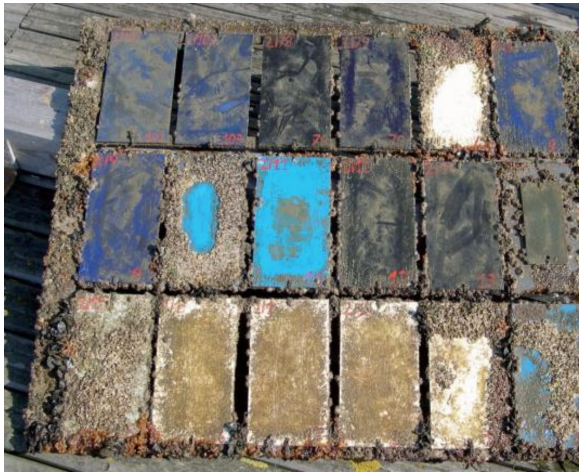
- **Biofouling phenomenon**: Biocides, usually highly polluting substances, most of them included in paints and polymeric agents.
- **Corrosion**: Expensive materials, substrates (stainless steels, Ni alloys, Titanium, etc.) and oversized designs for the purpose of increasing the whole life cycle of the component.

Faced with this scenario, there is a need for many industries to **develop environmentally** sustainable **solutions** to protect offshore structures. A technical solution based on **advanced coatings** with corrosion resistance and anti-fouling properties could improve the yield and reduce costs.

Overview

For certain applications, **paints** may have several disadvantages:

- Low resistance to scratching and wear
- Chemical stability problems at certain temperatures
- Low adherence (mechanical) to the substrate
- Usually they have to be replaced regularly to maintain the main properties.



Ceramic coatings could be a good environmentally friendly alternative in certain offshore components with high corrosion and biofouling resistance.

IK4 CIDETEC Research Alliance

Corrosion and fouling in offshore

Overview

PROPERTIES:

1. FUNCTIONAL:

1.1. Physical properties:
- Temperature resistance
- Resistance to thermal shock

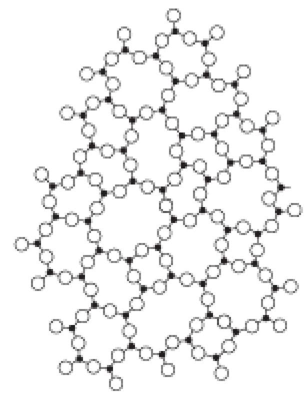
1.2. Chemical properties:
- Resistance to chemical agents
- Resistance to atmospheric agents
- Impermeability

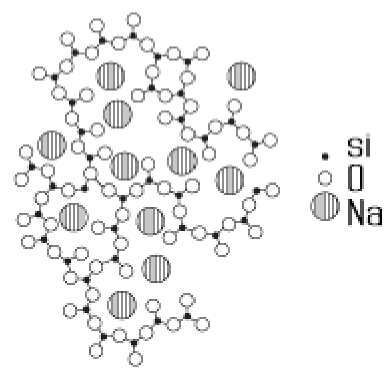
1.3. Mechanical properties:
- Hardness
- Scratch resistance
- Abrasión resistance
- Impact resistance

1.4. Hygienic properties:
- Inhibit bacterial growth
- Cleanability

2. AESTHETICS:

2.1. Finishings
2.2. Varied colors
2.3. Visual effects
2.4. Stability

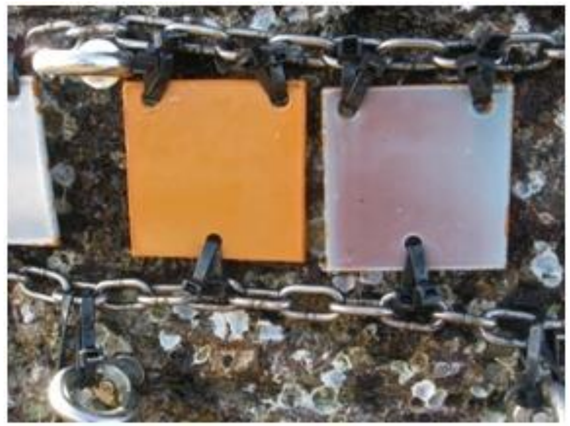




Corrosion and fouling in offshore

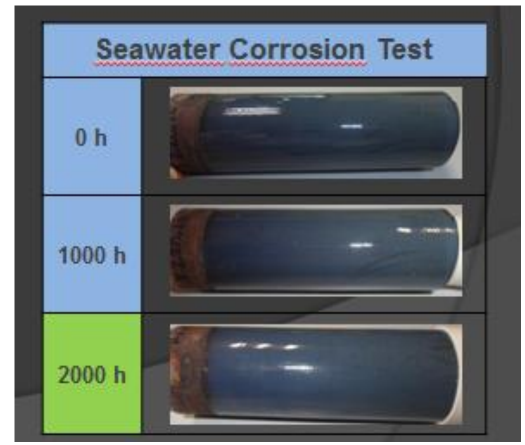
Ceramic approach with enamels coatings

Coatings with anticorrosive / anticlogging properties for Offshore systems

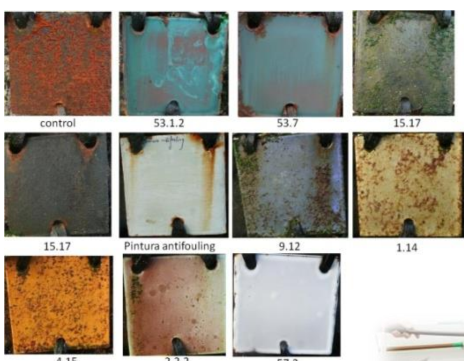


UNE-EN ISO 9227:2012

ASTM D5479-94 (2013), ASTM D6990-05 (2011)



Up-scaling and field test

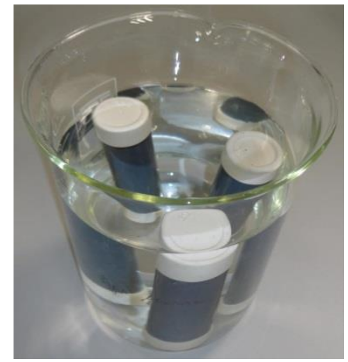


Development of vitreous coatings on carbon steel that has to overcome more than 20 years in offshore conditions without corrosive processes and antifouling

Corrosion and fouling in offshore

Ceramic approach with enamels coatings

- **Seawater Corrosion Resistance (Offshore):**
  - **Conditions**:
    - Solution: 3,5% NaCl at 22 ^{0}C
    - Visual inspection after test



Seawater Corrosion Test	
0 h	
1000 h	
2000 h	

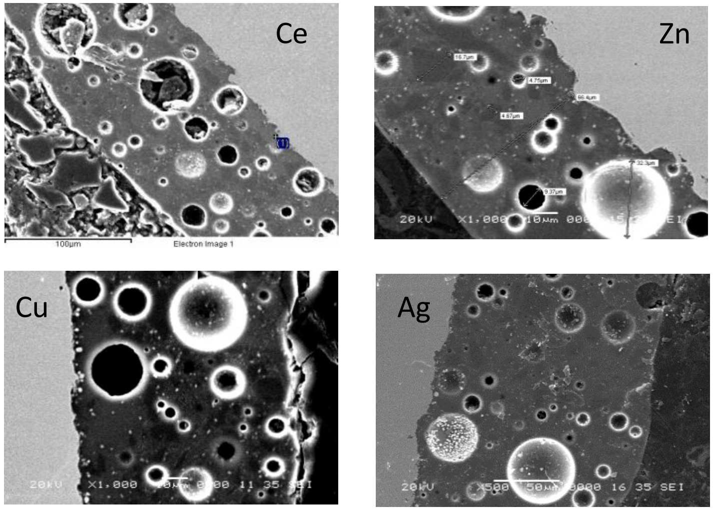
HIGH CORROSION RESISTANCE FOR OFFSHORE APPLICATIONS

Ceramic approach with enamels coatings

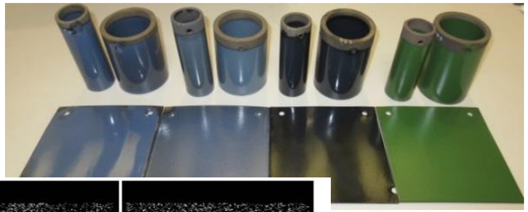
The application of **ceramic coatings based on advanced enamels** with antifouling properties in offshore structures is completely new.

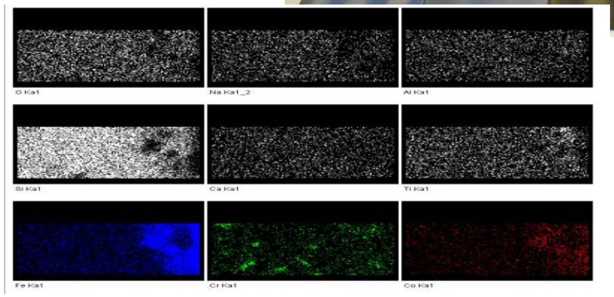
IK4-CIDETEC, is actually working on different projects based on the development of **ceramic coatings** with high corrosion resistance and antifouling properties under seawater immersion conditions:

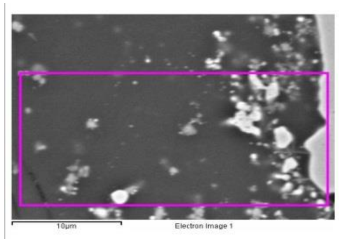
- Chemically bonded to the substrate
- Incorporating active ceramic particles against fouling as silver, copper, vanadium, cerium, zinc, titanium, etc.



SEM







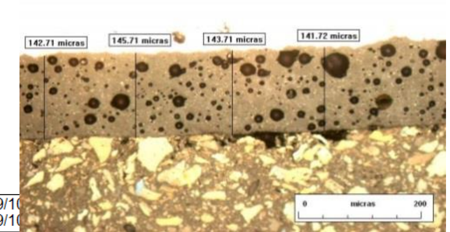
Mapping interface

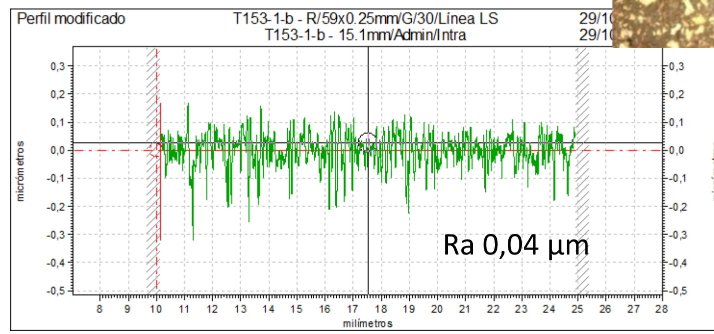
Corrosion and fouling in offshore

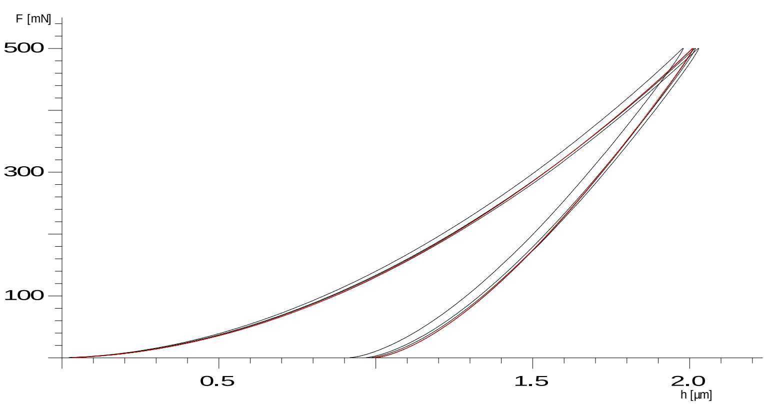
Ceramic approach with enamels coatings

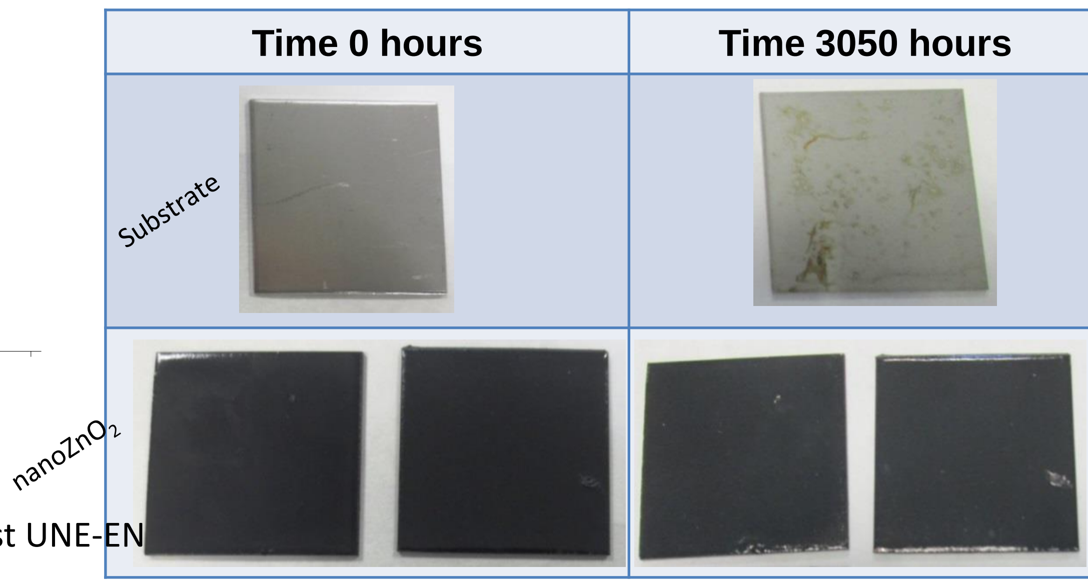
Properties

- Thickness: 100-150 mm.
- Corrosion resistance: good.
- Coating adherence (UNE-EN-10209): good.
- Roughness (ISO 25178): Ra = 0,03 - 0,06.
- Hardness (ASTM C 1327-03): 750-800 Hv.









Accelerated corrosion in Salt Spray test UNE-EN ISO 9227:2012

Ceramic approach with enamels coatings

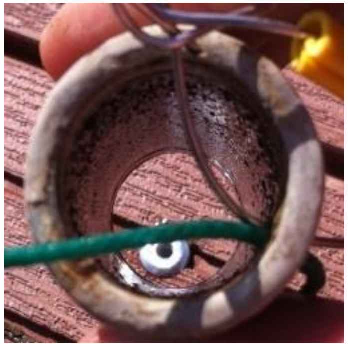
Proof of concept

Some ceramic formulations developed in IK4-CIDETEC are currently under evaluation in a test bench to analyse the effect of active ceramic nanoparticles in the antifouling properties, showing a good behaviour at early stages.

- Check corrosion resistance.
- Check biofouling.
- Check ease of cleaning.

Seawater immersion in Plentzia harbour (Cantabrian sea)

Initial development



nanoZnO

nanoCu

V_2O_5

Outcome

- Enamel coatings with chemical adherence to the metal substrate (better in carbon steel than in stainless steel)
- Enamel coatings with high corrosion resistance in salt medium
- Nanoparticles integration in ceramic structure trying to get the functionality at the surface with no lose of corrosion properties
- Smooth surface (low roughness) to try to avoid fouling adhesion
- Enamel coatings developed over sheet an tube coupons (inside the tube the proliferation of algae and molluscs is higher, calmest zone)
- Direct testing in test bench

Future Steps

- Monitoring the results.
- Adjust the formulations.
- Analyse the biocidal compounds distribution (specially in the interface substrate-ceramic)
- New biocidal compounds compatible with enamel vitreous structure.
- Effect of particle size (nanoparticles).
- Compare the results.