Recent Patents on Corrosion Science, **2010**, *2*, 22-33

Open Access

Corrosion Preventive Strategies as a Crucial Need for Decreasing Environmental Pollution and Saving Economics

A.A. El-Meligi*

National Research Centre, Physical Chemistry Dept, Dokki, Cairo, Egypt

Abstract: It is important to protect the environment by decreasing and controlling all causes, which damage and pollute the society, and affect the economy. Different hazards such as industrial pollution, transportation accidents and damage, radioactive pollution, water pollution, petroleum pollution…etc) occurs all the time. Corrosion is considered one of these causes because it can damage everything of materials, which are used to construct cars, water pipeline systems, bridges and buildings, petroleum constructions (e.g. pipelines, refineries)…etc. The Corrosion of materials cost the national income of developed countries (GDP) losses of 3-4%. Every year, billions of dollars are spent on capital replacement and control methods for corrosion infrastructure. Preventing corrosion is a crucial need to protect the environment and the economy. Accordingly, better corrosion management can be achieved using preventive strategies in nontechnical and technical areas. Therefore, many environmental protection legislation raised to prevent using the environmentally unacceptable materials such as the use of chromium salts is now restricted because chromium (Cr^{+6}) is highly toxic and carcinogenic. Rare earth elements can replace the chromium salts as corrosion inhibitors. Environmentally friendly compounds used in coating process are used to avoid the harmful effects of the currently used compounds.

Keywords: Materials corrosion, preventing corrosion, environmental pollution, environmentally corrosion inhibitors.

1. INTRODUCTION

Many pollutants, such as organic and inorganic compounds in different states are considered hazardous for human health, for animal and vegetal life or when they may cause damage to various materials, for example, metals and nonmetals [1-3]. Accordingly, there is an increasing demand to protect the environment by decreasing and controlling all causes, which damage and pollute the society, and affect the economy. Different hazards occur naturally and deliberately (such as industrial pollution, transportation accidents and damage, radioactive pollution, water pollution, petroleum pollution…etc). Corrosion is considered one of theses causes because it can damage everything of materials, which are used to construct cars, water pipeline systems, bridges and buildings, petroleum constructions (e.g. pipelines, refineries)…etc., [4]. Every year, billions of dollars are spent on capital replacement and control methods for corrosion infrastructure [5]. Therefore, environmental protection legislation raised to prevent using the environmentally unacceptable materials such as the use of chromium salts is now restricted because chromium (Cr^{+6}) is highly toxic and carcinogenic. There is a replacement with environmentally friendly compounds for alloys coating [6, 7]. For example, in United States, it has reportedly levied $10,000-a-day fines against companies when chromium invaded the water supply. In the past, various chromium-based inhibitors have been applied to alloys surfaces such as aluminum. These include strontium chromate, zinc chromate, and chrome phosphate. These are heavy metal-based and largely carcinogenic. In addition, the lead-based coatings were causing health complications in children. Small amounts of chromic acids or potassium dichromate can cause kidney failure, liver damage, and blood disorders. Chromate mists entering the lungs may eventually cause lung cancer. The effect of various oxyanions, MoO_4^{2-}, PO_4^{3-}, VO_4^{3-}, MnO_4^{6-}, SiO_4^{4-} and WO_4^{2-}, on the electrochemical behavior of the depleted uranium alloy in nitric acid has been explored including their ability to inhibit corrosion [8]. Results indicate that chemical or electrochemical activation of the depleted uranium alloy in 0.1 M HNO_3 + 0.025 M MoO_4^{2-} can lead to the formation of a rudimentary coating. As well, chemical pickling of the materials such as stainless steel (SS) is achieved by using HF-HNO_3 mixture [9-12]. However, the disadvantage of such pickling are nitrous gas emissions and nitrate effluents, which pollute the environment. Therefore, replacing traditional electrolytes by HNO_3-free environmentally friendly electrolytes is of increasing interest [13-16]. Such electrolytes contain at least one acid and one oxidizing agent. Hydrogen peroxide (H_2O_2) is an appropriate oxidizing agent and the acids usually used are HF, HCl and H_2SO_4. These acids increase the solubility of corrosion products. Generally, HCl and H_2SO_4 are preferred due to their low costs and low environmentally pollution. As known, these acids are used extensively in pickling carbon and low alloy steels, especially HCl [17-20]. The use of HCl in pickling of metals, acidization of oil wells and in cleaning of scales is more economical, efficient and trouble free, compared to other mineral acids [21]. The great advantage of the HCl over the other acids in cleaning and pickling operations lies in its ability to form metal chlorides, which are extremely soluble in aqueous phase, compared to sulphate, nitrate and phosphate. This higher rate of solubility of chloride salts causes the least polarizing effect and does not hamper the rate of reaction [22].

---

*Address correspondence to this author at the National Research Centre, Physical Chemistry Dept, Dokki, Cairo, Egypt; Tel: 020121488505; Fax: +202-3370931; E-mail: aelV̇meligi10@hotmail.com

1877-6108/10 2010 Bentham Open

Accordingly, researches must be directed towards developing environmentally friendly materials for metals and alloys protection from corrosion in different applications to safe the environment.

2. MATERIALS

A large variety of materials are used for different applications [23]. They are classified into two main categories, (A) Carbon Steels and (B) Stainless Steel and non-ferrous materials. The two categories include 13 types of materials [24], as in Table **1**. These materials are attacked and can be degraded by the corrosive environments. When a material has to be chosen for a given application that choice depends on a number of factors apart from corrosion resistance such as availability and costs of the materials, corrosion resistance, strength, workability and appearance. However, the corrosion resistance itself depends on a number of factors, the most important of which are electrochemical behavior, application in certain environments, mechanical properties, and metallurgical structure. As known, the environment impacts on the material applications. A metal may be corrosion resistance in a certain environment, whereas the opposite may be applied in another medium. For example, aluminum is highly resistant in many aqueous solutions but it will corrode rapidly in a dilute soda solution [25].

Furthermore, the decision as to whether a material is suitable or unsuitable is also co-determined by the application and the service life desired. However, there are a number of design rules should be followed to control the corrosion such as [23]:

1. Welded connections are generally preferable to riveted or screwed connections, which can often lead to crevice corrosion. Crevice corrosion and stress corrosion cracking were occurred in a vessel of stainless steel [26]. The damage was found mainly in the vicinity of welded area. There was a possibility of poor weld quality being the cause of failure. The dissimilar metal weldment joining Boiling Water Reactor is one of the more complex configurations in the entire recirculation system. Corrosion problems occurred due to deposit, which lead to intergranular stress corrosion cracking [27].
2. Tanks, reactor vessels …etc. should be so designed that they are easy to empty and clean.
3. The design should allow for simple, efficient and low cost maintenance and inspection.
4. Ensure that components (e.g. pumps, outlet pipes…etc.) expected to be liable to corrosion are simple and rapid to exchange.
5. Avoid mechanical stresses (to prevent stress corrosion).
6. Avoid sharp contact between dissimilar metals (to prevent erosion corrosion).
7. Avoid contact between dissimilar metals (to prevent contact corrosion or galvanic corrosion).
8. Avoid strong local heating because corrosion generally increases rapidly with temperature and occasionally evaporation leading to increased concentrations.
9. Wherever possible attempt to avoid contact with aggressive substances.
10. The most general rule is that heterogeneity should be avoided (local stress concentrations, temperature differences, sites where moisture and dirt can accumulate.

The corrosion engineer is primarily interested in the chemical properties (i.e., corrosion resistance) of these materials, but it is also necessary to have knowledge of their properties to verify desired materials performance. The properties of the materials are corrosion resistance and mechanical behavior (such as, ductility, tensile strength, fatigue, stress rupture, hardness, toughness and brittleness) [28, 29]. They are helpful in specifying their applications.

The aforementioned materials face 44 types of corrosion phenomena [24], for example, as coded in the 'Corrosion Atlas', 01- oxygen corrosion, 04- acid corrosion, 06- high temperature corrosion, 09- salt corrosion, 14- galvanic corrosion, 40- coating failures, and 44- 475 ºC embrittlement [30]. Also, there are 25 types of system from which the corroded part originates, for example 01- steam systems (boiler feed water systems, steam boiler,…etc.), 04- heating systems (central heating systems, hot water heating systems), 05-cold and hot tap-water systems (drinking water systems), 09- air conditioning systems, 12- cleaning systems and pickling baths, 19- aircraft, 20- automotive systems (cars, trains,…etc.), 21- ships and marine systems, and 25- other equipment and installation systems. Based of the 'Corrosion Atlas', there are many corrosion cases history are summarized, provided with complete description for each case [24]. The case history 01.01.01.01 represents the following, the first two digits (01) is for materials (carbon steel), the second two digits (01) is the system (boiler feed system), the third (01) is corrosion phenomena (oxygen corrosion), the last two digits are for numerical order. This case represents the corrosion of a boiler feed system (the part of the system is the feed line from deaerator to boiler). The C-steel part is subjected to deaerated feedwater (pH 5, chloride 10 ppm and temperature 105 ºC). The main cause of corrosion is oxygen, which is carried by feedwater due to malfunctioning deaerator. The deaerator should be improved and keeping the water alkaline.

In fact, carbon steel is the most widely used engineering material, accounts for approximately 85%, of the annual steel production worldwide [31]. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in marine applications, nuclear power and fossil fuel power plants, transportation, chemical processing, petroleum production, pipelines, mining, construction and metal-processing equipment. Because carbon steels represent the largest single class of alloys in use, both in terms of tonnage and total cost, it is easy to understand that the corrosion of carbon steels is a problem of enormous practical importance. This is the reason for the existence of entire industries devoted to providing protective systems for irons and steel such as using protective coating and corrosion inhibitors. Carbon steels are generally categorized according to their carbon content. Generally speaking, carbon steels

Table 1. Materials Classification as in the 'Corrosion Atlas' [24]

Carbon Steels	Stainless Steel and Non-Ferrous Materials
01. Unprotected carbon steel	04. Stainless Steel (304, 316, …etc. this material has to contain iron and must contain at least 10.5 % chromium)
02. Galvanized Steel	05. Nickel and Cobalt-base alloys
03. C-Steels provided with a coating other than Zn	06. Copper alloys
	07. Al-Mg and their alloys
	08. Lead (Pb), Tin (Sn) and Zinc (Zn)
	09. Noble and reactive metals (Silver (Ag), gold (Au)
	10. Plastics
	11. Concrete and cement mortar linings
	12. Coated metals
	13. Other materials (natural rubber, glass, wood, ceramics)

contain up to 2% total alloying elements and can be subdivided into low-carbon steels, medium-carbon steels, high-carbon steels, and ultrahigh-carbon steels [32].

Low-Carbon: Steels contain up to 0.30% C. The largest category of this class of steel is flat-rolled products (sheet or strip), usually in the cold-rolled and annealed condition. The carbon content for these high-formability steels is very low, less than 0.10% C, with up to 0.4% Mn. Typical uses are in automobile body panels, tin plate, and wire products.

For rolled steel structural plates and sections, the carbon content may be increased to approximately 0.30%, with higher manganese content up to 1.5%. These materials may be used for stampings, forgings, seamless tubes, and boiler plate.

Medium-Carbon: Steels are similar to low-carbon steels except that the carbon ranges from 0.30 to 0.60% and the manganese from 0.60 to 1.65%. Increasing the carbon content to approximately 0.5% with an accompanying increase in manganese allows medium carbon steels to be used in the quenched and tempered condition. The uses of medium carbon-manganese steels include shafts, axles, gears, crankshafts, couplings and forgings. Steels in the 0.40 to 0.60% C range are also used for rails, railway wheels and rail axles.

High-Carbon Steels: Contain from 0.60 to 1.00% C with manganese contents ranging from 0.30 to 0.90%. High-carbon steels are used for spring materials and high-strength wires.

Ultrahigh-Carbon: Steels are experimental alloys containing 1.25 to 2.0% C. These steels are thermomechanically processed to produce microstructures that consist of ultrafine, equiaxed grains of spherical, discontinuous proeutectoid carbide particles.

A number of cases histories are provided to show different corrosion phenomena, which deteriorate the materials used in different applications [24]. As presented in the case history 01.01.03.02, the corrosion of water tube boiler (14.5 MPa) (the part corroded of the system is the wall tube). C-steel part is attacked by caustic solution (high pH). There are deposits shield the metal from the bulk solution, such as magnetite. The main cause of corrosion is sodium hydroxide, which will first dissolve magnetite deposit, as in the following equation:

$$4NaOH + Fe_3O_4 \rightarrow 2NaFeO_2 + Na_2FeO_2 + 2H_2O \qquad (1)$$

The alloy surface will be attacked by NaOH:

$$Fe + 2NaOH \rightarrow Na2FeO2 + H_2 \qquad (2)$$

The formation of H_2 can lead to further corrosion. To overcome this problem, the amount of NaOH should be reduced by a water treatment programme based on coordinated phosphate. Also, the excessive water side deposition should be prevented by annual inspection and cleaning of the boiler if necessary.

Corrosion of carbon steel (case history 01.08.04.01) and bitumen-coated steel (case history 03.14.26.01) are presented in corrosion Atlas [24], respectively. First case is subjected to acid corrosion, which attack the pump impeller part of the waste water transport system. The conditions were water with some ppm phenol and temperature was 50 up to 100 ºC. There is a pH drop caused by contamination with H_2SO_4 as a result of a failure. To solve this problem: the pump must be constructed completely of AISI 316, the waste water has to diluted with cold water to reduce the acid concentration to maximum 1 % and temperature to maximum 50 ºC. The second case is the corrosion by stray current in underground pipe of gas supply system. The cause of corrosion is due to earthing current left the pipe and caused local attack. To overcome the problem, installation of an isolating plastic insert at the gas meter.

3. CORROSION PHENOMENA

In most environments, metals are not inherently stable but tend to revert to compounds, which are more stable; a process with is called corrosion [33]. Corrosion is derived from the Latin "corrosus" meaning gnawed away.

The definition of corrosion is "the chemical or electrochemical reaction between a material and its environment that produces deterioration of the material or of its properties". On the other hand, corrosion is considered as including combined forms of attack in which the simultaneous occurrence of corrosion by chemical or electrochemical attack [24, 34]. The chemical attack or dry corrosion occurs under dry conditions, such as high temperatures in gaseous environments, molten salts and liquid metals. Dry corrosion process is a direct reaction between a metal and the corrosive environment. Dry corrosion is of great importance in a number of petroleum refining processes. It includes the attack of hydrogen sulfide and other sulfur compounds on steel and various alloys at elevated temperatures. Solutions to this type of corrosion generally depend on metallurgical approaches, e.g. variations in composition, heat treatment of the selected metal or alloy. In fact, high temperature corrosion of metals and alloys always involves oxidation process. For example, a metal reacts with oxygen at high temperature by initial adsorption of oxygen, chemical reaction to form the surface oxide, oxide nucleation and lateral growth into a continuous film. Such film may protect the underlying metal [35]. One of the well known oxidation is the iron oxidation in oxygen (as pure metal or in carbon steel alloys) at high temperature [36]. Two types of oxide film (scale) can be formed:

1. Low temperature scale forms below 570 ºC. It consists of two layers, an internal layer of magnetite (Fe_3O_4) and an outer layer of heamatite (Fe_2O_3).
2. High temperature scale forms above 570 ºC. It has three layers of wustite (FeO) adjacent to the metal, a layer of magnetite and an outer layer of hematite. The thickness of the scale and the relative amounts of the different phases present depends on the temperature and heating rate, gas composition, alloying elements and time of scale formation.

Wet corrosion is an electrochemical process; in practice it is limited to nearly 232 ºC as an upper temperature. The electrochemical corrosion results from reaction between a metal surface and an ion-conducting environment. This process can occur if the metal contact with an electrolyte for transport of electric current. Most cases of electrochemical corrosion proceed in aqueous media such as natural water, atmospheric moisture, rain, and wet soil. Also, other environments e.g. acids, petroleum products, cooling water, chemical solutions,…etc. For example, water is presented in refinery by different sources, such as the crude itself, through injection of water of steam to aid in the steam distillation of various petroleum fractions, water washing or aqueous solution contacting various intermediate and product streams in refining and petrochemical processes. In refineries, acid (lower pH) attacks the active metals such as Fe, Cu, Zn, Al and others. The acidity is imported to refinery fluids by solution in the water phase of various gases, e.g. H_2S, hydrocyanic acid, CO_2, organic fatty acid and naphthenic acids and HCl. The HCl is formed in refinery by thermal decomposition and hydrolysis of Mg and Ca-chlorides. The problem of acidity in refineries is solved by using alkali to neutralize the medium, but the problem of alkali is the formation of scales. Other neutralizer used such as ammonia, and cyclohexylamine. Ammonia has high neutralizing power, low cost easy to handle and have low environmental effect [37].

In fact, the effect of the aggressive environments, such as, acid rains, chemical disposals, petroleum products (include corrosive media e.g. naphthenic acid, sulfur compounds), and others on the materials shows that there are consequences (technical and economic) and problems of corrosion affect the society [24, 34]. The naphthenic acids are generic name used for all the organic acids present in crude oils. These acids are most active at their boiling point and the most severe corrosion generally occurs on condensation of petroleum products [38-40]. Most of naphthenic acids are believed to have the chemical formula $R(CH_2)_nCOOH$ where R is a cyclopentane ring and n is typically greater than 12. Also, other than carbon and hydrogen, sulfur is the most abundant element in petroleum. It may be present as elemental sulfur, hydrogen sulfide, mercaptans, sulfides, and polysulfides. If the temperature is above 288 ºC (550 ºF), and very low naphthenic acid content, cladding with 5 % Cr or 12 % Cr is recommended for crude over 1% sulfur when no operating experience is available. When hydrogen sulfide is evolved, an alloy containing a minimum of 9% chromium is preferred. In contrast to high-temperature sulfidic corrosion, low-alloy steels containing up to 12% Cr do not seem to provide benefits over carbon steel in naphthenic acid service. 316 SS (with 2.5% Mo minimum) or better 317 SS with a higher Mo content (3.5% minimum) cladding of vacuum column is recommended when total acid number (TAN) is above 0.5 mg KOH/g and in atmospheric column when the TAN is above 2.0 mg KOH/g The case history 01.11.06.06 is presented in Corrosion Atlas [24]. It represents the corrosion of bottom effluent line of the refinery distillation column (made of carbon steel). The type of corrosion phenomenon is high-temperature corrosion (in presence of hydrocarbon and sulphur compounds originating from sulphur-containing crude oil, temperature is 390 ºC and pressure is 25 bar). The pipe fracture caused a fire which led to total destruction of the plant.

3.1. Technical Consequences

The working life of the industrial plants such as petroleum refiners and pipelines system, transports, bridges,…etc. will be shortened due to corrosion attack. They are sometimes accompanied by accidents, especially in case of a phenomenon such as stress corrosion cracking. Another technical consequence of corrosion is disturbance of the machine and equipment performance, e.g., the corrosion products becoming lodged between moving parts and blocking them and increasing the friction of these parts. This may lead to different accidents, such as fires or explosions. This process occurs because of leakage resulting from perforation of a material by pitting corrosion [37-39]. As well, there is a possibility for food contamination due to the dissolved corrosion products or using unacceptable materials for food preparation and storages. Therefore, contamination of consumer products, e.g. food during production, storage and/or transport, due to release of chemicals caused by contact with technical components and corrosion products is of great concern. Water contamination with the corrosion products due to perforation and breakdown (such as copper sulphate in water due to copper corrosion), and due to using oxidants such chlorine should be treated [40, 41]. The preservation of the biological stability of potable water during its storage in reservoir or its transport through the distribution systems can be achieved by (a) the use of chemical disinfectants (in particular by addition of chlorine) which is the widely used technique, but the use of chlorine induces a number of problems, in particular the development of oxidation by-products like trihalomethans (THM), among which some are recognized as carcinogenic products for animals. (b) The use of new techniques such as nanofiltration that can eliminate bacteria and significantly decrease the concentrations of organic matter at the inlet of the distribution network and in the potable water [42]. Nevertheless, chlorine has a disinfectant effect on planctonic bacteria, if considering that only around 10 % of free bacterial cells are living cells, i.e. are able of respiratory oxidation. However, the bacteria fixed on granular activated carbon particles can be resistant to chlorine, as well as bacteria in aggregates. Thus, the addition of chlorine in potable water does not inhibit the formation of a bio-film at the surface of pipe walls. In the same way, protozoa transported by potable water can resist to chlorine.

3.2. Economic Consequences

Like other natural hazards such as earthquakes, corrosion can cause dangerous and expensive damage to everything from cars, home appliances, bridges…etc. [4]. Therefore, corrosion is causing a heavy burden to economy all over the world. The corrosion costs should be drawn between the direct and indirect costs. The Direct costs of corrosion are:

- capital: replacement of buildings, installations and machinery.
- design and control: materials selection, corrosion allowances, special treatments (e.g. acid cleaning), control agents, maintenance and repair. The indirect corrosion costs are:
- depreciation and interest losses; -product and production loss, technical support; and -additional reserves, insurance.

British and American surveys have shown that the overall- direct plus indirect costs caused by corrosion amount to approximately 4.5 % of Gross National Products (GNP) [24]. That represents about $ 500 per annum per capita of the population of the industrialized countries. Fig. (**1**) shows the direct corrosion costs in USA. The corrosion costs by the five major industry categories in USA. (infrastructure, utilities, transportation, production and manufacturing, and government was $137.9 billion per annum [43]. Also, it is estimated that about 10 % of the world's steel output that is nearly 5 x 10^7 tonnes per year, is made for the purpose of replacing corroded steel. In the UK, it has been calculated that one tonne of steel is converted completely into rust every 90 seconds. Apart from the waste of metals, the energy required to produce one tonne of steel from iron ore is sufficient to provide an average family home with energy for 3 months [23]. As well, corrosion will lead to additional consumption of energy, loss of health due to toxic materials, and even loss of life caused by explosions or by transport (aircraft) due to corrosion degradation. The case history 01.11.06.06 presented in Corrosion Atlas [24] showed a catastrophic action due to distillation pipe failures, which caused a fire and lead to total destruction of the refinery plant. Accordingly, effective corrosion prevention and control may contribute towards the limitation of economic, social and personnel loss. All these consequences increased the pressure of society to control the corrosion attack and to safe the environment.

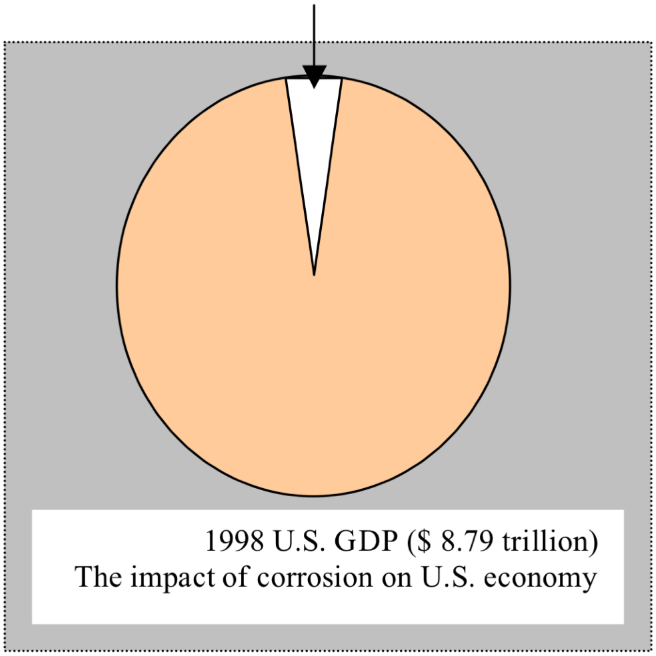

Fig. (1). Direct Corrosion Costs: $ 276 billion (3.1 % of U.S. GDP) [4].

4. CORROSION CONTROL

The control of corrosion is considered an integral part of the pressure, which load by society. Therefore, a number of measures are presented for the corrosion control, such as [4, 24]:

(I) Choice of different materials. Using more corrosion resistant and also putting into consideration the mechanical properties, and economic and environmental matters, for example, improving the oxidation, wear and corrosion resistant materials of TiAl alloy at high temperature for saving energy was processed by the ion implantation with some elements including Nb. High-temperature Nb ion implantation and Nb+C combined implantations are effective for improving the oxidation resistance of TiAl alloy [44]. Furthermore, the thin film coating of high-Al alloys such as CoNiCrAlY, TiAlN and NiCrAl provide a promising surface modification method for improving the oxidation, wear and corrosion resistance of steels and alloys at high temperature. These effects are based on formation of a protective Al_2O_3 oxide scale on material surfaces. For practical application to sliding seal materials the TiCrN film was applied to the actual seal ring for steam turbines, and its sliding properties were successful performance. Also, the life time of many steel structures can be remarkably improved by protecting the steel with zinc layers. The reduction of the corrosion rate of zinc is therefore an important topic. These results can be obtained by introducing zinc alloys with lower corrosion rate (ZnNi, ZnFe, etc.) or by protecting the zinc surface with organic or inorganic layers able to reduce the corrosion rate. In the past a very popular way to reduce the corrosion rate of zinc was the use of chemical conversion layers based on Cr^{6+}, able to increase the passivation tendency of the zinc (chromating) [45]. This procedure is quite effective also for improving the adhesion of organic coatings deposited on the zinc surface, but there is the important problem that the use of chromium salts is now restricted because of environmental protection legislation. It is therefore very important to develop new zinc surface treatments environmentally friendly to improve the corrosion resistance of zinc and the adhesion with the final organic protective layer.

(II) Design modifications. By adapting the design, treatment and construction, the part of the system can be rendered less vulnerable to corrosion.

(III) Application of coatings. The materials can be separated from the aggressive environment by using metallic, inorganic, non-metallic or organic coatings.

(IV) Change of environment. It is mainly done by using inhibitors.

(V) Intervention in the reactions, in particular with electrochemical methods, e.g. cathodic protection with sacrificial anodes or with inert anodes with impressed currents, and anodic protections (e.g. to protect stainless steel).

(VI) Changing the procedures: introduction or modification of procedures for start up, shut down, operation and storage, recommendation concerning inspection, corrosion monitoring and maintenance.

5. ENVIRONMENTALLY FRIENDLY COATINGS

The material can be protected from the aggressive environment using different types of coats such as metallic, inorganic, non-metallic or organic coatings [46, 47]. It will be very important to choose the materials, which are environmentally friendly, because pollution has become a problem in a conservation society. It has been estimated, in UK, for example, that about 360,000 tonnes of volatile organic compounds are released into the atmosphere every year as a result of paint application [23]. Solvents are added to coatings to disperse the other constituents of the formulation and to reduce viscosity, thereby enabling application of the coating. Solvents traditionally make up about 60% of the total formulation. A wide variety of solvents are used in paints, including aliphatic hydrocarbons, aromatic hydrocarbons (toluene, xylene, and the trimethyl benzenes), ketones (methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK)), alcohols, esters, and glycol ethers. These solvents are dangerous and not safe, so they are replaced with 'high solids water-based' formulations for less evaporation of undesirable materials. Also, dangerous lead (Pb) additives have mostly been replaced with harmless materials such as TiO_2, also, Chromium free" aluminum conversion treatments new bath formulations and treatment procedures in order to further improve the effectiveness of this kind of environmentally friendly aluminum pretreatment in a titanate baths [48]. Cerium and molybdenum were used to form conversion coatings on Al-alloys. the coating generated on both alloys was predominantly a hydrated aluminium oxide. It appeared from SEM and Scanning AES that the cerium was concentrated locally on the oxide. X-Ray Photo-electron Spectroscopy (XPS) indicated that the cerium was present in a mixture of Ce(III) and Ce(IV) oxidation states. Many of these cerium rich areas were associated with the constituent particles (large intermetallics). Mo(VI) was detected with XPS and there was evidence from SEM and AES to suggest that there was local enrichment of Mo around the intermetallic particles [6, 49, 50].

A new corrosion protection coating system for automotive steel has been developed through interface engineering affected by an energetic plasma process. In the plasma process, the steel substrate was subjected to plasma cleaning and in situ plasma polymerization deposition [51].

5.1. Coat Thickness and Particle Sizes

The thickness of the coat is an important factor for protection, as well; the particle size of the coat can affect the corrosion protection. Heavy duty in severe environments such as offshore use or water treatment and chemical applications, may require a combination of coating several millimeters thick, but a lacquer inside a can of food may be a little as 5 μm.

The particle size of the coating compounds can help to provide more efficient coat. Particularly, the surface of the materials (metal, alloys,…etc.) is not perfectly smooth. Figs. (**2**, **3**) show the surface morphology of the as-received materials of Al-alloy and C-steel alloy, respectively. The photomicrographs of both alloys show a rough and non-uniform surface with semi-cracks spreads on it [52, 53]. The imperfections of the surfaces have different widths (nearly up to 7μm and lengths (up to 70μm). As stated [23], metals are rarely uniform in composition or structure whether we consider them from a macroscopic or a microscopic viewpoint. Therefore, nano-materials may be more efficient than the other conventional materials' sizes because they can penetrate into the micro-voids and micro-cracks all over the surface to give the best protection for materials. The effect of the pigment (conventional ZnO and nano-ZnO)/binder ratio (P/B) on the corrosion resistance properties of polyurethane paints on carbon steel was investigated [54]. Better anticorrosive protection is achieved by the coatings pigmented with nano-ZnO and a lesser amount of nano-ZnO is required. Nowadays, nanocrystalline powders can easily prepared and applied in a wide variety of fields, such as Abrasives, catalysts, cosmetics, electronic devices, magnetics, corrosion protection, pigments and coatings, ceramics,…etc. Nano-ZnO is manufactured using a patented Physical Vapor Synthesis (PVS) process [55], as in Fig. (**4**). Also, other nano-oxides such as iron oxide (Fe_2O_3) can be obtained by using the PVS process (Fig. **5**).

Generally, there are a number of factors to take into account during selection of the coating compounds to help increasing the corrosion resistance of the materials and to safe the environment [28], as shown in Table **2**.

6. AN OVERVIEW OF INHIBITORS

6.1. Historical Perspectives

It is stated by Hackerman that "all corrosion reduction processes are inhibitors" [56]. However, by the common use, the term inhibitors is taken to mean retardation of the metal oxidation rate ($M \rightarrow M^{+n} + ne$) by the addition of chemicals to the system *via* the fluid phase. Corrosion inhibitor must be felt on the metal side of the metal/fluid interface (i.e. the inhibitor should be transported to the interface of the metal or alloys surface to perform inhibition) [57]. Therefore, metal and alloy surfaces are very important to be well processed and well finished. This is to decrease the surfaces' defects as possible as it can.

Table 2. Considerations for Optimum Selection of a Coating

Key Aspects	Considerations
-Project requirement	-Nature of structure -Lifetime required -Primer -Access for maintenance -Special requirements, e.g. contact with food
-Exposure conditions	-Climate -Atmospheric or immersed -Cathodic protection -Contact with chemicals -Impact and abrasion -Surface temperature
-Surface preparation	-Techniques and staff available -Contamination removal -Ability to achieve grade -Access available -Environment and safety
-Application and safety	-Techniques and staff available -Expected climatic conditions -Access available -Time and number of coats required -Environment and safety
-Economics	-Available budget -Can economics be made

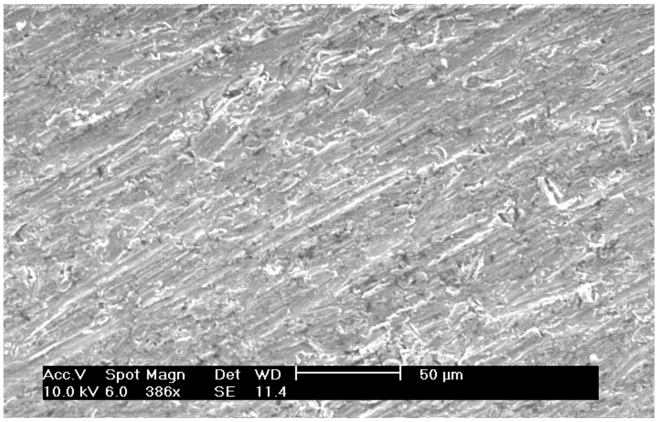

Fig. (2). Photomicrograph of the as-received Al-alloy surface. Surfaces roughness and semi-cracks are observed [52].

Failing to follow these considerations will lead to coating failure, as in the case history 03.21.40.06 in the 'Corrosion Atlas' [24]. As presented, the material is epoxy coating (two coats) on steel surface. This material is used in construction the interior seawater ballast tank of the ship. This part was in service for 6 months. The description of the corrosion phenomenon is rusty pinpoint area above clean area. The coating failure was due to many conditions such as poor application, fast drying or heavily pigmented cause dry spray, over spray, the second coat was applied over the first without removing the overspray…etc. To overcome this problem, better application procedures should be followed (proper gun adjustment and gun handling, removing overspray, closer application inspections. Also, apply slower-drying coating such as oil based materials or catalyzed epoxies.

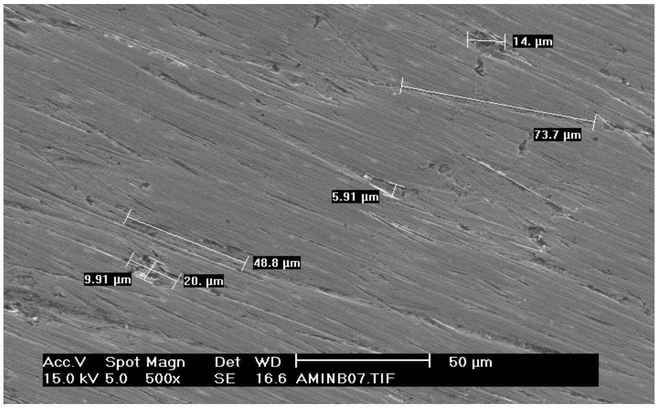

Fig. (3). Photomicrograph of the as-received C-steel alloy. The voids have different widths (nearly up to 7µm and lengths (up to 70µm)) [53].

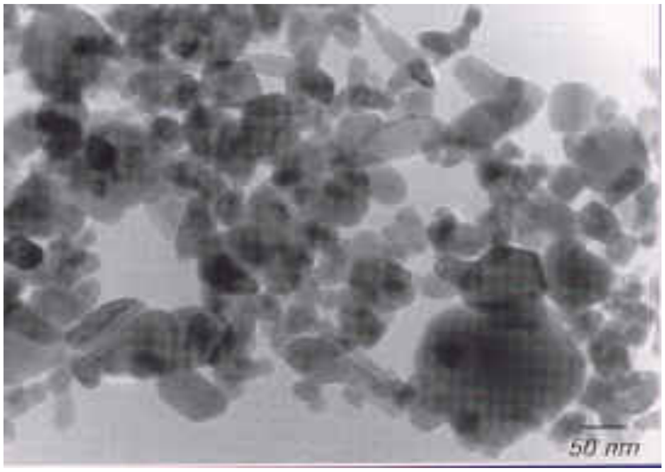

Fig. (4). TEM showing zinc oxide (ZnO) typical nano-particle size distribution [50].

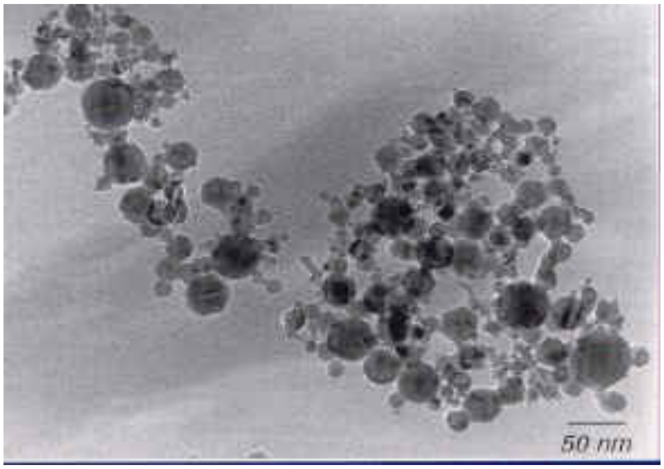

Fig. (5). TEM showing iron oxide (Fe_2O_3) typical nano-particle size distribution [55].

Referring to corrosion phenomena in the technical literature probably appear earlier but were available at least by the end of the 18th century [58]. The earliest corrosion inhibitors were made using naturally extracted compounds, which can be considered as environmentally friendly inhibitors, such as starch, molasses, egg white. The first patent in corrosion inhibition was to Baldwin, British patent 2327, which specified the use of molasses and vegetable oils for pickling steel in acids [32].

6.2. Selection of Inhibitors

As defined, the corrosion inhibitors are substances, when added to corrosive environment, decrease the rate of attack on a metal or alloy [59]. It is mainly used to control the corrosion rate, which is usually expressed by different means such as the change in material mass, the depth of the surface, which has been corroded and the number and quantity of pits formed [60]. The inhibitors are classified according to their effect on the electrochemical reactions, which make up the overall corrosion process, into three main types [61, 62]:

6.2.1. Anodic Inhibitors

These inhibitors affect the anodic reaction and its polarization curve. They show an increase in the polarization (a large potential change results from a small current flow).

The anodic reaction whereby a metal dissolves while releasing electrons is:

$$Fe \rightarrow Fe2^{+} + 2e \qquad (3)$$

or is converted into solid compound, such as:

$$2Al + 3H_2O \rightarrow Al2O3 + 6H^{+} + 6e \qquad (4)$$

The potential shifts to more positive direction (anodic direction), as shown in Fig. (**6**) [37]. The anodic inhibitors function to reduce the dissolution rate of the passivating oxide [60] to repassivate the surface by repairing or reformation the oxide film, to repair the oxide film by plugging pore with insoluble compounds and to prevent the adsorption of aggressive anions.

An example of this type of inhibitors is chromate ions, which must be replaced by more environmentally inhibitors, such as rare earth elements [63, 64], also, molybdate, nitrite and phosphate [65]. Organic compounds such as formaldehyde, pyridine and polyethylene polymer used to inhibit steel corrosion. These types of inhibitors are considered "dangerous inhibitors", especially, at lower concentrations pores and defects can arise on the oxide layer, where the attack will be increased causing corrosion acceleration.

6.2.2. Cathodic Inhibitors

These types of inhibitors are mainly influence the cathodic reaction and the cathodic polarization curve, as shown in Fig. (**6**).

For example, cathodic reaction proceeds in acid solution:

$$2H^{+} + 2e \rightarrow H_2 \qquad (5)$$

Potential shifts towards more negative values (cathodic direction). Examples of the cathodic inhibitors are polypposphate (sodium polyphosphate ($Na_2P_2O_7$), Sodium tripolyphosphate ($Na_5P_3O_{10}$)). Organic compounds such as N-heterocyclic e.g. imidazole and benzimidazole. These inhibitors are added to boilers to prevent adherent deposites of calcium and magnesium [66]. There are some cathodic inhibitors such as arsenates, sulfides and selenides used to poisons the cathodic process by interferring with the cathodic reaction (hydrogen atom formation and hydrogen gas evolution in acid medium, equation 5). These inhibitors are environmentally unacceptable because they are toxic [67].

Generally, cathodic inhibitors are considered "safe inhibitors", because they provide inhibition of the cathodic reaction even with a very low concentartion of the inhibitor.

6.2.3. Mixed Inhibitors

These inhibitors work to inhibit both anode and cathode reactions, as in Fig. (**6**). Benzotriazole is used widely for copper and copper alloy protection [68, 69]. Quniolines and thiourea used to inhibit the dissolution of mild steel in H_2SO_4. Amines, amides, acridines used to inhibit steel corrosion in HCl.

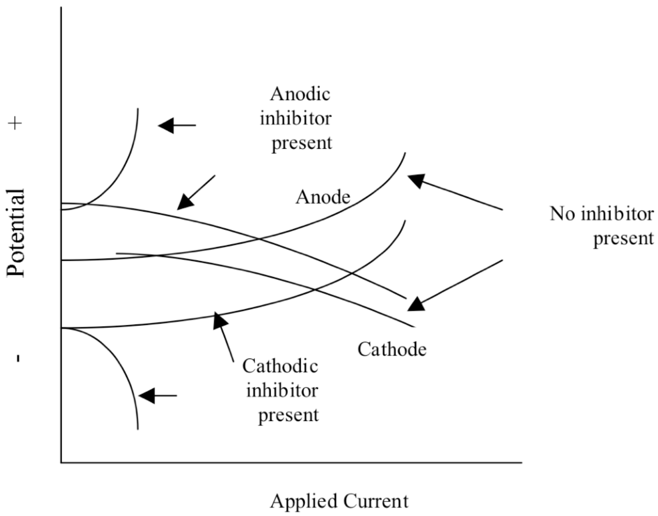

Fig. (6). Schematic diagram shows effect of inhibitors on polarization curve.

The inhibition is accomplished by one or more of some mechanisms such as [23, 24]:

1. Some inhibitors retard corrosion by adsorption to form a thin and invisible film on the material surface.
2. Others form visible bulky precipitates, which coat the metal and protect it from attack.
3. Another common mechanism consists of causing the metal to corrode in such a way that a combination of adsorption and corrosion product forms a passive layer.

The inhibitor can be transported to the metal surface from [70]:

- A liquid corrosive environment, in which the inhibiotr is present in dissolved or dispersed form.
- A corrosion preventing fluid with an additive of inhibitor.
- The atmosphere in a package, in this case inhibitor is required having a suitable vapour pressure. It is called

volatile corrosion inhibitor or vapor phase inhibitors. They are transported in a closed system to the site of corrosion by volatilization from a source. In boilers, volatile inhibitors such as morpholine or octadecylamine are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide. In closed vapor spaces, such as shipping containers, volatile solids such as carbonate, and benzoate salts of dicyclohexylamine are used.

7. ENVIRONMENTALLY FRIENDLY INHIBITORS

In fact, much attention should be given when selecting inhibitors for investigation or application to ensure the environmental regulations. The inhibitor must be environmentally friendly to replace the older, which is more toxic and harmful to the environment [71, 72]. When applying the ideas of green chemistry to the area of corrosion inhibitors, the major improvement is in the area of eliminating environmentally toxic compounds, such as chromates, dichromate and nitrites, and replacing them with more environmentally friendly chemicals. Most attention has been focused on the use of nontoxic oxyanions such as molybdates [73], sodium molybdate, Na_2MoO_4, which is a non-toxic, environment friendly corrosion inhibitor for the protection of soft water cooling systems [74], organic compounds such as thioglycolates [75], and phosphonates [76] or mixtures of inorganic compounds such as phosphates, borates, silicates and surfactants e.g. phosphonates and sulfonates [77-79].

Among all the lanthanides compounds, cerium salts have successfully been used as corrosion inhibitors on different metals and alloys [80-86]. Cerium carboxylates (cerium salicylate, cerium anthranilate and cerium glycolate) are used as effective inhibitors for mild steel in NaCl solutions [87]. Cerium salicylate offers the highest inhibition efficiency, particularly at low concentrations.

Goldi and McCarrol first demonstrated the effectiveness of rare-earth metal (REM) salts as environmentally friendly corrosion inhibitors [88]. They found that concentrations of 0.001 M cerium or lanthanum nitrate produced corrosion inhibition efficiencies of 91 % and 82 %, respectively, with steel in 3.5 % sodium chloride (NaCl) solutions. Also, the corrosion inhibition of environmentally acceptable cerium and lanthanum cinnamate based compounds are applied for steel exposed to NaCl soluiton of neutral pH [89]. The protection mechanism was explained that the rare earth metal-cinnamate compounds adsorb on the surface of the alloy followed by the hydrolysis of the rare earth elements to form a barrier oxide on the steel surface. Environmentally friendly corrosion inhibitors are studied (chromium III, molybdate, permanganate and cerium III) and compared to the standard corrosion inhibitor, i.e. hexavalent chromium [90]. The results show that the morphology of sol–gel and the solubility of the additive play a role in the effectiveness of corrosion protection for a long term.

Hinton's group, also investigated the potential of the rare earth metal salts of cerium, lanthanum and yttrium as corrosion inhibitors to replace the classic systems based on chromates [91]. Their work showed the inhibiting action of the cerium salts on corrosion of aluminum alloys [92, 93], zinc [94], and mild steel [95] in aqueous solutions was due to the suppression of the cathodic half of the corrosion process. It was proposed that cathodic processes generated alkaline conditions close to the metal surface, leading to localized precipitation of hydrated rare-earth oxide and the formation of a protective film [96, 97]. Zinc (plated on gold) is inhibited in acidic solution, by inorganic environmentally safe inhibitors such as sodium silicate, sodium molybdate and cerium nitrate. Cerium conversion coating, as alternative for the chromate, increased the corrosion resistance of Mg and its alloys [98]. The acid (HCl) pretreatment increased the corrosion resistance of the coated alloys. After five days of imersion in chloride environment the untreated samples showed localized corrosion while the chemical conversion coated sample appeared unaffected.

Recent research has been focused on the use of rare earth metals as a green alternative for the chromuim species not only because their effectiveness but also due to null toxicity for most of them. Ce-saltes used as inhibitors for tinplate (low C-steel sheet coated on both faces with tin) [85, 99, 100]. Tinplate is used for equipment and containers for a wide variety of poducts, from food can to cleaners in from of aerosols. Hybrid organic–inorganic sol–gel-matrices, with up to 20 wt.% incorporated ceria nanoparticles, have been employed as coatings for an AA2024-T3 aluminium alloy. The morphology of the coatings and associated nanoparticles has been examined by conventional and high-resolution transmission electron microscopy, revealing a relatively uniform distribution of 5 nm size nanoparticles across the coating thickness. Electrochemical studies indicate a general beneficial effect of incorporation of ceria nanoparticles, although the performance of the coated alloy depends on the nanoparticle content [101]. The synergistic inhibition effect of rare earth cerium (IV) ion and 3, 4-dihydroxybenzaldehye (DHBA) on corrosion of cold rolled steel (CRS) in H_2SO_4 solution was first investigated by weight loss and potentiodynamic polarization methods [102]. The results reveal that DHBA has moderate inhibitive effect and its adsorption obeys Temkin adsorption isotherm. For the cerium (IV) ion, it has negligible effect. However, incorporation of Ce^{4+} with DHBA improves the inhibition performance significantly, and produces strong synergistic inhibition effect.

Natural products are extracted and used as environmentally friendly corrosion inhibitors, e.g. henna extract (*Lawsonia inermis*) and its main constituents (lawsone, gallic acid, α-d-Glucose and tannic acid) on corrosion of mild steel in 1 M HCl solution was investigated through electrochemical techniques and surface analysis [103]. Polarization measurements indicate that all the examined compounds act as a mixed inhibitor and inhibition efficiency increases with inhibitor concentration.

Finally, safety precautions should be followed to deal with inhibitors, especially, toxic compounds. For example, handling the toxic inhibitors must be considered in processes where compounds may be inhaled or contacted [32]. Extreme care must be taken to avoid the use of toxic compounds in or near food processing equipment and potable water suppliers…etc. Also, disposal of such compounds must be considered, because a number of inhibitors contain ions and compounds which are toxic, such as chromate.

8. CONCLUSION

As presented, recent trends are focusing on the compounds that are environmentally friendly and less toxic to the environment. The governements regulations become more stringent for use and disposal of chemicals all over the world. The research has been focused on the use the environmentally friendly compounds to replace harmful substances. As presented, one of the most toxic and harmful compounds is the chromate-based compounds, lead-based coatings and pickling solutions contain nitric acid. Small amounts of chromic acids or potassium dichromate are very dangerous for human health. Therefore, different compounds are developed such as rare earth metals as a green alternative for the chromium species. The rare earth metals show sound inhibition for different metals and alloys in different aggressive environments, such as acids, alkaline medium. They are non-toxic and can replace the chromium species. The toxicity of the chemical products is classified according to the parameter lethal dose 50 (LD50), which corresponds to the dose of the substance under study that would cause the death to the 50 % of the animal population tested [104]. As an indicative result, lanthanide chloride exhibit values for the LD50 similar to the sodium salt [105]. Therefore, preventing corrosion is a crucial need to safe the environment and the economy. Accordingly, better corrosion management can be achieved using preventive strategies in nontechnical and technical areas. These strategies are identified as follows [4]:

- Increase awareness of significant corrosion costs and potential cost savings.
- Change the misconception that nothing can be done about corrosion.
- Change policies, regulations, standards and management practices to increase corrosion cost savings through sound corrosion management.
- Improve education and training of staff in the recognition of corrosion control.
- Implement advanced life-prediction and performance-assessments methods.
- Implement advanced design practices for better corrosion management.
- Improve corrosion technology through research, development and implementation.

REFERENCES

[1] Deborde M, Gunten U, Reactions of chlorine with inorganic and organic compounds during water treatment-kinetics and mechanism: A critical review. Water Res 2008; 42(1-2): 13.

[2] Seinfeld JH. Atmospheric chemistry physics of air pollution. New York: Wiley 1986; p. 303.

[3] Gatz DF. Urban precipitation chemistry: A review and synthesis. Atmos Environ 1991; 25B: 1.

[4] U.S. Report on Corrosion Costs and Preventive Strategies in the United States. www.corrosioncost.com, July 2002.

[5] Cherry BW, Skerry BS, Clayton Vic. Corrosion in Australia: the report of the Australian National Centre for Corrosion Prevention and Control feasibility study. Department of Materials Engineering. Monash University: Australia 1983.

[6] Hughes AE, Gorman JD, Paterson PJK. The characterization of Ce-Mo-based conversion coatings on Al-alloys: Part I. Corrosion Sci 1996; 38(11): 7-1976.

[7] Schem M, Schmidt T, Gerwann J, *et al.* CeO_2-filled sol–gel coatings for corrosion protection of AA2024-T3 aluminum alloy. Corrosion Sci 2009; 51: 2304.

[8] Roeper DF, Chidambaram D, Clayton CR, Halada GP. Development of an environmentally friendly protective coating for the depleted uranium-0.75 wt.% titanium alloy: Part I. Surface morphology and electrochemistry. Electrochim Acta 2005; 50(18): 3622.

[9] Tamba A, Azzerri N. Anodic pickling of stainless steels in sulphuric acid. J Appl Electrochem 1972; 2: 175.

[10] Henriet D, Lacombe P, Baroux B, Beranger G, Eds. Stainless steel. Phys Les Ulis 1993; p. 823.

[11] Sutter EMM, Goetz-Grandmont GJ. The behaviour of titanium in nitric-hydrofluoric acid solutions. Corrosion Sci 1990; 30: 461.

[12] Pedrazzini C, Giordani P. Process for stainless steel pickling and passivation without using nitric acid. US Patent 6068001, 2001.

[13] Fortunati S, Novaro E, Pedrazzini, Pollastrelli C. Conference proceedings of Innovation stainless steel. Florence: Italy 1993; vol. 2: pp. 119-28.

[14] Sanders NJ. Environmentally friendly stainless steel pickling. Anti-Corrosion Method Mater 1997; 44(1): 20.

[15] Li LF, Caenen P, Daerden M, *et al.* Mechanism of single and multiple step pickling of 304 stainless steel in acid electrolytes. Corrosion Sci 2005; 47: 1307.

[16] Malingreaux JP, Morleghem PH. The new continuous cold rolling and annealing line of Ugine at Isbergues (France). Rev Metel 2000; 10: 1177.

[17] Groshart EC. Preparation of basis metals for plating. Met Finish 2000; 98: 194.

[18] Rudy SF. Pickling and acid dipping. Met Finish 2007; 105: 139.

[19] Hudson DM, The use of contact angle analysis to determine surface cleanliness. Met Finish 1997; 95: 26.

[20] Rudy SF. Pickling and acid dipping. Met Finish 2001; 99: 183.

[21] Goode BJ, Jones RD, Howells JNH. Kinetics of pickling of low carbon steel. Iron Mak Steel Mak 1996; 23: 164.

[22] Singh DD, Singh TB, Gaur B. The role of metal cations in improving the inhibitive performance of hexamine on the corrosion of steel in hydrochloric acid solution. Corrosion Sci 1995; 37(6): 1005.

[23] Trethewey KR, Chamberlain J. Corrosion for science and engineering. 2nd ed. New York: Longman Group Limited 1995.

[24] During EDD. Corrosion Atlas. 3rd ed. NewYork: Elsevier Science 1997.

[25] Doche ML, Rameau JJ, Durand R, Novel-Cattin F. Electrochemical behaviour of aluminium in concentrated NaOH solutions. Corrosion Sci 1999; 41: 805.

[26] Linton VM, Laycock NJ, Thomsen SJ, Klumpers A. Failure of a super duplex stainless steel reaction vessel. Eng Fail Anal 2004; 11(2): 243.

[27] Smith RE, Hanfordand R, Cheng SC. Pressure vessel nozzle repair. Nucl Eng Des/Fusion 1990; 124(1-2): 79.

[28] Fontana MG, Greene ND. Corrosion engineering. Chapter 5. New York: McGraw-Hill Book 1967.

[29] Schweitzer PA, Dekker M. Corrosion engineering handbook. New York: McGraw-Hill Book 1996.

[30] Iacoviello F, Casari F, Gialanella S. Effect of 475 °C embrittlement on duplex stainless steels localized corrosion resistance. Corrosion Sci 2005; 47(4): 909.

[31] Kay to Metals. Classification of carbon steel and low alloys steels. www.key-to-steel.com, 2005.

[32] National Association of Corrosion Engineers (NACE). Corrosion basics: an introduction. NACE 1984.

[33] Heusler KE. Present state and future problems of corrosion science and engineering. Corrosion Sci 1990; 31: 753.

[34] Craig HL. Naphthenic acid corrosion in the refinery. Corrosion/95. National association of corrosion engineers, Houston: Texas 1995; p. 333.

[35] Kofstad P. High Temperature corrosion. New York: Elsevier Applied Science Publishers Ltd 1988.

[36] Fontana MJ. Corrosion engineering. High temperature corrosion. Chap 11. 3rd ed. London: McGraw-Hill 1988.

[37] Nathan CC. Corrosion Inhibitors. NACE, Houston: Texas 1981.

[38] Corrosion and Materials Technology Site, www.hghouston.com, June 2005.

[39] González JA, Morcillo M, Escudero E, López V, Otero E. Atmospheric corrosion of bare and anodized aluminium in a wide

range of environmental conditions. Part I: Visual observations and gravimetric results. Surf Coat Technol 2002; 153(2-3): 225.
[40] Garcia-Alonso MC, Macchi G, Brugnoni C, Stroosnijder MF. Electrochemical release testing of a stainless steel in a glucose solution using thin layer activation. Corrosion Sci 2002; 44(1): 129.
[41] Rabold GJ, Charles WH, David RS, *et al.* Cyclospora outbreak associated with chlorinated drinking water. Lancet 1994; 344: 1360.
[42] Rogers A. Europe to set tougher targets for bathing and drinking water. Lancet 1996; 384: 1728.
[43] Ross T, Lott N. Billion Dollar U.S. Weather Disasters 1980-2001. Asheville, NC: National Climatic Data Center. National Oceanic and Atmospheric Administration 2001.
[44] Zhu Y, Fujita K, Iwamoto N, Nagasaka H, Kataoka T. Influence of boron ion implantation on the wear resistance of TiAlN coatings. Surf Coat Technol 2002; 158: 664.
[45] Gundry RD. Corrosion/93 plenary & keynote lectures. NACE International: Houston TX 1993.
[46] Long DG. Paper 103 in Corrosion 94, Baltimore MD, NACE International: Houston TX 1994.
[47] Munger CG. Corrosion prevention by protective coatings. NACE International: Houston TX 1985.
[48] Fedrizzi L, Deflorian F, Bonora PL. Corrosion behaviour of fluotitanate pretreated and painted aluminium sheets. Electrochim Acta 1997; 42(6): 969.
[49] Gorman JD, Johnson ST, Johnston PN, Paterson PJK, Hughes AE, The characterization of Ce-Mo-based coatings on Al-allos: Part II. Corrosion Sci 1996; 38(11): 1977.
[50] Conde A, Arenas MA, de Frutos A, de Damborenea J. Effective corrosion protection of 8090 alloy by cerium conversion coatings. Electrochim Acta 2008; 53(26): 7760-8.
[51] Lin TJ, Antonelli JA, Yang DJ, Yasuda HK, Wang FT. Plasma treatment of automotive steel for corrosion protection – a dry energetic process for coatings. Prog Org Coat 1997; 31(4): 351.
[52] El-Meligi AA, Ismail AA, Sanad SH, Baraka AM. Corrosion penetration and crystal structure of AA5022 in HCl and rare earth elements. J Mater Sci Technol 2005; 21 (3): 1-7.
[53] El-Meligi AA. Effect of the heating rate on the formable oxide scale on a C-steel surface. J Mater Sci Technol 2004; 20(5): 591.
[54] Yang LH, Liu FC, Han EH. Effects of P/B on the properties of anticorrosive coatings with different particle size. Prog Org Coat 2005; 53(2): 91.
[55] Kemco International Associates, USA, http://www.kemcointernationalcom/ITO.htm
[56] Hackerman N. Review on corrosion inhibitor science and technology. National Association of Corrosion Engineers (NACE) 1989.
[57] Talbot D, Talbot J. Corrosion science and technology. New York: CRC Press 1998.
[58] Putilova IN, Balezin SA, Barannik VP. Metallic corrosion inhibitors. New York: Pergammon Press 1960.
[59] Dean SW, Derby JR, Van Den Bussche GT. Materials performance. NACE 1981; 47.
[60] Uhlig UH. Corrosion and corrosion control. Chap 16. New York: John Wiley and Sons 1963.
[61] Thomas JGN, Shreir LL. Corrosion. London: Newers-Butter Worth 1976; vol. 2: p. 18.
[62] Trabanalli G. Corrosion mechanism. Chap. 3. Corrosion inhibitors. In: Mansfeld F, Ed. New York: Marcel Dekker 1987.
[63] O'Keefe JM, Geng S, Joshi S. Cerium-based conversion coatings as alternatives to hex chrome: Rare-earth compounds provide resistance against corrosion for aluminum alloys in military applications. Met Finish 2007; 105: 25.
[64] Gunasekaran G, Palanisamy N, Appa Rao BV, Muralidharan VS. Synergistic inhibition in low chloride media. Electrochim Acta 1997; 42: 1427.
[65] Blin F, Leary SG, Wilson K, Deacon GB, Junk C, Forsyth M. Corrosion mitigation of mild steel by new rare earth cinnamate compounds. J Appl Electrochem 2004; 34: 591.
[66] Munn P. The testing of corrosion inhibitors for central heating systems. Corros Sci 1993; 35(5-8): 1495.
[67] Wolson K, Forsyth M, Deacon GB, Forsyth C, Cosgriff J. Proceedings University of Ferrara: Ferrara, Italy 2000; vol. 2: pp. 1125-1140.
[68] Lorenz WJ, Mansfeld F. Determination of corrosion rates by electrochemical DC and AC methods. Corrosion Sci 1981; 21: 647.
[69] Aksut AA, Lorenz WJ, Mansfield F. The determination of corrosion rates by electrochemical D.C and A.C methods — II. Systems with discontinuous steady state polarization behavior. Corrosion Sci 1982; 22: 611.
[70] Mattsso E. Basic Corrosion Technology for Scientists and Engineers. 2nd ed. The Institute of Material Science: London 1996.
[71] Blaser RW. American Hot-Dip Galvanizers Association Semi-Annual Meeting, Montréal: Canada 1976.
[72] Anatas PT, Williamson TC. Acs Symp Series no. 626, Washington, DC: American Chemical Society, New York 1996.
[73] Airey K, Armstrong RD, Handyside T. The use of molybdates combined with etidronic acid as corrosion inhibitors for iron. Corrosion Sci 1988; 28: 449.
[74] Shams El Din AM, Wang L. Mechanism of corrosion inhibition by sodium molybdate. Desalination 1996; 107(1): 29.
[75] Hewins MAH, McLoughlin VCR. An evaluation of corrosion inhibitors for aluminium alloys. Ministry of Defence: London, UK 1980.
[76] McCoy JW. Chemical Treatment of Cooling water. 2nd ed. New York: Chemical Publishing Co 1974; p. 147.
[77] Yabuki A, Sakai M. Anodic films formed on magnesium in organic, silicate-containing electrolytes. Corrosion Sci 2009; 51: 793.
[78] Bethencourt M, Botana FJ, Calvino JJ, Marcos M, Rodriguz-Chacon MA. Lanthanide compounds as environmentally-friendly corrosion inhibitors of aluminium alloys: a review. Corros Sci 1998; 40(11): 1803.
[79] Salasi M, Shahrabi T, Roayaei E, Aliofkhazraei M. The electrochemical behaviour of environment-friendly inhibitors of silicate and phosphonate in corrosion control of carbon steel in soft water media. Mater Chem Phy 2007; 104(1): 183.
[80] Arnott DR, Hinton BR, Ryan NE. Cationic film-forming inhibitors for the protection of the AA 7075 aluminum alloy against corrosion in aqueous chloride solution. Corrosion 1989; 45: 12.
[81] Arenas MA, Bethencourt M, Botana FJ, de Damborenea JJ, Marcos M. Inhibition of 5083 aluminium alloy and galvanised steel by lanthanide salts. Corrosion Sci 2001; 43: 157.
[82] Xingwen Y, Chunan C, Zhiming Y, Derui Z. Zhongda Y. Corrosion behavior of rare earth metal (REM) conversion coatings on aluminum alloy LY12. Mater Sci Eng A 2000; 284: 56.
[83] Virtanen S, Ives MB, Sproule GI, Schmuki P, Graham MJ. A surface analytical and electrochemical study on the role of cerium in the chemical surface treatment of stainless steels. Corrosion Sci 1997; 39 (10-11): 1897.
[84] Powell SM, Mcmurray HN, Worsley DA. Use of the scanning reference electrode technique for the evaluation of environmentally friendly nonchromate corrosion inhibitors. Corrosion 1999; 55 (11): 1040.
[85] Breslin CB, Geary M. Inhibition of copper corrosion with Schiff base derived from 3-methoxysalicylaldehyde and o-phenyldiamine. Corrosion 1998; 54 (12): 964.
[86] Forsyth M, Willson K, Behrsing T, Forsyth C, Deacon GB, Phanasgoankar A. Effectiveness of rare earth metal compounds as corrosion inhibitors on steel. Corrosion 2002; 58(11): 953.
[87] Forsyth M, Forsyth CM, Wilson K, Behrsing T, Deacon GB. ATR characterisation ofsynergistic corrosion inhibition of mild steel surfaces by cerium salicylate. Corrosion Sci 2002; 44: 2651.
[88] Goldie BPF, McCarroll JJ. Methods of inhibiting corrosion in aqueous systems. Australian Patent 32947/84, 1984.
[89] Blin F, Leary SG, Deaco GB, Junk C, Forsyth M. The nature of the surface film on steel treated with cerium and lanthanum cinnamate based corrosion inhibitors. Corrosion Sci 2006; 48: 404.
[90] Moutarlier V, Neveu B, Gigandet MP. Evaluation of corrosion protection for sol-gel coatings doped with inorganic inhibitors. Surf Coat Technol 2008; 202(10): 2052.
[91] Hinton BRW. Corrosion inhibition with rare earth metal salts. J Alloys Compd 1992; 180(1-2): 15.
[92] Hughes AE, Mol JMC, Hinton BRW, van der Zwaag S. A morphological study of filiform corrosive attack on cerated AA2024-T351 aluminium alloy. Corrosion Sci 2005; 47; 107.
[93] Arnott DR, Ryan NE, Hinton BRW, Sexton BA, Hughes AE. Auger and XPS studies of cerium corrosion inhibition on 7075 aluminum alloy. Appl Surf Sci 1985; 22: 236.
[94] Hinton BRW, Wilson L. The corrosion inhibition of zinc with cerous chloride. Corrosion Sci 1989; 29: 967.

[95] Trathen PN, Wilson L, Ryan NE. Proceedings of 28th Australian Corrosion Association Conference, Vic, Australia 1988.

[96] Issacs HS, Daveport AJ, Shipley A. The electrochemical response of steel to the presence of dissolved cerium. J Electrochem Soc 1991; 138: 390.

[97] Lai PK, Hinton BRW. Proceedings of 13th International Corrosion Conference, Paper no. 336, Vic, Australia, 1996; pp. 1-8.

[98] Brunelli K, Dabala M, Calliari I, Magrini M. Effect of HCl pre-treatment on corrosion resistance of cerium-based conversion coatings on magnesium and magnesium alloys. Corrosion Sci 2005; 47(4): 989.

[99] Arenas MA, Conde A, de Damborenea JJ. Cerium: a suitable green corrosion inhibitor for tinplate. Corrosion Sci 2002; 44: 511.

[100] Shreir LL, Jarman RA, Burstein GT. Corrosion metal environment reaction. London: Butterworth-Heinemann 1994; vol. 1: pp. 4-160.

[101] Schem M, Schmidt T, Gerwann J, *et al.* CeO_2-filled sol-gel coatings for corrosion protection of AA2024-T3 aluminium alloy. Corrosion Sci 2009; 51(10): 2304.

[102] Xianghong Li, Shuduan Deng, Hui Fu, Guannan Mu. Synergistis inhibition effect of rare earth cerium (IV) ion and 3,4-dihydroxybenaldehde on the corrosion of cold rolled steel in H_2SO_4 solution. Corrosion Sci 2009; 51(11): 2639.

[103] Ostovari A, Hoseinieh SM, Peikari M, Shadizadeh SR, Hashemi SJ. Corrosion inhibition of mild steel in 1M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawsone, Gallic acid, α-d-Glucose and Tannic acid). Corrosion Sci 2009; 51(9): 1935.

[104] Haley TJ. Toxicity handbook on the physics and chemistry of rare earths. J Pharm Sci 1963; 54: 633.

[105] DHHS-NIOSH, Reg of Toxic Effects of Chemicals Substances, DHHS-NIOSH Pub. MDL Information Systems. 14600 Catalina Street, San Leandro, California USA1986; vol. 86: p. 103.

Received: September 16, 2009 Revised: October 30, 2009 Accepted: November 17, 2009