Improvements and New Technologies for Corrosion Control in Industrial Process Installations

Author: Giovanni Franchi-Chemical Engineer- Cooperation Contract -University UCBM – Rome (Italy)

1.Theme Description

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. It's called "anti-metallurgy" because it tends to bring the metals back to their state of being in nature, mixed with other elements (especially with O_2). Deterioration by physical causes is not called corrosion, but erosion, galling, or wear[1],[2].There are different types of corrosion: uniform, pitting, crevice, intergranular, galvanic, etc., and are related to different sectors: infrastructure, utilities, production, manufacturing and transportation .Corrosion costs are due to lost production, health, safety and environmental issues. In the USA, referring only on direct costs, corrosion costs grew up from 276 billion US$ in 1998[3] to 1.1 trillion US$ in 2016.[4]

Table 1 reports the Global Corrosion Costs referring to 2013.

Economic Regions	Agriculture CoC US$ billion	Industry CoC US$ billion	Services CoC US$ billion	Total CoC US$ billion	Total GDP US$ billion	CoC % GDP
United States	2.0	303.2	146.0	451.3	16,720	2.7%
India	17.7	20.3	32.3	70.3	1,670	4.2%
European Region	3.5	401	297	701.5	18,331	3.8%
Arab World	13.3	34.2	92.6	140.1	2,789	5.0%
China	56.2	192.5	146.2	394.9	9,330	4.2%
Russia	5.4	37.2	41.9	84.5	2,113	4.0%
Japan	0.6	45.9	5.1	51.6	5,002	1.0%
Four Asian Tigers + Macau	1.5	29.9	27.3	58.6	2,302	2.5%
Rest of the World	52.4	382.5	117.6	552.5	16,057	3.4%
Global	**152.7**	**1446.7**	**906.0**	**2505.4**	**74,314**	**3.4%**

Table 1 – Global Corrosion Costs (2013)[5]

As can be seen, these costs reached 2.5 trillion US$ corresponding to 3.4% of Global Gross Domestic Product. The Nace International Institute has estimated that the application of techniques for preventing corrosion can save 375-875 billion US$ (15-35% of the total cost).[6]

The following sections described the most common types of corrosion in industrial processes such a soil and gas refining and corrosion due to water and in soil. Finally, methods to prevent and monitoring corrosion are described.

2. Corrosion in Industrial Processes

2.1 Corrosion in Oil and Gas Refining

Corrosion is widespread in oil and gas refining; indeed, refining processes works at high level of pressure and temperature. In addition, due to harmful fluids, specific corrosions (sulfidic corrosion, naphthenic acid corrosion, sour water corrosion etc.) are related.

The European Commission's report on "Corrosion Related Accidents in Petroleum Refineries" highlights that the most sensitive equipment, in the 99 refineries analysed, is the distillation unit (23% of failures) followed by hydrotreatments equipment (20%); 17% of failures occurred in the pipeline for transport between units, 4% in tubes of heat exchanger and cooling equipment, 15% took place in storage tanks, whereas the rest involved other equipment component like trays, drums and towers.[7]

2.2 Corrosion in Water

Water is very aggressive natural electrolyte for many metals and alloys due to oxygen dissolved. Other elements that affect corrosion are: pH, chloride, Total Dissolved Solids (TDS), hardness and high temperature.

Langelier Saturation Index (LSI) is one of the most common index used to evaluate the water corrosion:

$$LSI = pH - pH_s$$

where

- pH_S = pH at saturation conditions.
- LSI < 0 the water is corrosive and could damage metal surface.
- -5 < LSI < -3, treatments are recommended.[8]

Local corrosion is accelerated by the presence of nitrates and nitrites.[9]

2.3 Soil Corrosion

Soil corrosivity depends on electrical conductivity, oxygen concentration, salts and acids content. It's common in storage tanks, cables and pipelines. Soil aeration is a well manner to reduce corrosion because the ground has higher rates of evaporation and lower water retention.[10]

3.Methods for Corrosion Reduction, Measurement and Monitoring

As abovementioned, corrosion costs are very high. Therefore, it is necessary to prevent and monitor the corrosion development during equipment operation.

3.1 Corrosion Prevention

Corrosion could be reduced by using:

- **suitable materials**, i.e. titanium alloys in heat exchanger and condenser tubes show a great resistance (Figure 1).[11]

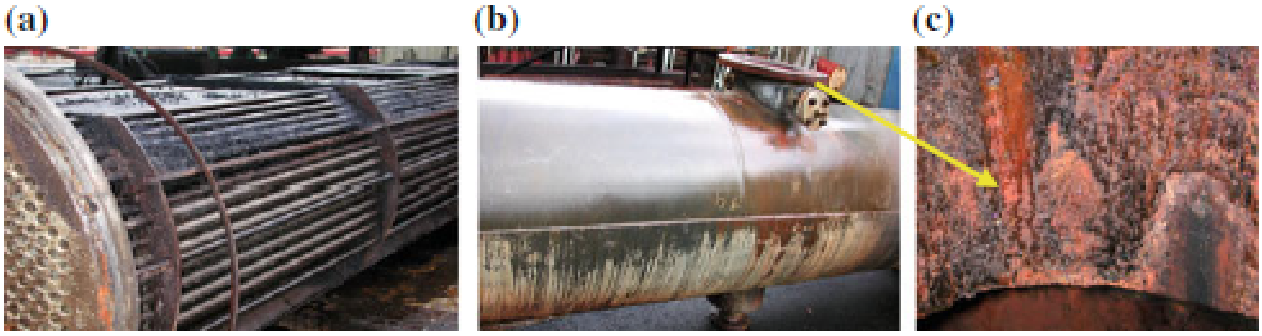

Figure 1 – (a) tube bundle (Titanium Gr.12) of overhead vacuum condenser (b) carbon steel shell (c) detail of inlet nozzle corroded by acids gases (11)

- **cathodic protection** where the metal that needs to be save is transformed into the cathode in an electrochemical reaction or cell. It's used to control corrosion in marine environments, but it can't prevent MIC (Microbiological Influenced Corrosion)[12]. It's also very common in soil corrosion prevention10;
- **protective coatings** like fiberglass-reinforced plastics (FRP). They combine the properties of resin (i.e. polyester, epoxy and vinyl ester) with that of glass fibers. The former allows the chemical resistance while the latter gives mechanical strength and resistance to external damage[13];
- **corrosion inhibitors** are usually adsorbed on the surface of the metal forming a protective film.[14]

3.2 Corrosion Monitoring

There are several techniques for corrosion measurements and can be divided into Non- Destructive Techniques and Corrosion Monitoring Techniques[15].

Non- Destructive Techniques are used when it isn't possible to remove damaged materials and include:

- **X-ray techniques** use electromagnetic waves from 1pm to 10nm with energy between 0.1keV and 1MeV. There are different methods such as: X-ray fluorescence analysis (XRF), X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS). The XRF and XPS are very similar, the X-ray energies let to some electrons to jump from the atom as photoelectrons. The generated holes are occupied by nearby shells electrons releasing energy. In the XRF the energy released is measured, while the XPS is measured the energy associated to photoelectrons. The XRD uses waves of 0.1 nm, corresponding to lattice spacing, that are scattered by the electrons in the atoms with a certain angle. By measuring this angle is possible to know the chemical composition of the element.[16]

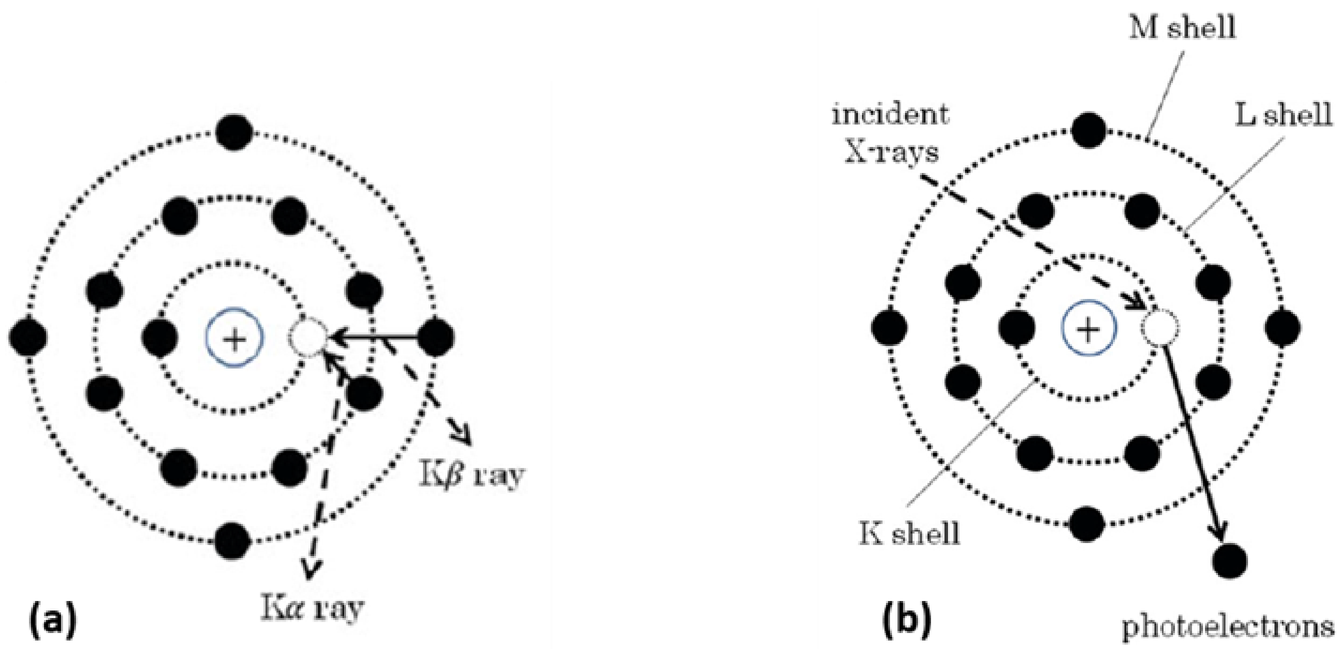

Figure 2 – (a) XRF, (b) XPS where K,L,M represent the energy levels (16)

- **Ultrasonic Technique** is an online technique that allows to analyse general and localized corrosion. The system consists of a transducer (a piezoelectric material), the object to be analysed and a liquid placed between them.

When the piezoelectric material oscillates, a wave is transmitted into the object. By measuring the time that wave employs to go across the material it is possible to know the thickness. It can detect wall losses of about 0.1 mm.[17]

- **Eddy Current Technique**, is used in thin materials (aircraft skin, sheet stock etc.). It uses the principle of electromagnetic inductions where by means of altering currents, eddy currents are induced in the material to be analysed. These currents induce, in turn, an alternating current in the sensor coil. The change of the two current fields let to measure the corrosion rate.16 New techniques have been studied as: Photoinductive Imaging (PI) and Pulsed EddyCurrent (PEC). The former uses an argon ion laser to generate eddy current obtaining a microscopic resolution. The latter uses low frequencies spectrum that allows to have information at different depths.[18]

Corrosion Monitoring Techniques include:

- **Electrical Resistance (ER),** an online method that measures the changing in electrical resistance of a conducting elements. Indeed, referring to the second Ohm’s law the resistance of an element is equal to:

$$R = \rho \frac{l}{S}$$

where

- ρ = resistivity;
- l = element length;
- S = cross section area of the element.

- If S decreases due to corrosion, the element resistance increases. By plotting corrosion loss over time, it is possible to work out the corrosion rate.[19] This method can’t be used in liquid metals and conductive molten salts.[20]There are different types of Electrical Resistance on market: wire loop, cylindrical, tube loop, spiral loop, large/small flush and atmospheric.
- **Linear Polarization Resistance (LPR)** uses the first Ohm’s law:

$$R = \frac{\Delta V}{I}$$

where

- ΔV = difference voltage applied to the electrodes;
- I = current between the electrodes.

Two or three electrode probes are inserted into the process system. A potential of about 20 mV is applied between the elements and current is measured. This method allows to monitoring general and galvanic corrosion and qualitatively local corrosion like pitting and crevice corrosion[21]. It’s suitable to evaluate corrosion rate in real time.[22]

- **Corrosion Coupons** are small bars of same alloy or similar chemical composition of the equipment that is being monitored (i.e. mild steel, copper, stainless steel, nickel, etc.)[23]. They are introduced into the system through a side stream coupon rack.[24]There are several kinds of corrosion coupons: strip, rod, flush disc and disc (Figure 3). Corrosion coupon are certified by its serial number, weight in grams, dimensions, material and surface finish.[25]Referring to corrosion in water, as example, corrosion coupons are removed from coupon rack after 30-90 days and return to laboratory. Where the rate of corrosion is determined from loss of weight (mils/year)[26]. In this way, it is also possible to understand the type of corrosion that occurred.[27]

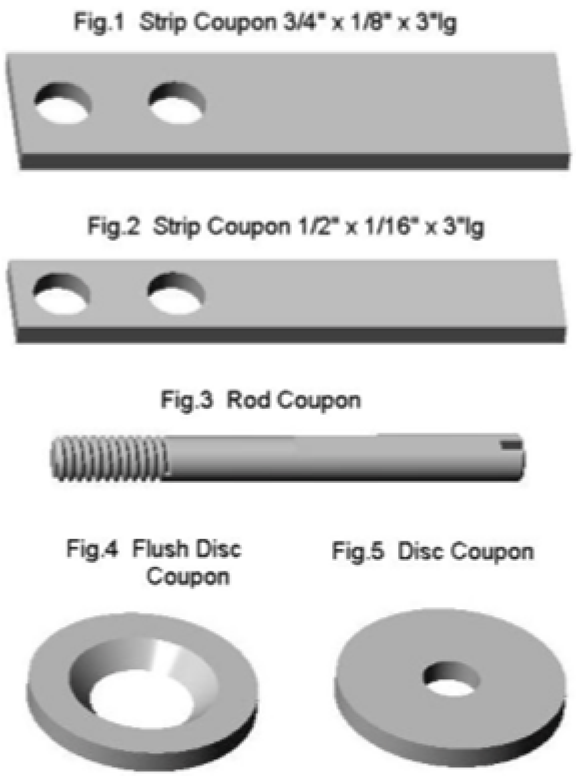

Figure 3 – Different configurations of corrosion coupons from CAPROCO27

3.3 New Approaches in Corrosion Control

Techniques described above are stand-alone methods for corrosion control that don't allow to monitor corrosion in real time (Figure 4).

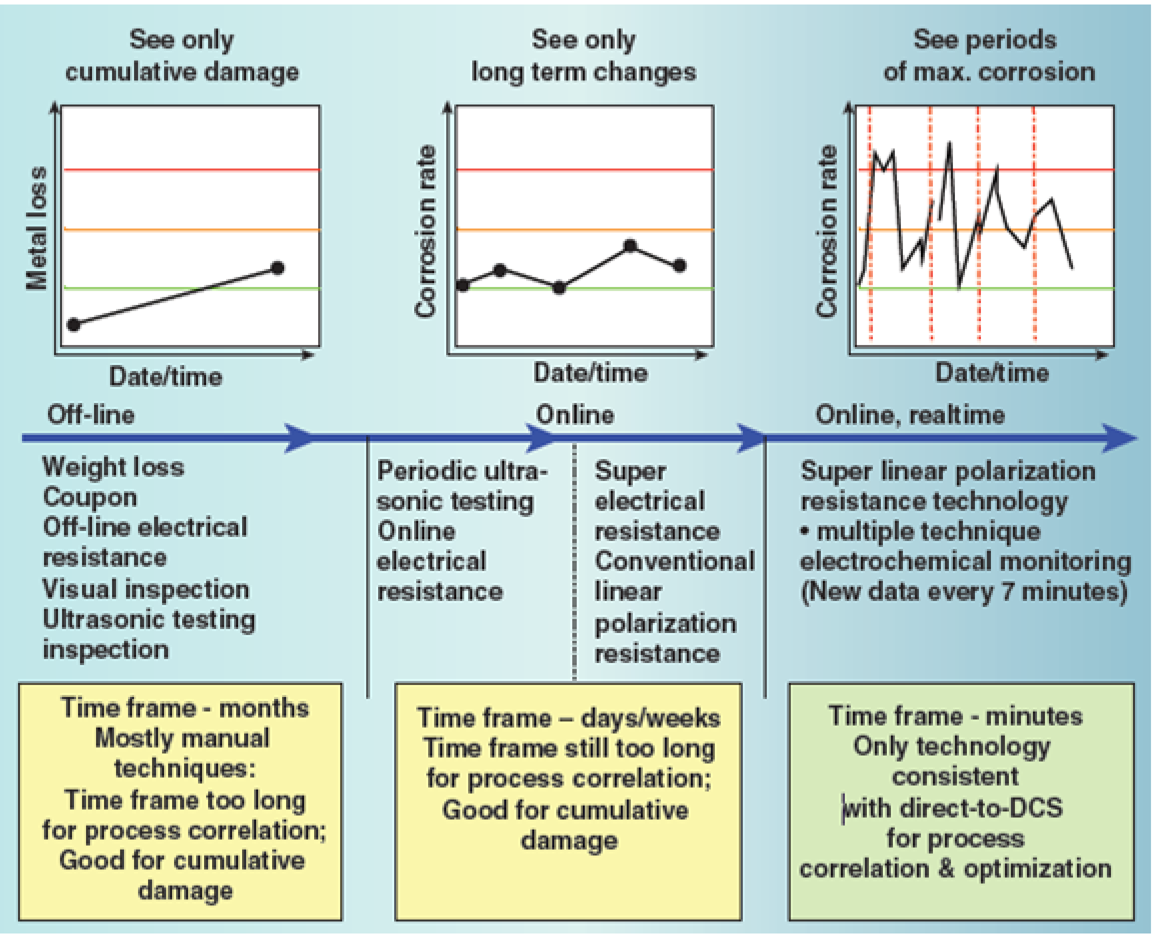

Figure 4 – Differences between off-line, online and online measurements[28]

In the last few years, with the development of automation and Distributed Control System (DCS) it could be possible to control corrosion in real time and optimize system productivity (Figure 5).

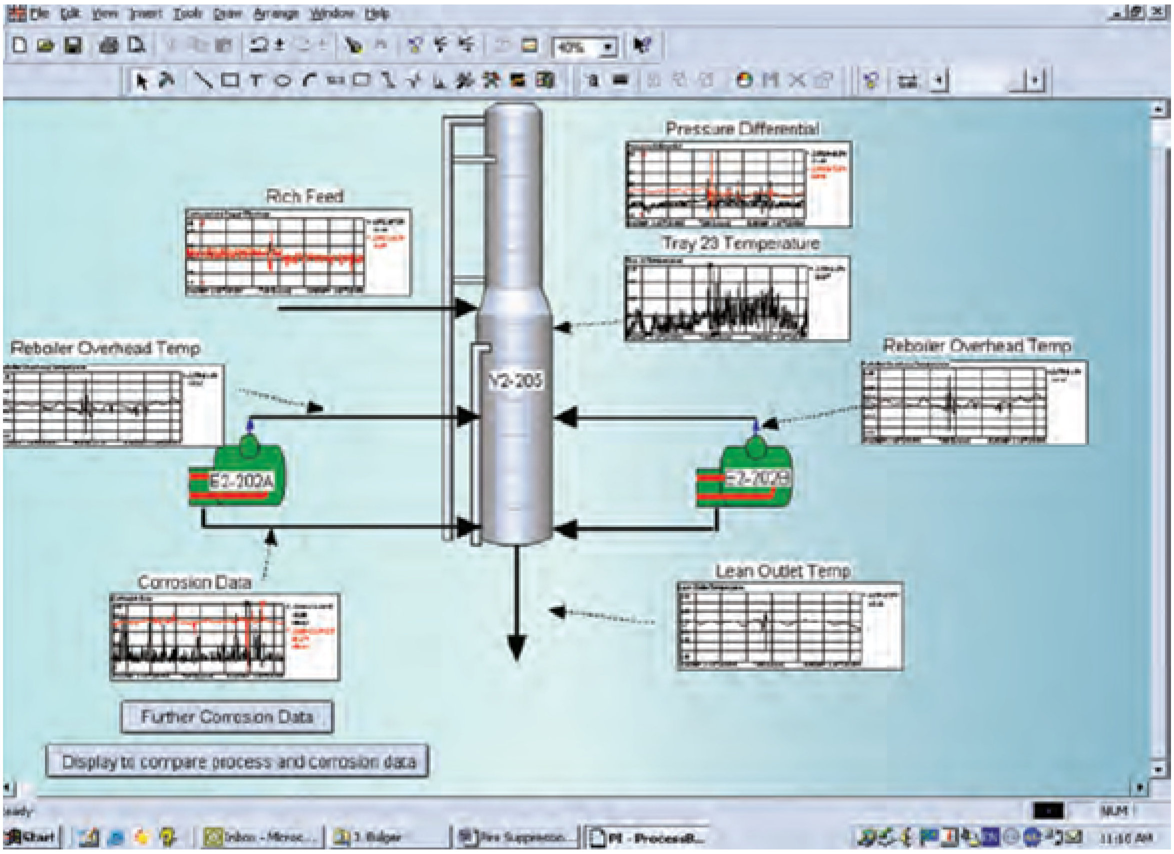

Figure 5 – Example of corrosion monitoring integrated with other process variables (28)

However, problems of integrating corrosion measurements within DCS exist due to qualitative and not quantitative measurements (28). Therefore, they can't be used as process variables that can be manipulated. At the same time there isn't a method that can evaluate all different kinds of corrosion. Recently new multivariable corrosion transmitter[29] and wireless[30]systems have been developed, but further efforts are needed to reduce the risks of corrosion.

4. Conclusions

Corrosion control is a real problem for industrial processes. It covers all sectors and with reference to hazardous plants such as oil refining, it can create serious damage to environments and people (i.e. Sinopec Gas Pipeline Explosion)[31]. Several methods for corrosion mitigation (cathodic protection, protective coating etc.) and monitoring (eddy current techniques, corrosion coupons etc.) exist. Despite this, corrosion causes trillion US$ losses. Nowadays these costs are 3-4% of Global Gross Domestic Production. Therefore, is necessary to control corrosion by integrating corrosion transmitters within DCS system (i.e. SmartCET)29 and equipping skilled professionals with the latest generation technologies.

---

[1] R. Winston Revie, *Corrosion and Corrosion Control, An Introduction to Corrosion Science and technology*, fourth edition, Wiley-Interscience, 2008.

[2] P. Pedeferri, *Corrosione e protezione dei materiali metallici*, Polipress, 2010.

[3]https://www.nace.org/Publications/Cost-of-Corrosion-Study/

[4] http://www.g2mtlabs.com/corrosion/cost-of-corrosion/

[5] http://impact.nace.org/economic-impact.aspx

[6] https://www.nace.org/Newsroom/NACE-News/Study-Sets-Course-Toward-Corrosion-Management-Practices-to-Increase-Safety,-Decrease-$2-5-Trillion-Global-Cost-of-Corrosion/

[7]M.H. Wood et al., *Corrosion-Related Accidents in Petroleum Refineries*, European Commission Joint Research Centre, 2013.

[8] http://www.water-research.net/index.php/drinking-water-issues-corrosive-water-lead-copper-aluminum-zinc-and-more

[9]B. Valdez et al., *Corrosion Control in Industry*, Chapter2, *Environmental and Industrial Corrosion – Practical and*

Theoretical Aspects, Intech 2012. http://dx.doi.org/10.5772/51987

[10] https://www.corrosionpedia.com/an-introduction-to-soil-corrosion/2/1431

[11]A. Groysman, *Corrosion Problems and Solutions in Oil Refining and Petrochemical Industry,* Springer 2016.

[12]Günter Schmitt, *Global Needs for Knowledge Dissemination, Research, and Development in Materials Deterioration and Corrosion Control*, World Corrosion Organization, 2009.

[13] https://www.plasticoncomposites.com/composites-material/frp-material

[14]G.Camila, Corrosion Inhibitors – Principles, Mechanisms and Applications, INTECH, 2014. http://dx.doi.org/10.5772/57255

[15]http://www.alspi.com/introduction.htm

[16]H. Kanematsu and D.M. Barry, *Corrosion Control and Surface Finishing, Environmentally Friendly Approaches*, Springer, 2016.

[17]S. Papavinasam, *Corrosion Control in the Oil and Gas Industry*, 1st Edition, Gulf Professional Publishing, 2013.

[18] https://www.nde-ed.org/EducationResources/CommunityCollege/EddyCurrents/Introduction/presentstateofET.htm

[19] http://www.caproco.com/catalog/pdf/Probes-Instruments/Electrical-Resistance/Electrical-Resistance-General-Information.pdf

[20] https://www.cosasco.com/corrosion-monitoring-standard-electrical-resistance.html

[21] L. Yang, Techniques for corrosion monitoring, Woodhead Publishing in Materials, 2008.

[22] http://www.alspi.com/lprintro.htm

[23] https://www.cosasco.com/corrosion-monitoring-corrosion-coupons.html

[24] http://www.gwt-inc.com/resources/corrosion-monitoring/

[25] http://www.assetintegrityengineering.com/introduction-corrosion-coupons/

[26] http://www.chemaqua.com/downloads/cases/catb2-009_9-10.pdf

[27]http://www.caproco.com/catalog/pdf/Coupons-Holders/Corrosion-Coupons/Corrosion-Coupons.pdf

[28]R.D.Kane, A new approach to corrosion monitoring, Chemical Engineering, 2007-honeywellprocess.com

[29] https://www.honeywellprocess.com/library/support/Public/Documents/Corrosion_Solution-%20Cooling_Water-70-82-57-24.pdf

[30] https://www.controleng.com/single-article/wireless-based-corrosion-monitoring-system/603fc2cec90abd585879e8ac14ae6efb.html

[31]https://www.nace.org/CORROSION-FAILURES-Sinopec-Gas-Pipeline-Explosion.aspx