Coatings systems for carbon steel protection against biocorrosion and biofouling in seawater. A Laboratory and field study

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Abstract

The performance of various coatings systems was assessed in laboratory and field experiments to avoid biocorrosion and biofouling deleterious effects on navy carbon steel in polluted harbor seawater. Microfouling and corrosion attack were observed by scanning electron microscopy (SEM) and corrosion products were characterized by X-ray diffraction (XRD).The effectiveness of antifouling coatings was assessed by means of seawater immersion tests during a time period of 16 months. A coating system based on lamellar zinc and modified with an extender and an inhibitor has been used as primer. This formulation offered an antifouling high dissolution rate and showed the best performance.

Key-words: anticorrosive primer, lamellar zinc, antifouling coatings, carbon steel, seawater, biocorrosion, biofouling

Introduction

Marine biofouling develops within a few hours on all metal surfaces exposed to natural marine environments. At long exposure times, marine fouling occurs in the form of a complex community of plants, animals and microorganisms that considerably alter and influence the immediate surroundings of the metal surface (1).
Biofouling and biofilm formation are the result of an accumulation process which is not necessarily uniform in time and space (2). In an aggressive medium like seawater, metal dissolution takes place simultaneously with biofilm formation. Thus, a very active interaction between the corrosion process and biofouling settlement can be expected. A new "biologically conditioned" metal/solution interface is formed and a reciprocal conditioning between the corrosion products layers and biofilms is established (3).

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Biofilms and their accumulation as biofouling are influenced by both the substratum and the bulk phase. On an active metal like carbon steel, the gelatinous structure of the biofilm, formed by extracellular polymeric materials (EPS), bacterial cells and water is mixed with corrosion products that are formed within the same time scale (4).
The cohesive effect of EPS in biofouling deposits depends on several environmental and biological factors influencing biocorrosion /biofouling interactions.
Macrofouling is divided in engineering terms as “soft fouling” (algae, soft corals, sponges, anemones, tunicates and hydroids) and “hard fouling” (crustose algae, barnacles, mussels, tubeworms, and other organisms).
Biocorrosion and biofouling effects are relevant factors in the corrosion of carbon steel when the level of pollution of seawater is high as in the case of the harbor of Cartagena, Colombia, where this study has been performed.
The aim of this work was to assess several formulations of antifouling coatings for protecting carbon steel from the deleterious effects of biocorrosion and marine biofouling. Coatings performance was evaluated by means of laboratory and field experiments.
Optical microscopy and scanning electron microscopy (SEM) were used to observe biofouling characteristics and corrosion attack. Corrosion products characterization was made by using energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD).

Experimental

Seawater characterization

A physicochemical characterization of the harbor seawater was made taking into account the following parameters: light availability; temperature, dissolved oxygen, pH, redox potential, alkalinity and salinity.
The biological characterization of macrofouling deposits was made by taking samples from metal surfaces without antifouling protection, carrying out a classification of different groups of organisms and a corresponding counting of each of these groups.

Anticorrosive and antifouling coatings

The protection of carbon steel against corrosion attack was made by using zinc rich coatings (5, 6). These coatings provide corrosion protection by using sacrificial anodes provided by pure zinc particles dispersed into a film forming material (binder). They can be formulated by using spherical or laminar zinc particles. Coatings containing laminar zinc particles attain a higher superficial area/weight relationship than those elaborated with spherical zinc particles providing a better electric contact with the metal (7).
In the soluble antifouling coatings the toxicant and the film forming material are simultaneously dissolved. An effective performance of antifouling coatings was reached by using soluble resins such as rosin or calcium resinate properly plasticized. As toxicant, red cuprous oxide was added to coating formulation. A critical leaching rate between 9 and 13 $\mu g.cm^{-2.}day^{-1}$ is recommended to avoid fixation of barnacles and algae, respectively (8).

Materials characterization

Corrosion products characterization was made by using an XRD diffractometer Bruker AXS D8 with an X ray source of Co Kα, λ = 1.78897 Å or a Siemens D5000 diffractometer with an X ray source of Cu Kα, λ = 1.5406 Å.
SEM observations and EDS analysis were made by using a Jeol JSM 5910 LV. A general flow

sheet of the experimental procedures used in this work is shown in Figure 1.

Results and discussion

The Geographical location of Cartagena Harbor as determined by GPS is N 10^{o} 19'46"; W 0.75^{o} 30'52".
Different depths were considered between 0.00 and 7.35 m. Results of light transparency showed that 50 % of daylight attenuation is reached at 0.44 m and the average limit of the brightness zone is located approximately at 2.96 m. Within these limits the higher photosynthetic activity is developed by microscopic algae (phytoplankton). Below brightness zone anaerobic organisms grow by using both organic residues produced by the phytoplankton and the organic pollutants contained in the harbor seawater.
The pH values varied between 7.6 and 7.9, which are lower than the usual lightly alkaline seawater pH range of 8.0 – 8.2, owing to the high level of pollutants of Cartagena harbor.
Concerning the temperature, the measured values remained nearly constant above 30-32 ^{o}C during all the day long which can be attributed to the tropical location of the site.
Oxygen levels, the highest values at the bright zone, were 10.82 mg.l^{-1} and 4.59 mg. l^{-1} for the dark zones.
Redox-potential profiles are shown in Figure 2. A simultaneous decrease of redox potential and an increase of salinity can be observed. Both factors are relevant and closely related to the conductivity and corrosiveness of seawater.
To assess biological activity of macrofouling in the seawater, a ship bottom without any antifouling protection was used as reference. The ship remained anchored for two years with a very limited time of navigation. Experimental results (Figure 3) show a marked colonization of the substratum with c.a.1100 organisms in 900 cm^2 involving 8 species. Predominant specie was *Balanus* sp. which shows higher resistance to biocides than other species of organisms like oysters (*Crassostreas rizophora*), *Mitilus* (*Mitilopsis* sp.), sponges, etc.
Raft trials were programmed in order to carry out periodical evaluations of the coated panels and to record fouling settlement. Excellent results were reached with some experimental compositions during partial observation after 16 months of seawater immersion (Figure 4). Presently, testing goes on to carry out future inspections to get conclusions for longer periods of time. Thus, some antifouling coatings formulated with the above mentioned raw materials achieved a fast dissolution steady state and leached the biocide on the surface with a leaching rate at enough level for controlling fouling settlement.
Reference tests were made by using metallic panels also located on the raft. These assays showed a relevant weight increase due to macrofouling settlement, of approximately 4.7 kg on a surface of 1200 cm^2 for a time period of 156 days (Figure 5).
Corrosion products characterization began with optical microscope observations to assess the characteristics and thickness of the deposits. Later identification was made by using SEM/EDS and XRD. Metallographic microscope observations showed that corrosion product average thickness was c.a. 178.22 μm. XRD results allowed the identification of lepidochrocite, goethite, smythite and magnetite and/or maghemite. The two former products (oxyhydroxides) are usually present in corroded steel surfaces in seawater although in less amounts than iron oxide (magnetite). Smythite can be associated to SRB bacteria which would provide the sulfur component.

Conclusions

1) The assessment of the biofouling of Cartagena harbor seawater revealed a high degree of biological activity supported by a wide variety of biological species of well known aggressiveness.
2) Laboratory tests with coatings based on lamellar zinc primers carried out in salt fog chamber (1000 hours) and 100% relativity humidity cabinet (800 hours) showed very good both corrosion and blistering resistance. Lamellar zinc coatings modified with an extender and an inhibitor showed the best performance. These coatings were used as primer in all protective strategies where antifouling coatings were tested.
3) The performance of antifouling coatings assayed in this work at a preliminary testing time of 16 months, has been satisfactory especially in the case of antifouling coatings containing binders of high dissolution rate in their formulation. Coatings based on disproportionate calcium resinate attained a steady state quickly after immersion avoiding the rapid initial toxicant loss and thickness decrease of films containing rosin as soluble resinous material.
4) Experimental results of the laboratory tests confirm the biocidal behavior; some coatings showed proper bioactivity by preventing both biofilm formation and macrofouling settlement with a copper-leaching rate less than 10 μg $Cu_2O.cm^{-2}.day^{-1}$ corroborating conclusions reached by other authors.

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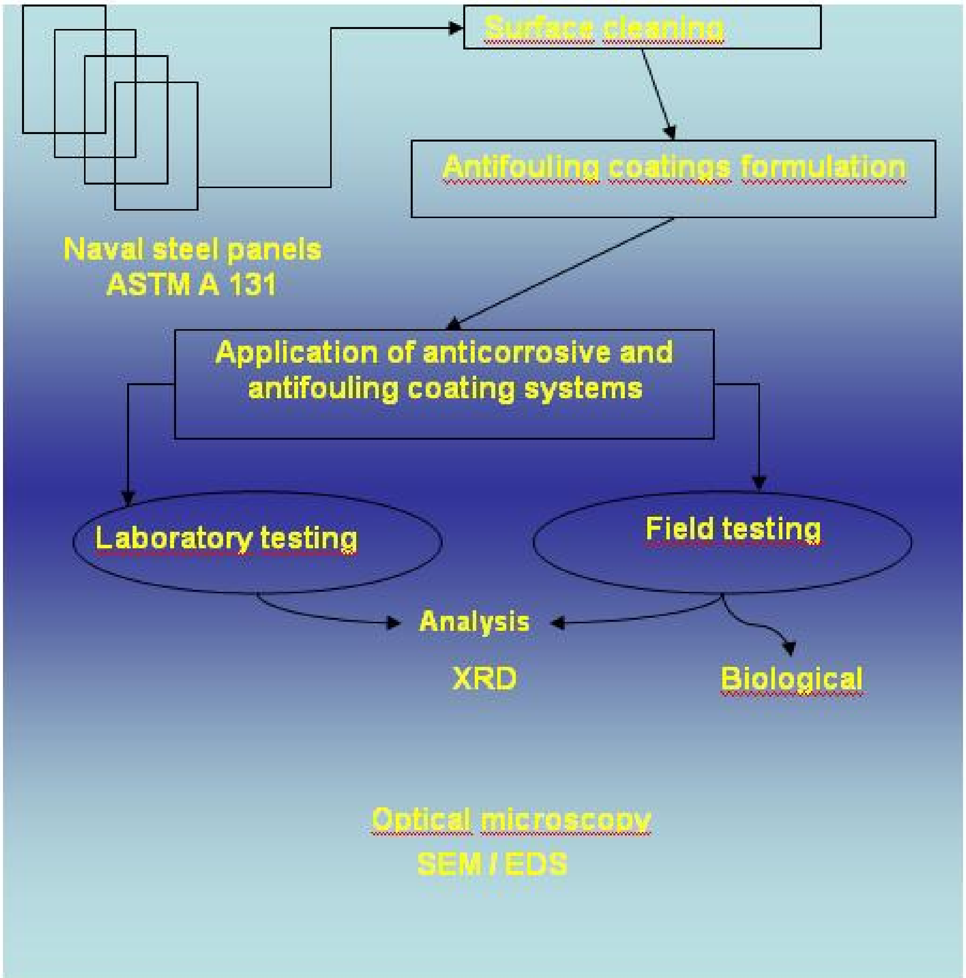

Figure 1 – Flow sheet of experimental studies

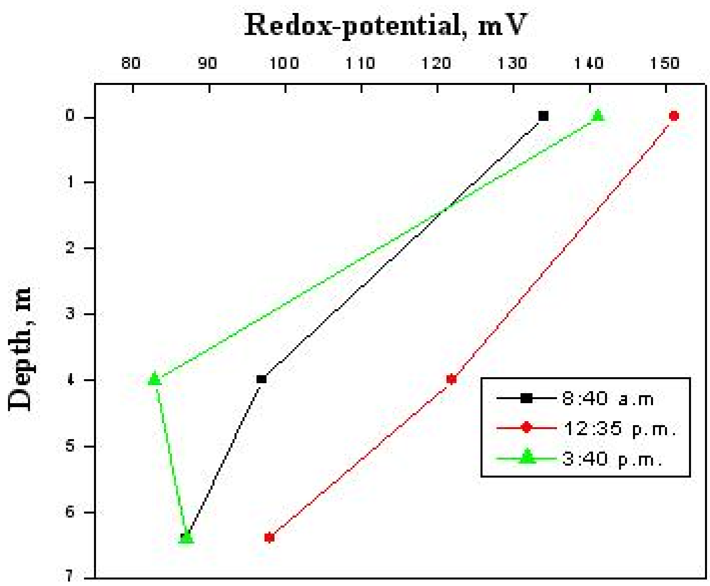

Figure 2: Redox-potential profiles of seawater corresponding to experimental environment

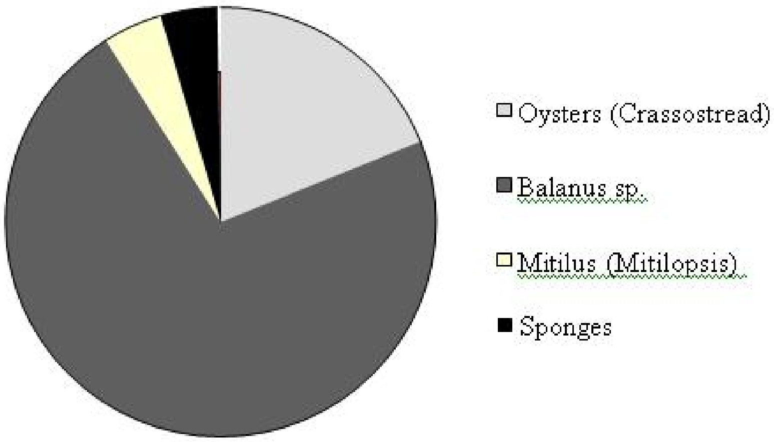

Figure 3: Biological species on a ship bottom anchored at Cartagena harbor for two years

Figure 4: Biofouling settlement control with an efficient antifouling coating

Figure 5: Macrofouling fixation on a metallic panel without any antifouling protection (156 days)