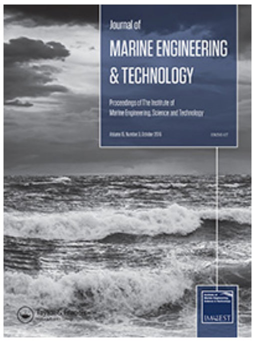

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Corrosion assessment of infrastructure assets in coastal seas

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ABSTRACT

The seas play an essential role for the peoples living on their coastal regions, since the marine infrastructure is located in the coasts. Seawater is a corrosive environment that affects infrastructure particularly in polluted seawater. Corrosion and pollution are pernicious chemical, physical processes that impair the quality of the environment and the durability of the marine structures and materials. They are aggravated by the discharge into the sea coast of municipal, industrial and agricultural effluents, which contain and produce toxic and highly corrosive components by biological and chemical degradation. Reinforced concrete and carbon steel are the main engineering materials used for the construction of marine installations and equipment but other metals and alloys: aluminium; copper, stainless steels are applied, too. Laboratory and field corrosion tests in seawater were carried out applying gravimetric, electrochemical and surface examination methods, based on American Society of Testing and Materials (ASTM) and National Association of Corrosion Engineers (NACE) standards. This work is the result of a cooperation between academic institutions in Mexico and Israel. The data generated advance the management of sea corrosion prevention and mitigation, and provide a guide for marine infrastructure maintenance and corrosion control. Several cases of corrosion in the sea coasts based on the authors experience and knowledge are presented.

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Introduction

The seas played an essential role for the humans living on the coastal regions of the world. These ancient maritime civilisations were widespread by peoples of the Mediterranean, Arabian and China seas and the Atlantic and Pacific Oceans; managing complex systems of harbours, shipyards and seafaring for trade, conquest and colonising expeditions. The maritime heritage of the Phoenicians, Greeks, Romans, Vikings, Byzantines and Spaniards navigators has been implemented, through the millennia by the modern maritime nations (Leon H. Charney School of Marine Sciences 2016).

The coast and its adjacent areas onshore and offshore are an important part of local ecosystems, forming gulfs, bay and estuaries, sometimes mixing fresh and salty waters.

The seas energy is enormous, tides rise and fall twice daily, and swift currents flow towards the coast. Offshore electricity generators and waterfront industries such as liquefied natural gas (LNG) regasification plants, with their cryogenic ships and mooring ports will power coastal and inland cities (Valdez et al. 2011).

The Gulf of Mexico (GOM), an extension of the Atlantic Ocean, characterised by its tropical climate, reaching the coasts of Mexico and U.S., displaying elements of infrastructure, was evaluated in the framework of this work. The GOM was chosen as a typical seacoast of two countries seriously affected by corrosion and pollution (Hernandez et al. 1995; Acuña et al. 2002).

Additional gulfs and areas with infrastructure assets and environmental characteristics similar to those encountered in the GOM exist in the worldwide tropical zone, for example, Gulf of California, of Panama, of Suez, of Aqaba, the Arabian, the Persian, the Bengal Bay and the Strait of Singapore. The experience, knowledge and information gathered in this work will contribute to corrosion control and preservation of the infrastructure in these marine, tropical regions.

The aim of this investigation is to build a body of knowledge useful for the selection of corrosion-resistant engineering materials for materials for the marine infrastructure and naval industry.

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Corrosion and pollution interaction

Corrosion and pollution are interrelated processes since many pollutants produced by power stations burning fossil fuels, accelerate corrosion and corrosion products such as rust, oxides and salts, pollute water bodies. Both are pernicious processes that impair the quality of the environment and the durability of the marine structures and construction materials (Raichev et al. 2009).

They are permanent problems in the fluvial and marine environments, in maritime activities and naval industries. This situation is aggravated when industrial, municipal and agricultural pollutants flow into the river, the port and its surroundings, damaging its structures, installations, equipment and machinery, The physical, chemical, biological and thermal characteristics of these effluents affect the entire sea coast environment and influence the corrosion processes, types and mechanisms. These natural and anthropogenic pollutants increase the corrosion extent of steel, reinforced concrete and other engineering materials of the infrastructure assets. The knowledge of their source and characteristics contributes to the establishment and management of technologies to control water pollution and industrial corrosion, applying corrosion monitoring and corrosion risk assessment. Furthermore, water pollutants, even when present at very low levels, impair human health, aquatic life and seawater quality. The avoidance of pollution is therefore an important part of corrosion prevention and control (Marcos et al. 2006).

Climate change

There is nowadays a deep universal concern about the influence of climate change (CC), global warming and greenhouse emissions (all interrelated complex phenomena) on the corrosive and deterioration effects of the marine environment on maritime activities. Higher temperatures promote melting of polar and glacial ice and snow; sea-level rise affects the coast structures and changes atmospheric moisture and rain precipitation patterns. The climate and extreme-weather-related events (such as floodings, strong winds and storms coming from the seas that erode the coasts; prolonged heat waves, dust and particulate matter flowing in the air) seriously affect the environment and society in a variety of ways, acting through destruction of the infrastructure, famine, disease, and social and economic upheaval. But, the powerful floods that ripped roads and bridges are the most devastating events wreaking havoc across vast regions with great loss of life and property.

This growing concern has been expressed by IMarEST, the Institute of Marine Engineering, Science and Technology, UK, which recognise that CC is the most serious threat facing humanity, resulting in significant warming of the oceans and the marine atmosphere. Furthermore, the Institute of Materials, Minerals and Mining (IOM3), London, published a special issue of its journal: Corrosion Engineering, Science and Technology, entitled 'Relationship of Corrosion with Warming and Climate Change', which brings together papers examining CC induced corrosion (Valdez et al. 2010). Roberge (2010) reports on three aspects of the effect of CC: corrosivity at coastal regions; increased stress on marine systems; pluvial precipitation pattern that may change the corrosive behaviour of the environment and increase the risk of corrosion failures. Measurements are presented of coastal erosion and corrosion and flooding of the British coasts. Corrosivity maps for 2000 and 2100 illustrate the present and future situation (Roberge 2010).

Seas and rivers

Human civilisation begins and spreads along the riverbanks; when the population increase, cities are created and ports built. The major cities of Europe and America were installed on the banks of the Danube, Thames, Guadalquivir, Tiber, Mississippi, Parana, which flow into deltas, estuaries, and finally into the seas of their regions. The dominant presence of water affects the stability of materials and engineering structures, by physicochemical processes of absorption, penetration, dissolution, hydration, hydrolysis, oxidation, carbonation, erosion, corrosion and degradation; therefore, modern technologies of prevention, protection and control are applied (Marcos et al. 2006).

The river flow is not constant; melting snow and heavy rains increase its flow, causing flooding and damaging turbulence, that cover vast expanses of land, degrading and destroying buildings, bridges, roads, structures and facilities.

The sea is a dynamic system in permanent motion, with complex surface currents and winds blowing over its surface generating waves that reach the coast, its facilities and installations. In splash zones, violent, rough waves break down, generating whitish, oxygenated foam, hence increasing local corrosion. Sometimes, these high, powerful waves erode and devastate the coast.

Seawater consists of a solution of many salts and numerous organic and inorganic particles in suspension. Its main characteristics are salinity and chlorinity and, from the corrosion point of view, dissolved oxygen (DO) content, which ranges from 4 to 8 mg/l, depending on temperature and depth. Its minor components include dissolved gases – CO_2, NH_3 and H_2S – found in seawater contaminated by urban sewage. The oceans house algae, bacteria and phytoplankton generate about half of the oxygen in the atmosphere (Melcher 2005).

Ocean surface salinity is determined by the balance between water lost by evaporation and water gained by precipitation. The salt concentration, particularly NaCl, varies from 3.5% to 2.0%, according to the sea location and the massive addition of fresh river water. For instance, in the Red Sea (an enclosed basin), salinity at high summer temperatures is 4.1%, but in the Baltic Sea it is about 2.0% since many rivers feed into it.

The expansion of industry, transportation and the energy sector increases the CO_2 air content. This CO_2 dissolves in the seas, decreasing their pH from 8.11 to 8.06, acidifying with carbonic acid (H_2CO_3), particularly near the coast where the fossil-fuel power stations are located. Acidic water affects the life of marine calcifying organisms such as coral, molluscs and plankton (Bonilla et al. 2011; Anonimous 2013).

Marine infrastructure

The infrastructure of a nation constitutes the physical base of its economic activity; its quality represents a crucial index of the industrial and social vitality of a country. During processes of growth and development, national governments emphasise the maintenance and modernisation of the infrastructure to assure the long life of these assets. Budgets and huge efforts are spent to operate, maintain and upgrade the coastal seas infrastructure, which are composed of two types of structures: fixed and mobile. Fixed structures are on the gulfs and bays commercial and industrial ports, shipyards, rail yards, fuel terminal, naval bases, platforms for oil drilling, production, processing and storage; submarine pipelines and communication cables and electricity grid lines along the coasts (Valdez et al. 2015).

The mobile structures include all types of ships large and small: civil, commercial and military. These include general bulk cargo vessels, for cereals, chemicals, minerals, cryogenic vessels for LNG, cruise tourist and recreational yachts, fishing vessels, container ships, oil tankers, military ships including cruisers, aircraft-carriers, patrol boats, light, nuclear and conventional submarines. The International Maritime Organization (IMO), a United Nations Agency, estimates that at any time about 100,000 ships and vessels roam through the oceans and seas of the world!

The infrastructure elements are located along the coastline. Many infrastructure assets (roads, railways, bridges) were not planned or constructed to handle the actual traffic loads and need repair and rehabilitation work. There are 70,000 structurally deficient U.S. bridges, and more than 15% are at risk of catastrophic, corrosion-related failures (Hummel 2014).

Table 1 presents a summary of the elements of infrastructure, existing on the seacoast and the adjoining mainland. They are made of a great variety of materials of construction: steels, SS, reinforced concrete, plastics and composites, elastomers for lining of storage tanks and pipelines. The correct selection of construction materials will assure the infrastructure resiliency in case of weather extremes.

Ports, shipyards and ships

Ports for maritime commerce, and shipyards for the construction of wooden, seagoing sailing vessels, were established in ancient times, along the coasts of the Mediterranean Sea, by the Phoenicians, the Greeks and the Romans.

Today, a marine port situated near a large city belongs to a coastal ecosystem that comprises industrial parks, agricultural fields and a hydrologic basin with streams

Table 1. Sea coasts infrastructure.

Infrastructure	Assets	Corrosion problems, protection and maintenance
Energy generation	Thermoelectric, nucleoelectric, eolic and hydroelectric plants, dams, electricity grids: cables and towers	Hot corrosion by fossil-fuel combustion gases control of fuel sulphur and vanadium contamination. Erosion-corrosion and stress corrosion cracking in turbines. Feed water treatment
Waterworks	Water supply: pipelines and pump stations, sewage systems water and wastewater treatment plants, pluvial drainage	Control of corrosion, scaling and fouling by correct design. Selection of materials and coatings. Cathodic protection for steel pipelines. Coatings for concrete and steel pipelines
Petroleum industry	Offshore platforms, production wells, marine oil terminals, submarine and land oil and gas pipelines, refineries. LNG regasification plants	Corrosion by sour and sweet gas and crude. Corrosion control with inhibitors. Cathodic protection for steel platforms and pipelines. Control of corrosive emissions
Transportation	Harbours, shipyards, airports, river, railway and seawater bridges, railways, highways and roads, waterways, public transportation	Asphalt pavement deterioration. Repair and restoration of steel reinforced concrete structures. Use of coatings and cathodic protection. De-icing of roads and bridges deck
Communication	Underground cables: telephone, TV, electricity. Communication towers and antennae	Protection of buildings from atmospheric marine corrosion with water repellent plastics and paints. Restoration of facades with polymeric concrete
Construction	Housing, public buildings: hospitals, hotels, stadia, urban recreation areas, parking sites	Building protection from weather by paints and coatings. Restoration of facades with polymeric concrete
Fishing	Harbours, marine vessels, freezing and packaging plants	Marine corrosion and fouling. Anti-corrosive and antifouling paints and cathodic protection

that flow into the sea, in the vicinity of the port. Modern ports are the central link between maritime and land transportation, responsible for the exports and imports that ensure the prosperity of a nation. The ports access, with its dredged channels to maintain a sufficient depth, allows the manoeuvring of ships. This active traffic depends on the port installations and equipment, their quays, wharves and docks, tugs, internal trains and warehouses. Breakwaters, which protect the port from powerful waves, are built entirely of large stones or rocks, or seawater resistant concrete boulders or tetrapods. With the growth of trade, commerce and tourism and the increase in the size of oil tankers, passenger and cargo ships, many ports are being enlarged, their dock accommodations extended and their entry channels deepened. This modernisation of port facilities and equipment is a national priority, and is being actively implemented.

The shipyards operate two types of docks: a floating one and a dry one. The first serves for inspection, maintenance and repairs of ships; it incurs in high maintenance costs because the steel structure requires regular removal of corrosion products, sea fouling and scale and periodical painting, to prevent or minimise corrosion. A floating dock consists of a structure with a U-shaped profile, built of steel, with a double wall deck and a high lateral series of ballast chambers, which, upon filling with seawater, causes the dock to become submerged. In this way, the entry of the ship to be repaired is facilitated and upon emptying the chambers by pumps, the dock emerges from the water with the ship resting on its dry deck. Floating docks incur high maintenance costs because the steel structure, being continuously afloat, requires the regular removal of sea fouling and scale and occasional painting, as the hull of a ship does, to prevent or minimise corrosion. When the water in a port is contaminated and the sea soil beneath the floating dock contains corrosive sediments, accelerated corrosion results in a large number of cavities and perforations in the floating dock floor and the seawater chambers (Schorr and Valdez 2005).

A dry dock is a narrow basin made of concrete, closed by steel gates, used for the building of ships. After the ship is completed the dock is flooded, and it slides slowly into the sea coast, ready to cross the oceans. The dock is also employed for repair and maintenance of all kind of watercrafts. Modern merchant and military ships built mainly from steel are sailing the seas and oceans or moored at piers ports; therefore they are affected by corrosion and fouling.

In biblical times, Noah coated his ark 'within and without with pitch' (Genesis 6 : 14); the Phoenicians, Greeks and Romans protected their wooden vessels with natural materials: pitch, tar, wax, sulphur, asphalt, resins and tallow. The Royal British Navy applied copper sheets to avoid the attachment of fouling organisms. Applying modern marine paints constitute the primary method of corrosion control, with cathodic protection, by impressed current or sacrificial anodes, as a supplementary method. The hull plates of a ship are pre-treated with a phosphate coating, before ship assembly at the shipyard, so as to protect them against corrosion (Valdez 2016).

Ancient and modern ship wrecks are investigated by scientists and divers, trained in coastal and underwater archeology, to discover the corrosion mechanism of metallic artefacts buried in the seafloor for centuries. Artefacts recovered include military suppliers (produced from wrought- and cast-iron), religious jewellery (made of gold, silver, copper and bronze) and ship hardware. These activities constitute the base for the study of maritime civilisation.

Nowadays, Europe, Japan, South Korea and Singapore yards are building large oil barges, oil rigs and drill-ships designed for work at the deepest water, such in the GOM. These are a new generation of fuel-efficient, cheap to run 'ecoships'. These platforms, and the metallic underwater pipelines used to transfer oil and gas from the borehole to the surface, are fitted with sacrificial anodes for corrosion control by cathodic protection. They are towed out to sea and installed at various depths around the world.

Ballast water technology (BWT)

Huge petroleum-tankers haul crude and derivatives from the coast sea terminals to the refineries and consuming markets. They suffer from corrosion in the steel holds; when they cross back to the terminals, the holds are full of ballast seawater, protected with corrosion inhibitors (CIs) (4th Ballast Water Technology Conference 2015). They are added to the ballast seawater as a fine powder, which converts the seawater into a colloidal suspension with particles dispersed in the water that are adsorbed on the steel surface, forming a thin, protective film.

A study has been carried out by analysing the water corrosivity, composition, hardness conductivity and pH. The mechanism of the formation of a gelatinous white precipitate is based on the combination of the water Ca^{2+} and Mg^{2+} ions with the CI chemical structure (Cheng et al. 2016).

About 4400 petroleum transportation tankers from oil-producing countries cross the oceans and seas of the world to energy-consuming countries. If, on average, each tanker has 10 cargo holds, it means 44,000 holds require a CI for their ballast seawater.

Petroleum steel tankers (Figure 1) are cheaper and more efficient than submarine pipelines installed on the seabed for oil transportation. For their trip back, the

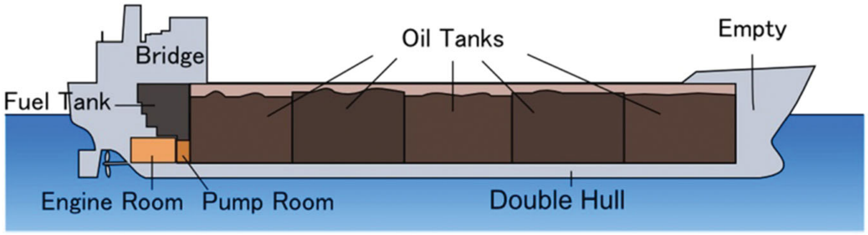

Figure 1. Petroleum transportation tanker showing holds.

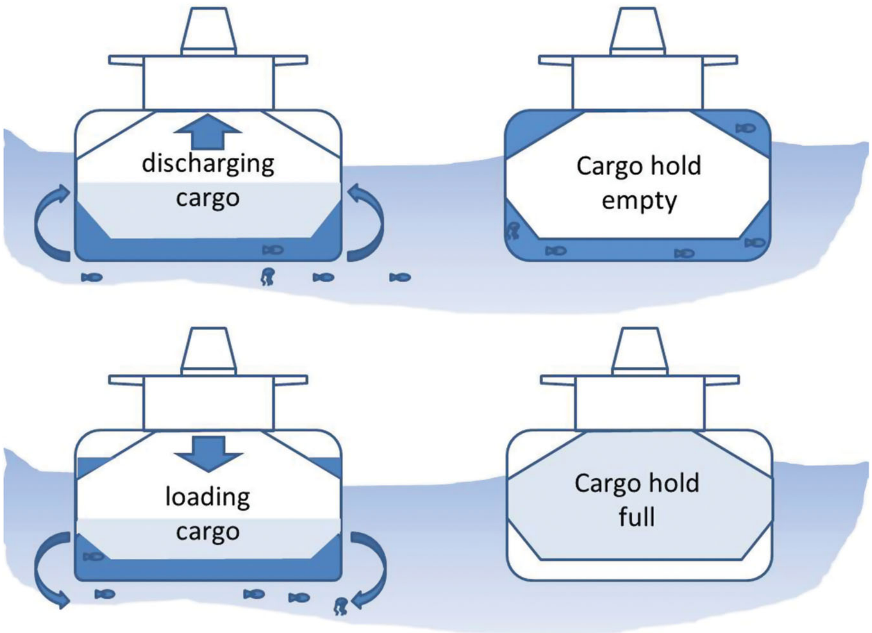

Figure 2. Diagram of ballast water intake and cargo discharge and loading.

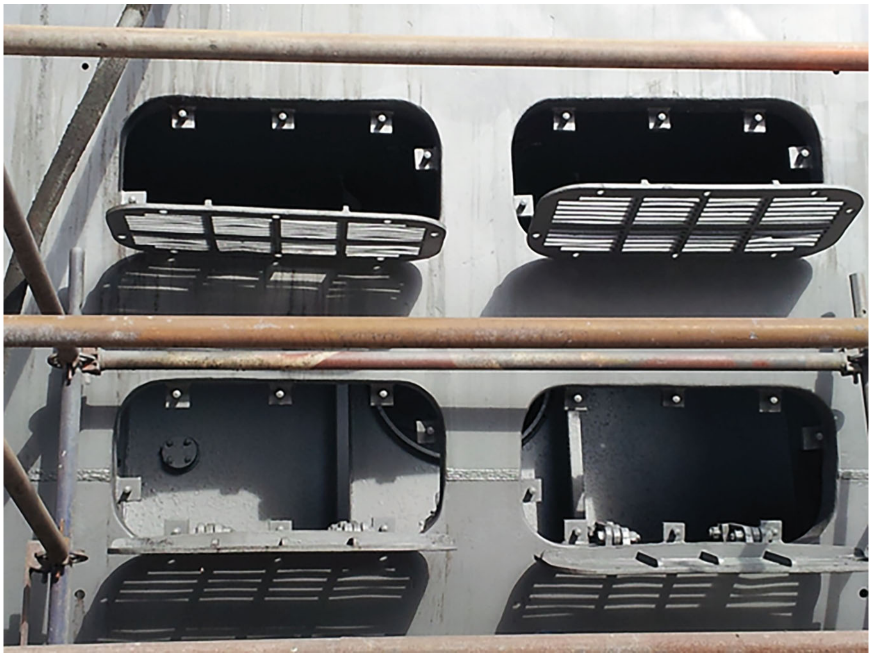

Figure 3. Ship opening, fitted with screens, for ballast water intake and discharge.

tanker holds are filled with seawater to provide adequate stability (Figures 2 and 3) and safety.

Recently, the 5th IMarEST Ballast Water Technology Conference was held in London to deal with the challenges facing the shipping industry. The two main concerns are the avoidance of the ship holds corrosion and the pollution of the ports and the adjacent sea regions, by discharging non-native aquatic species. Two central maritime entities – IMO and the US Coast Guard (USCG) – are involved with the regulations managing these key issues (18th ICMCF 2016).

Marine corrosion

In recent decades the concept of corrosion has been expanded to cover the deterioration in seawater of structures and equipment manufactured from nonmetallic materials, for example, polymers and composites, used for the fabrication of recreation boats, naval vessels and coastguard ships. However, the aqueous corrosion of metallic structures in marine environments is an electrochemical process that occurs on the metal surface by interaction between it and the constituents of saline water. The dominant factors are salinity and the concentration of DO. Salinity influences the conductivity of the water and the chloride (Cl^-) ions also affect the oxide layer formed on the metal surface. When Cl^- penetrates the passive film, it can initiate pitting and crevice corrosion at localised sites, with breakdown of passivity.

During the corrosion process, marine structures lose wall thickness at a rate which varies with depth. Normal corrosion rates (CRs) for steel in seawater lie in the range 0.1–0.3 mm y^{-1} but can increase to 2–4 mm y^{-1} in seawater contaminated with corrosive effluents. Typical cases of severe corrosion are found in the steel retaining walls that separate the land and water in ports. The walls are formed from steel sheet piling about 26 m in length, 3–5 m wide and 10–12 mm in thickness, driven into the marine soil. The sheets interlock together with grooves or guides along each edge, producing a unit of great strength and stiffness. The walls lose thickness by corrosion until perforation of the plate eventually occurs. The corrosion is accelerated by the impact of waves, which break the fragile rust layer that is removed and falls on the sea bed near the wall. With time, the corroded plates must be repaired or replaced to protect the port.

Steel and aluminium alloys are the main metallic materials utilised for the manufacture of civil, industrial and military ships. Their limited corrosion resistance means that they need to be protected by paints and coating and by cathodic protection. The corrosion extent is increased in turbulent flow conditions since it destroys the rust or scale barrier and provides more DO. Fouling tends to reduce corrosion attack by restricting access to DO but corrosion takes place under the fouling by acidic excreta. Polluted seawater greatly accelerates the attack on steel. Naval aluminium vessels are built of the 5XXX alloys series in which magnesium (Mg) is the principal alloying element. UNS A95052 is the main alloy used for marine environments. In steel-hulled ships the upper structures are constructed with Al-Mg alloys (Eliezer et al. 2010). Modern navies and coast guards of many nations use vessels built with A95052, which provide long-life service. The underwater hull is the most vulnerable part but corrosion also appears in the propeller shaft and blades, pumps, engines and fittings. When a badly corroded propeller breaks down, the boat is soon adrift.

A ship navigating in coastal shallow water and the open sea is exposed to three diverse environments and corrosive conditions: (a) the underwater hull, submerged in seawater, covered with marine fouling and supplied with plentiful oxygen; (b) the deck area exposed to sweeping waves, salt spray and heated by solar radiation and (c) the upper structure exposed to marine atmospheric corrosion. A similar situation occurs with three levels of corrosion at sea-installed petroleum platforms.

Stainless steels (SS) are an important class of alloys extensively used in marine environments, in particular in the oil and gas industry, because they combine high mechanical properties and satisfactory corrosion resistance. They are utilised in the offshore petroleum as platforms, serving in areas as such drilling, subsea piping, pumps valves, flanges and fittings. Austenitic and duplex SS are required for high-temperature tubulars and raiser pipes.

An International Congress on Marine Corrosion and Fouling has been held recently in France, with IMarEST as one of the sponsors. It provided an interdisciplinary programme that highlights research efforts understanding biofouling and corrosion of materials and structures immersed in the marine environment. The congress dealt with the basic sciences of sea chemistry, biology, microbiology, paints coatings but also with real problems of marine structures such as biofouling, adhesive strength, biocides, inhibitors and protection.

Marine biofouling

The corrosion of metallic surfaces such as the ship hull in permanent contact with seawater is caused by the accumulation of macro and micro-organisms: algae, molluscs, barnacles, zebra mussels, bacteria, etc. Their adhesion is mediated by the secretion of glue-like substances of extracellular polymers. Corrosion occurs by anodic and cathodic electrochemical reactions promoted by the

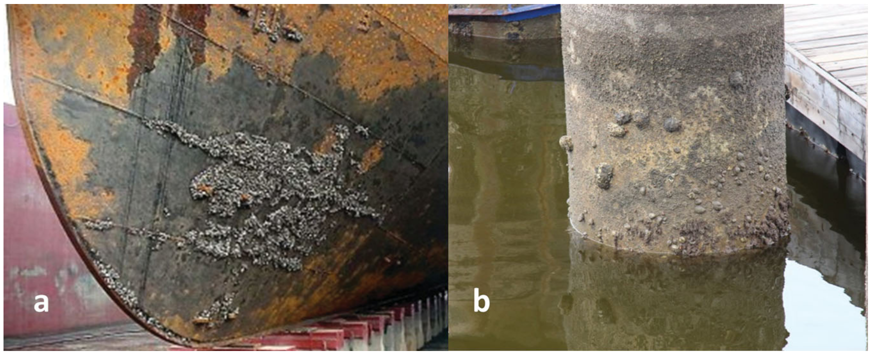

Figure 4. Biofouling cover, (a) ship hall, (b) steel pile for mooring boats.

corrosive metabolites produced by the biofouling fauna and flora (Railkin 2004).

Biofouling on marine vessels can raise the hydrodynamic volume of the vessel, augment the frictional effects loading to an increased drag, reduce the ship speed and rise its fuel consumption.

Many fluvial and marine structures are affected: ports, steel retention wall, shipyards, buoys, oil and gas platforms, coaling water towers of power plants. The physicochemical properties of the marine structure's surfaces such as roughness, texture, construction material, wettability, interfacial alkalinity affect the settlement of marine organisms during biofouling community development (Schultz et al. 2011; Huang et al. 2016) (Figure 4).

The control of marine biofouling is realised, essentially, by application of paints and coatings containing special biocides that are liberated when they come into contact with seawater, preventing the attachment of the marine, fouling organisms. Non-toxic, antifouling coatings, which contain polymers with antimicrobial activity, have been developed and applied (Hellio and Yebra 2009).

The economic importance of the anti-biofouling activities, in particular in the shipping industry, is demonstrated by the involvement of national and international organisations which regulate the industry such as International Maritime Organizations (IMO), Integrated Pollution and Control (European Commission); International Antifouling System (IAFS); International Chamber of Shipping; International Convention for the Control and Management of Ships Ballast Water and Sediments; International Council for the Exploration of the Sea and more.

Influence of pollutants

The quality of the river water that flows into a sea port and its surroundings depends on its physical, chemical, biological and thermal characteristics. The pollutants arrive with the industrial, agricultural and municipal wastes generated in the region. The industrial plants located around the river, produce agrochemicals, petrochemicals, industrial acids (sulphuric, nitric, phosphoric, etc.), plastics, food and beverages, electronic equipment, petroleum distillates and lubricants. They supply soluble pollutants such as acids and salts, insoluble inorganic minerals and heavy metal compounds. During periods of intense irrigation or copious rain, fields sloping towards the river that are used for agricultural purposes contribute pollutants containing biodegradable organic matter and nutrients (phosphorous, nitrogen and potash) from the synthetic and organic fertilisers dispersed thereon. In addition, numerous meat and seafood packaging and cold storage plants; dairy, poultry and pig farms, sometimes pour waste loaded with organic compounds into the river. Biological and chemical processes convert this matter into toxic and corrosive substances. For example, hydrogen sulphide (H_2S), with an unpleasant smell of rotten eggs, is biologically oxidised and converted into sulphuric acid, which is extremely corrosive towards steel and reinforced concrete (Schorr et al. 2006):

$$H_2S + 2O_2 \rightarrow H_2SO_4$$

Power plants, producing electricity by the combustion of fossil fuels, cool their condensers with seawater or river water. The hot cooling water is then discharged into the river, accelerating the chemical and biological processes of decomposition and putrefaction, producing methane (CH_4) and ammonia (NH_3) gases. Effluents with suspended solid particles that float towards the port and the coast are slowly deposited on the sea bed, forming a thick mud composed of silt, clay, sand, alumina, silicates, organic matter (carbohydrates, proteins and fats) and mineral components: oxides, hydroxides and compounds of heavy metals. These settled pollutants may persist for many years; so they have to be removed periodically by dredging, and the soil is remediated and restored. They contain toxic and corrosive components

Table 2. Concentration of pollutants for typical river water and seacoast.

Pollutant	Range(mg/l)
Total solids dissolved and suspended	350–1200
BOD (biological oxygen demand)	100–500
COD (chemical oxygen demand)	200–1000
TOC (total organic carbon)	100–400
Nitrogen (N, total)	50–100
Ammonia (NH_3)	20–100
Phosphor (P, total)	100–1000
Organic sulphide (S)	50–100
Fat and oil	50–100
Heavy metals	100–1000

that annihilate the aquatic, vegetal and animal life, thus enlarging the quantity of organic matter and increasing its biological decomposition, with the production of H_2S, a corrosive agent. The smell of the decomposition products constitutes an early environmental alert of the probable risks and damage to the port infrastructure. The range of pollutants in typical sea coast or river water receiving industrial, agricultural and municipal wastes is presented in Table 2. The concentration varies with the season, type of industry, agricultural activity and the effluents discharged.

Results

The corrosive substances that affect the fluvial and marine coastal infrastructure assets originate directly from the natural environment, from the industrial effluents formed *in situ* by biological and chemical conversion of the organic matter supplied by the agricultural and municipal wastes (Table 2).

Corrosion testing

Laboratory and field corrosion test in seawater and/or artificial seawater were carried out applying gravimetric, electrochemical and surface examination methods, based on ASTM, NACE appropriate standards (ASTM 1963; NACE 2000). The practices recommended in the following standards were followed:

- G1, preparing, cleaning and evaluating corrosion test specimens.
- G3, electrochemical measurements in corrosion testing.
- G4, conducting corrosion test in field applications.
- G5, potentiostatic and potentiodynamic anodic polarisation measurements.
- G31, laboratory immersion corrosion testing of metals.
- G59, conducting potentiodynamic polarisation resistance measurements.
- D1441, preparation of substitute ocean water.
- NACE TM 0169-2000, laboratory corrosion testing of metals.

Metals and specimens

The diversity of the materials used for shipbuilding is conditioned by the requirements of the ship's structural components, their function and the ship operating characteristics. The chemical composition of the alloys selected for corrosion testing is listed in Table 3.

For the sake of brevity, they are classified into three groups:

- Steels, including carbon steels (called hull steels), low-alloyed steel and SS.
- Copper-based alloys, such as bronzes and brasses, that serve in the ship for water supply and sanitary systems, air-conditioning, heat-exchangers, propellers, piping and fitting, etc.
- Aluminium-based alloys, pertaining to the series 5XXX, for example, UNS A95052 for the manufacture of navy, fast vessels and recreation boats.

Corrosion measurements

The corrosion measurements were performed in several marine locations:

- In the GOM coast, at the State of Veracruz, near the mouth of rivers, Mexico.

Table 3. Chemical composition of alloys tested.

		Chemical composition																	
Materials	UNS	Fe	C	Mn	S	P	Si	Cr	Mo	Ni	N	Cu	Sn	Pb	Al	Zn	Mg	V	Ti
Carbon steel	G10450	Bal.	0.43–0.50	0.60–0.90	0.05	0.04	–	–	–	–	–	–	–	–		–	–	–	–
Stainless steel	S31600	Bal.	0.08	2.0	0.03	0.045	0.75	16.0–18.0	2.00–3.00	10.0–14.0	0.10	–	–	–		–	–	–	–
Copper	C12200	–	–	–	–	0.02	–	–	–	–	–	99.90	–	–		–	–	–	–
Bronze	C52100	0.10	–	–	–	0.30	–	–	–	–	–	Bal.	8.00	0.05		0.20	–	–	–
Brass	C26000	0.05	–	–	–	–	–	–	–	–	–	70	–	0.07		Bal.	–	–	–
Aluminium	A91050	0.4	–	–	–	–	0.25	–	–	–	–	0.05	–	–	Bal.	0.05	0.05	0.05	0.03
Aluminium	A95052	–	–	–	–	–	–	0.25	–	–	–	–	–	–	97.2	–	2.5	–	–

Figure 5. The marina at Ensenada port, México.

- In the Lerma naval base, a part of the Sound of Campeche, in the state of Campeche, Mexico.
- The Ensenada port, on the Pacific Ocean, in the state of Baja California (Figure 5). Ensenada port seawater was brought to the Institute of Engineering, at Mexicali, for additional corrosion tests.
- At the Ashdod port on the Mediterranean Sea, done by the Corrosion Research Centre of the Sami Shamoon College of Engineering, Israel.

Corrosion tests were performed by two techniques:

- Electrochemical tests based on ASTM standards, G3 and G5, to determine the electrode potential and the corrosion current density, which is expressed as CR in mm/y. The arrangement comprises a polarisation cell containing a three-electrode system: a specimen of the metal being tested (the working electrode), an auxiliary electrode and a reference electrode, immersed in seawater. A potentiostat was used to obtain the electrochemical parameters.
- A weight loss technique was applied, expressing the loss of wall thickness, in mm/y.

The results presented in Tables 45–6 are representative of the tests done in several marine locations, as described above.

Table 4 indicates the CRs of the alloys tested in GOM water. The active alloys (e.g. carbon steel, bronze and brass) show a similar CR in the range 0.10–0.22 mm/y. On the other side, passive alloys display a reduced CR.

Table 4. Corrosion rates of alloys tested in GOM seawater.

		Seawater		
Material	UNS	type	Location	CR(mm/y)[a]
Carbon steel	G10450	Natural	Campeche	0.22
Stainless steel	S31600	Natural	Campeche	0.0033
Copper	C12200	Synthetic	UV	0.059
Bronze	C52100	Natural	UV	0.10
Brass	C26000	Synthetic	UV	0.20
Aluminium	A91050	Natural	UV	0.018

[a]CR: Corrosion rate, Sound of Campeche, UV: Universidad Veracruzana, Anticorrosion Unity.

Table 5. Corrosion rates of steel and aluminium in sea and river waters.

			Corrosion rate[a]	
Alloy	Water	pH	mm/y	Mpy[b]
Carbon steel	Sea	7.5	0.28	11.2
Carbon steel	River	2 to 3	0.82	32.3
A 95052	Sea	7.5	0.05	2.05
A 95052	River	2 to 3	1.2	42.5

[a]Laboratory test by weight loss simulating conditions in the Kishon port an river.
[b]mpy = miliinch per year.

Laboratory tests in sea and acidified river water (to simulate the condition of water contaminated by acidic waste effluent) show higher CRs than those of passive alloy A95052 (Table 5).

Alloy A95052 exposed in two seas: the Pacific Ocean and the Mediterranean Sea under diverse flow conditions shows a similar open circuit potential but different CRs. The CR measures in the Ashdod port marina is greater than that obtained under laboratory conditions, due to the sea dynamic conditions and the plenty supply of DO (Table 6).

Table 6. Electrochemical characteristics of UNS a95052 in seawater, at Ensenada, Mexico and ashdod, Israel seaports.

Port	Laboratory[a]	Condition	Potential(V)	CR[a](mm/y)
Ashdod Marina	–	Flow	−0.9 to −1.0	1.25 to 1.75
Ensenada	II	Stagnant	−0.8 to −1.2	0.58 to 0.68
Ensenada	II	Flow	−0.8 to −1.2	0.11 to 0.53
Ashdod	CRC	Stagnant	−0.8 to −1.0	0.60 to 0.70
Ashdod	CRC	Flow	−0.9 to −1.0	0.24 to 0.020

[a]II: Institute of Engineering, University of Baja California, Mexico; CRC: Corrosion Research Center, Sami Shamoon College of Engineering, Israel; CR: Corrosion rate.

Conclusions

- The ancient maritime civilisations gradually developed in the sea coasts. Their maritime technologies were adapted and further improved by the modern seafaring nations.
- Combined corrosion and pollution of the marine environment, aggravated by the discharge of industrial, municipal and agricultural effluents, should be treated by methods of prevention, monitoring and control.
- Ports, shipyards and ships are primordial assets of the marine infrastructure that should be protected against corrosion applying paints and coatings and cathodic protection.
- The corrosion resistance value of the metals and alloys tested (listed in Table 4) is expressed by the following sequence:

$$\text{CS} < \text{Al alloys} < \text{Cu alloys} < \text{SS}$$

Local and national environmental organisations such as EPA, in USA and SEMARNAT, in Mexico, in collaboration with ports and rivers authorities and with the assistance of ecologist groups, need to develop and implement regulations covering the prevention of the degradation of their installations, materials and structures.

- To rehabilitate the sea coasts, their rivers and their surrounding environment, the regional enterprises must stop down loading their effluents, clean the river bed by dredging, remediate the soil, restore aquatic life and develop the river landscape for the benefit of the general public.

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