An appraisal of the harmful and widespread nature of corrosion and the ways to avoid corrosion by education and knowledge, corrosion testing, material selection and corrosion protection methods   Ronald Scott, FREng., BSc, C Eng., FIMMM

1. Background

Corrosion is a destructive mode of failure caused by a reaction between a susceptible material and the chemical elements present in an operating or service environment. This may include an aqueous connection with another more noble metal or alloy or contact with a corrosive fluid or the presence of elevated temperatures with a corrosive gas.

Corrosion can also occur in either wet or dry conditions. Dry corrosion occurs when there is no water or moisture to aid the corrosion, and the metal oxidises in contact with the oxygen in the atmosphere. This is typically important at high operating temperatures. In addition, any corrosion could also be combined with cyclic service stress, residual stress, microbes or wear conditions that would result in the mode of deterioration consisting of a combination of modes of failure such as: corrosion fatigue, stress corrosion cracking (SCC), intergranular cracking (IGC), environmentally assisted cracking (EAC), microbial induced corrosion (MIC) or fretting fatigue. (See Figure 1)
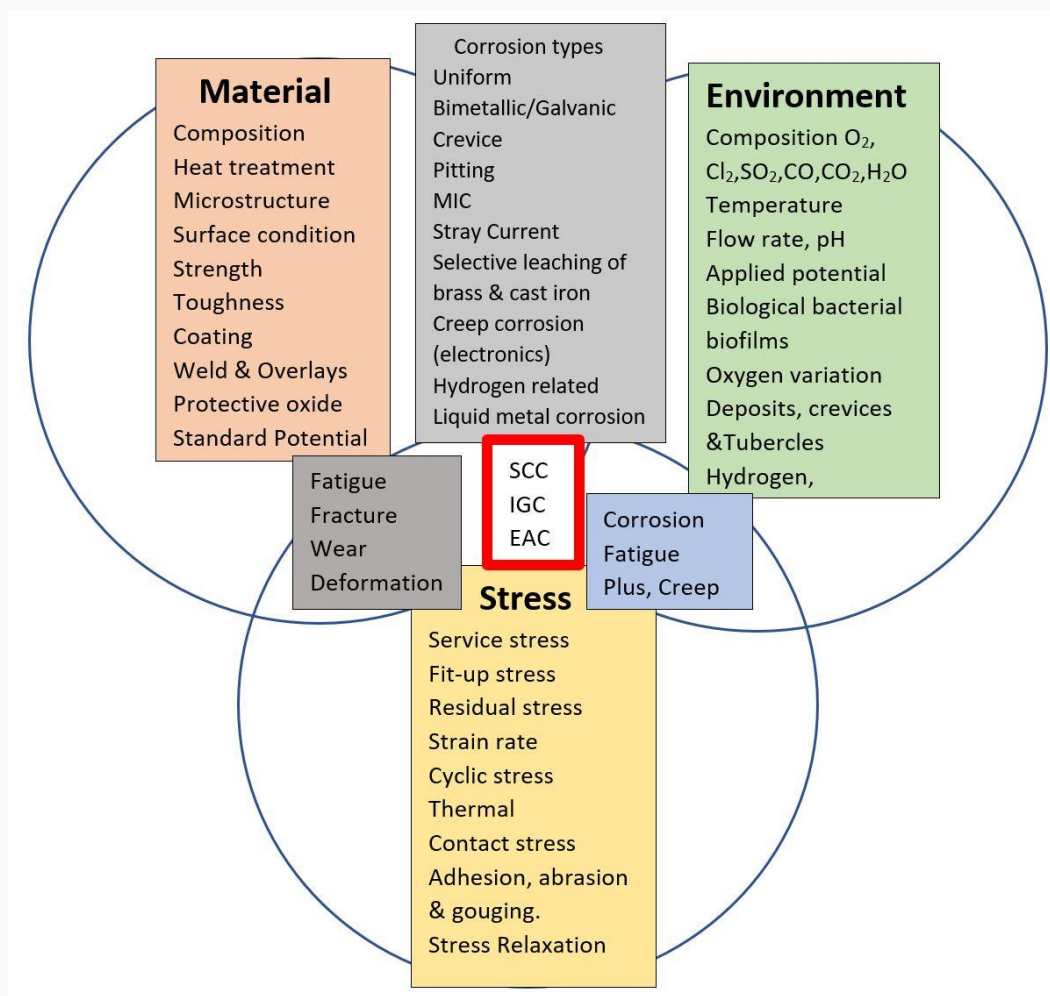

Corrosion types
Uniform
Bimetallic/Galvanic
Crevice
Pitting
MIC
Stray Current
Selective leaching of brass & cast iron
Creep corrosion (electronics)
Hydrogen related
Liquid metal corrosion

Material
Composition
Heat treatment
Microstructure
Surface condition
Strength
Toughness
Coating
Weld & Overlays
Protective oxide
Standard Potential

Environment
Composition O_2, Cl_2,SO_2,CO,CO_2,H_2O
Temperature
Flow rate, pH
Applied potential
Biological bacterial biofilms
Oxygen variation
Deposits, crevices &Tubercles
Hydrogen,

Fatigue
Fracture
Wear
Deformation

SCC
IGC
EAC

Corrosion
Fatigue
Plus, Creep

Stress
Service stress
Fit-up stress
Residual stress
Strain rate
Cyclic stress
Thermal
Contact stress
Adhesion, abrasion & gouging.
Stress Relaxation

Figure 1 Corrosion is the response of metals to the service environment

1.1.   The scientific path to understanding corrosion

A summary of the key events on the long journey towards the elucidation of corrosion mechanisms can be found on the web site of the Institute of Corrosion.[1]
In addition, V. S. Sastri et al in their 2007 book, "Corrosion Prevention and Protection Practical Solutions" outlined a more detailed list of key events on pages 6 to 8.[2]

The cited observations on the Institute of Corrosion web site include a description of events such as the fact that the Romans covered copper utensils with a thin layer of tin to prevent corrosion and in the early 1900's it was discovered that an addition of 10% chromium to iron caused the surface to passivate which created a steel resistant to corrosion and laid the foundation of stainless-steel manufacture. Stainless steel was a remarkable discovery by providing a cost-effective corrosion resistant material which made a significant contribution to many areas of industrial development. Subsequent R&D moved on from the ferritic and martensitic grades to the austenitic and duplex and then to the super martensitic, super austenitic and super duplex. It became the material of choice for a diverse range of products from cutlery to nuclear power vessels, desalination, waste water treatment plants and the oil and gas industry.

It is interesting to note the environmental credentials of the Romans. The Romans preferred the use of earthen ware pipes for the transportation of drinking water instead of lead pipes which could contaminated the water. Vitruvius, who wrote during the time of Augustus, explained: *"Water conducted through earthen pipes is more wholesome than that through lead; indeed, that conveyed in lead must be injurious, because from it white lead [PbCO3, lead carbonate] is obtained, and this is said to be injurious to the human system"* [3]

In the UK the building regulations changed in1969 to ban the use of lead pipes for houses was built in or after 1970. Some years later we took the lead out of petrol and then decide to use diesel and introduce cancer causing particulates into the atmosphere. We are now removing lead from brass fittings and using lead free solders to minimise the pickup of lead in drinking water.

In 1928 Ulick Richardson Evans (1889-1980) who had then studied corrosion for around 10 years and is often referred to by many as "the father of corrosion science" described the search for the understanding of corrosion as *"the winding road that leads to the understanding of corrosion".* The same publication presented in the USA also covered the topics of passivation and differential aeration describing his experimental work including simple measurements of electrode potential.[4]

Graduates of the late 1960's generation (the author of this document) that studied corrosion at university had the benefit of several sound text books on corrosion science published in the early 1960's. In 1963 U. R. Evans published "An Introduction to Metallic Corrosion"[5],

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[1] https://www.icorr.org/world-corrosion-science/
[2] Corrosion Prevention and Protection Practical Solution V. S. Sastri, Edward Ghali, Mimoun Elboujdaini, John Wiley and Sons, 2007
[3] Lead Poisoning and Rome,
https://penelope.uchicago.edu/~grout/encyclopaedia_romana/wine/leadpoisoning.html
[4] Ulick R. Evans, Passivity of Metals and Its Relation to Problems of Corrosion (Annual Lecture). Transactions of the American Institute of Mines and Metallurgical Engineers and The Institute of Metals, 1929 page 7, https://archive.org/stream/transactionsofth007789mbp/transactionsofth007789mbp_djvu.txt
[5] U. R. Evans, An Introduction to Metallic Corrosion, Hodder & Stoughton Educational; 2nd Revised edition, 1963.

L. L. Sheir "Corrosion"[6], H. H. Uhlig "Corrosion and Corrosion Control"[7], F. L. La Que and H. R. Copson "Corrosion Resistance of Metals and Alloys"[8]. In 1966 M. Pourbaix published "Atlas of Electrochemical Equilibria in Aqueous Solutions" and J. C. Scully "The Fundamentals of Corrosion"[9]. The students in the late 1960's had the advantage of technical book shops near the campus to browse and select books.

This was during the pre-internet era when the university library was generally the key source of information. This was supplemented by the wealth, knowledge and experience of the professors and lecturers. Figure 2 shows the "sources of knowledge" provided for students of my generation. These books are still in use worldwide by students involved with the study of corrosion.

Figure 2 Corrosion books published in the early 1960's

To understand and appreciate corrosion science in the 2020's, we need to be aware that there has been a new generation of text books published in the last 15 years which provide even better clarity to the important aspects of corrosion. These books are shown in the next section of this document that covers aspects of "Education and Knowledge" (See Figure 3)

1.2.   Education, Knowledge and Training in Corrosion Science in the materials era

To solve corrosion problems and to develop the skill to apply corrosion technology, to real corrosion issues and concerns, requires a basic understanding of the theory and practice of corrosion engineering. This requires the use of appropriate educational formats such as online lectures, case studies, problem solving and access to suitable professional development such as mentoring and self-audit techniques.

The practical application of these techniques can allow the complex aspects of corrosion to be presented in a simplified manner and can accelerate the personal acquisition of corrosion knowledge. Many of the recent excellent books on corrosion and the short internet courses provided by corrosion institutions and universities has resulted in improvement in self-study methods.

The early work on corrosion related to metals carried out by metallurgists. Despite a number of different definitions during the past 100 years, there is now a basic understanding that

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[6] L. L. Sheir , Corrosion, Pub George Newnes Ltd. 1963

[7] Uhlig, H.H, Corrosion and Corrosion Control : An Introduction to Corrosion Science and Engineering, Published by John Wiley and Sons, 1963

[8] F. L. Laque and H. R. Copson, Corrosion Resistance of Metals and Alloys, Second Edition January 1, 1963, Reinhold Publishing 1963

[9] J. C. Scully, The Fundamentals of Corrosion, Publisher: Pergamon Press, 1966

corrosion is the result of interaction between materials and the environment in which they operate.

Up to the 1960s, the term corrosion was restricted only to metals and their alloys and it did not incorporate ceramics, polymers, composites and semiconductors fully into its scope. This was changed as more interest was given to non-metallic materials such as the work of Mars Fontana (1910-1988) who replaced the word "metals" with "materials" in the definition of corrosion.[10]

"*Corrosion is the deterioration of materials as a result of reaction with its environment (Fontana)*"

The term corrosion now covers all types of natural and man-made materials including, polymers, ceramics, concrete, elastomers, rubbers, biomaterials and nanomaterials, and it is not confined to metals and alloys alone. The scope of corrosion is consistent with the revolutionary changes in materials development witnessed in past 40 years.

To be an effective corrosion technologist there is a need for an interdisciplinary approach which, as a minimum, combines the knowledge and wisdom of a physicist, electrochemist and metallurgist.

This specialist corrosion knowledge base has been made more accessible with the publication of some recent excellent text books. Some images of these books is shown in Figure 3. A list is shown at the end of this document after the references section.

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[10] Mars Fontana, Corrosion Engineering, https://automaterials.files.wordpress.com/2019/01/corrosion-engineering.pdf
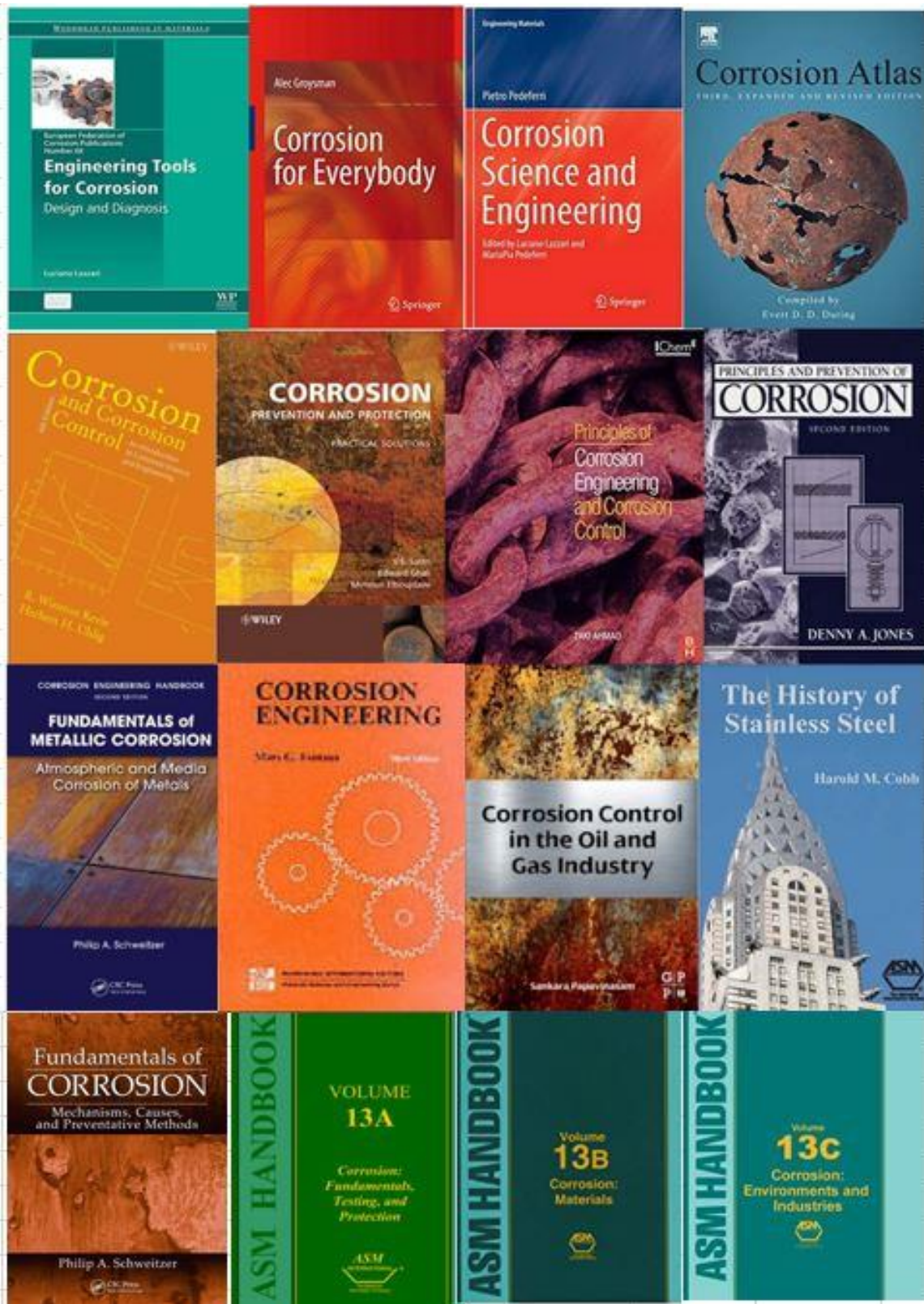
Figure 3 Recent books on corrosion

1.3. The cost of corrosion damage

Governments were also aware of the cost to both national economies and to nature itself. A technique used by one author to emphasis the problem was a comment that during the time you have been reading this document 10 tonnes of iron have corroded on the planet.

Government funds have been applied to both quantifying the cost of corrosion and methods to mitigate its effects. One of the first estimates of the cost of corrosion was done by Robert Hatfield in 1922 when he estimated that the rusting of worldwide iron and steel would cost £700 million.

A recent review of the cost of corrosion was carried out by Baorong Hou et al which was published in 2017[11]. Table 1 taken from this review summarises the cost estimates from several previous surveys. The cost of corrosion was identified as being between 2% and 4% of the gross national product. (See Table 1) It was also estimated that at least 25% of this cost could be saved by appropriate education and known methods of corrosion prevention.

A similar analysis by NACE in 2013 is shown in Table 2. The global cost of corrosion was estimated to be US$2,505 billion, which is equivalent to 3.4% of the global GDP (2013)[12]

Country	Year	Cost	Percentage of the GNP (%)
USA[1]	1949	USD$5.5 billion	2.1
West Germany[9]	1969	USD$6 billion	3
UK[4]	1971	£1365 billion pounds	3.5
Australia[10]	1972	AUD$900 million	3.5
Australia[11]	1974	AUD$470 million	1.5
Japan[2]	1977	USD $9.2 billion	1.8
USA[5]	1978	USD $70 billion	4.5 (GDP)
Australia[6]	1983	AUD$2 billion	1.5
Kuwait[7]	1995	USD $1 billion	5.2 (GDP)
USA[8]	1998	USD $276 billion	3.1 (GDP)
Japan[3]	1999	3.9 trillion Yen (Uhlig) 5.3 trillion Yen (Hoar) 9.7 trillion Yen (input/output)	0.77 (Uhlig) 1.02 (Hoar) 1.88 (input/output)

Table 1. Summary of reviews of the estimated cost of corrosion (11)

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 2 Global Cost of Corrosion by Region by Sector (Billion US$ 2013) (12)

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[11] Baorong Hou et al, The cost of corrosion in China, npj Materials Degradation (2017), https://www.nature.com/articles/s41529-017-0005-2.pdf
[12] http://impact.nace.org/economic-impact.aspx

1.4. The USA National Academies Study in 2011

An important recent contribution to the science has been the USA National Academies Study to prioritise the future R &D needs. Several experts contributed to this document which was published in 2011 along with a distinctive logo which outlined their vision which is shown in Figure 3 on the LHS.[13] Each of the four triangles represent, themes, which the committee called the four corrosion grand challenges (CGCs). They summaries the themes as:

CGC I: Development of cost-effective, environment-friendly, corrosion-resistant materials and coatings;
CGC II: High-fidelity modelling for the prediction of corrosion degradation in actual service environments;
CGC III: Accelerated corrosion testing under controlled laboratory conditions that quantitatively correlates with the long-term behaviour observed in service environments; and
CGC IV: Accurate forecasting of remaining service time until major repair, replacement, or overhaul becomes necessary—i.e., corrosion prognosis.

A horizontal white bar on the triangle denotes the importance of "dissemination" of information and the whole of chapter 4 of their document was devoted to this topic. It outlines that many corrosion problems could be solved by the application of accepted corrosion prevention principles. However, many engineers involved in design activities lack understanding of the issues associated with corrosion. The need for education and continued professional development to exploit new improvements was a major part of their plan.
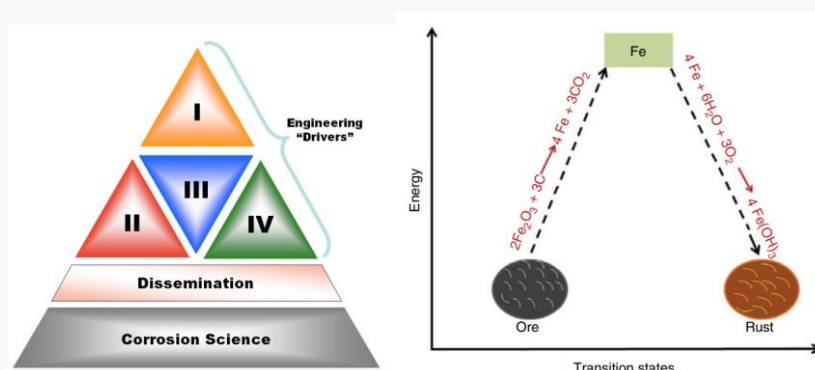

Figure 4 LHS=Hierarchy of the four corrosion grand challenges identified by the USA National Academies Study committee (13). RHS= Energy is supplied to iron ore to convert it into iron and when the latter rusts in use energy is released (14)

2. Back to basics-From ores to metals and then metals back to ores

Metal manufacture involves the processing of metal ores by using energy in the form of a reducing agent to remove the non-metallic elements such as oxide, carbonate, sulphide or chloride.

A typical example would be the reduction of magnetite (Fe_3O_4) with carbon monoxide in a blast furnace with coke, limestone an air blast and high temperatures. Following the metal extraction from their ores, and the use of metals by engineers, the metals have a strong driving force to react with the oxygen in the environment and to return back to its lower

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[13] RESEARCH OPPORTUNITIES IN CORROSION SCIENCE AND ENGINEERING, United States National Academy of Sciences 2011,
http://www2.me.rochester.edu/projects/QGroup/assets/Documents/Research%20Opp%20in%20Corrosion%20by%20NAP.pdf

energy oxide state (See Figure 4 RHS). The return of metals to their initial oxide state is referred to as corrosion. Although this process is inevitable, corrosion control methods such as protective coatings, paints and inhibitors are used to slow the progress and to allow an appropriate service life.[14]

Alan Weisman in his 2007 book "The World Without Us",[15] presented an interesting speculative perspective regarding corrosion and metals converting back to ores free from human intervention. He considered planet Earth devoid of humans and suggested that only metals such as copper and its alloys with good corrosion resistance would be amongst the few structural materials likely to survive in the earth's atmosphere beyond thousands of years. It would be interesting to see how the stainless alloys would perform but it is a certainty that we will never know the answer!

Consideration of the series of events that result in corrosive damage can give a better insight and understanding of the process. These events are typically described as follows:

1. Ions move from the metal surface and into solution (usually water) (anodic reaction)
2. The metal needs to dispose of free electrons left by the ions going into solution to allow corrosion reaction to proceed (cathode reaction required)
3. A compound is formed on the surface of the metal which could form a protective barrier (oxide) or may proceed to a further reaction.
4. Oxygen is known to take part in the process and needs to be available
5. For the corrosion to occur the above sequence of events need to happen and the associated reactions need to be thermodynamically and kinetically favourable.

The main value of this simple analysis is that if any of the sequence of events can be prevented the corrosion will be terminated. Figure 5 provides an image of these events.
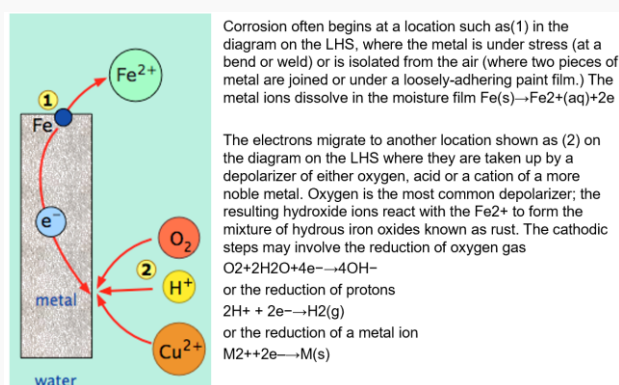

Corrosion often begins at a location such as(1) in the diagram on the LHS, where the metal is under stress (at a bend or weld) or is isolated from the air (where two pieces of metal are joined or under a loosely-adhering paint film.) The metal ions dissolve in the moisture film $Fe(s) \rightarrow Fe2+(aq)+2e$

The electrons migrate to another location shown as (2) on the diagram on the LHS where they are taken up by a depolarizer of either oxygen, acid or a cation of a more noble metal. Oxygen is the most common depolarizer; the resulting hydroxide ions react with the Fe2+ to form the mixture of hydrous iron oxides known as rust. The cathodic steps may involve the reduction of oxygen gas
$O2+2H2O+4e- \rightarrow 4OH-$
or the reduction of protons
$2H+ + 2e- \rightarrow H2(g)$
or the reduction of a metal ion
$M2++2e- \longrightarrow M(s)$

Figure 5 Corrosion is a two-step process (modified image from[16]

3. Corrosion Mechanisms and identification of the types and causes of corrosion

The general view at this moment in time is that corrosion consists of two basically different mechanisms. These were outlined in a book, which I used as a study aid, by J C Scully "The Fundamentals of Corrosion" and continued using the text by the purchase of the 1975 (second edition) in the as chapter 1-Oxidation and Chapter 2 Aqueous Corrosion.

3.1 Oxidation.

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[14] Corrosion Failures: Theory, Case Studies, and Solutions K. Elayaperuma and V.S. Raja K. 2015
[15] Alan Weisman, The World Without Us, Thomas Dunne Books, New York, 2007
[16] http://www.chem1.com/acad/webtext/virtualtextbook.html

The corrosion occurs at high temperature where metals are exposed to hot gas, for example, in furnaces, in power station boilers. It usually includes corrosion by other gases, such as Cl2, SO2, H2S, NOx and also liquid metal corrosion. They all involve chemical reactions, which obey the thermodynamic laws. Since hot corrosion involves the formation of protective layers (typically oxides) the kinetics of the corrosion process are generally more complicated and depend on a range of factors such as adhesion, consistence, porosity, type of conduction (ionic or electronic) and film conductivity. One of the most famous contributions to the oxide integrity was the Pilling and Bedworth ratio.

N.B. Pilling and R.E. Bedworth concluded in1923 that metals can be classed into two categories:
- Metals that form protective oxides,
- Metals that do not form protective oxide.

Pilling – Bedworth ratio indicates whether the volume of the corrosion product is greater or less than the volume of the metal from which the corrosion product formed. The oxide layer would be unprotective if the ratio is less than unity because the film that forms on the metal surface is porous and/or cracked. Conversely, the metals with the ratio higher than 1 tend to be protective because they form an effective barrier that prevents the gas from further oxidizing the metal.

Figure 6 Scheme of the oxide structure and the Pilling-Bedworth ratio.[17]

On the basis of measurements, the following connection can be shown:

- R_{PB} < 1: the oxide coating layer is too thin, likely broken and provides no protective effect (for example magnesium)
- R_{PB} > 2: the oxide coating chips off and provides no protective effect (example iron)
- 1 < R_{PB} < 2: the oxide coating is passivating and provides a protecting effect against further surface oxidation (example aluminium, titanium and stainless steels).

3.2. Aqueous Corrosion.

Corrosion in an aqueous conducting electrolyte that occurs when metals are exposed to waters, soil, chloride contaminated or carbonated concrete and many process fluids These involve an electrochemical process which is the result of two simultaneous and complementary reactions, one anodic and one cathodic, where the flow of electrons play an important role. Wet corrosion follows thermodynamic laws and electrochemistry kinetics.

In general terms these two mechanisms are also referred to as wet and dry conditions of exposure. However, this simplification cannot always be followed. For example, parts used on vehicle exhaust gases such as exhaust gas recirculation systems or truck exhaust brakes can be both hot and cold and wet during the vehicles service life and can be attacked by more than one corrosion mechanism. The differences between Dry corrosion and Wet corrosion are summarised in Table 2.

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[17] https://en.wikipedia.org/wiki/Pilling%E2%80%93Bedworth_ratio

Dry Corrosion	Wet Corrosion
It takes place in the absence of moisture	It takes place in the presence of moisture
It involves the direct reaction with atmospheric gases	It involves the development of a number of small galvanic cells
It is a less frequent occurrence	It is a frequent occurrence
It can be explained by a chemical reaction	It can be explained by electrochemical theory and practice
It is a relatively slow process	It is a fast process
The corrosion is generally uniform	The corrosion is non-uniform since the metal loss occurs at the anode region and not at the cathode region

Table 2 Some of the differences between Dry corrosion and Wet corrosion

3.3. Listing the Corrosion Mechanisms

One important aspect to allow investigators to identify the corrosion mechanism responsible for a particular corrosion problem was the idea of describing the various types of corrosion damage of metals based on appearance. This has been carried out at various times, by various authors with similar observation.[18] The main list that is often used was put together by Fontana and Green and used eight main forms of corrosion:
1. Uniform or general corrosion
2. Galvanic or bimetallic corrosion
3. Crevice corrosion
4. Pitting corrosion
5. Intergranular corrosion
6. Selective leaching or dealloying
7. Impact corrosion (erosion corrosion, impingement corrosion, cavitation corrosion, and fretting corrosion)
8. Stress corrosion cracking (including corrosion fatigue)

Figure 7 An alternative method to categorise the various forms of corrosion damage[19]

This type of list is also been found useful as a training aid and many of the text books include a list of mechanisms. However, the final list can be a personal choice especially since corrosion problems in service often involve more than one mechanism.

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[18] https://corrosion-doctors.org/Corrosion-History/Eight.htm
[19] Giel Notten, Corrosion Engineering Guide, ISBN 9789073168299

The overall intention is to aid the identification of in-service problems. Some of the mechanisms are shown in Figure 1. One of the best collections of corrosion damage and failures is the book compiled by Evert D.D "Corrosion Atlas A Collection of Illustrated Case Histories Third, Expanded and revised Edition".[20] An examination of published documents shows that it has almost become a challenge to establish the longest list with a recent Chinese web site suggesting 23[21] Figure 8 shows some examples of corrosion mechanisms

Corrosion failure in oil and gas refining are common. The refining processes works at high level of pressure and temperature and handle fluids that are harmful to many metals and corrosion reactions such as sulfidic corrosion, naphthenic acid corrosion, sour water corrosion can be experienced. API 571 provides a guidance on Damage Mechanisms Affecting Fixed Equipment in the Refining Industry. This includes typical images of the various corrosion mechanisms[22]

The European Commission's report on "Corrosion Related Accidents in Petroleum Refineries" highlights that the most sensitive equipment, in the 99 refineries analysed, were 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 such as trays, drums and towers.[23]
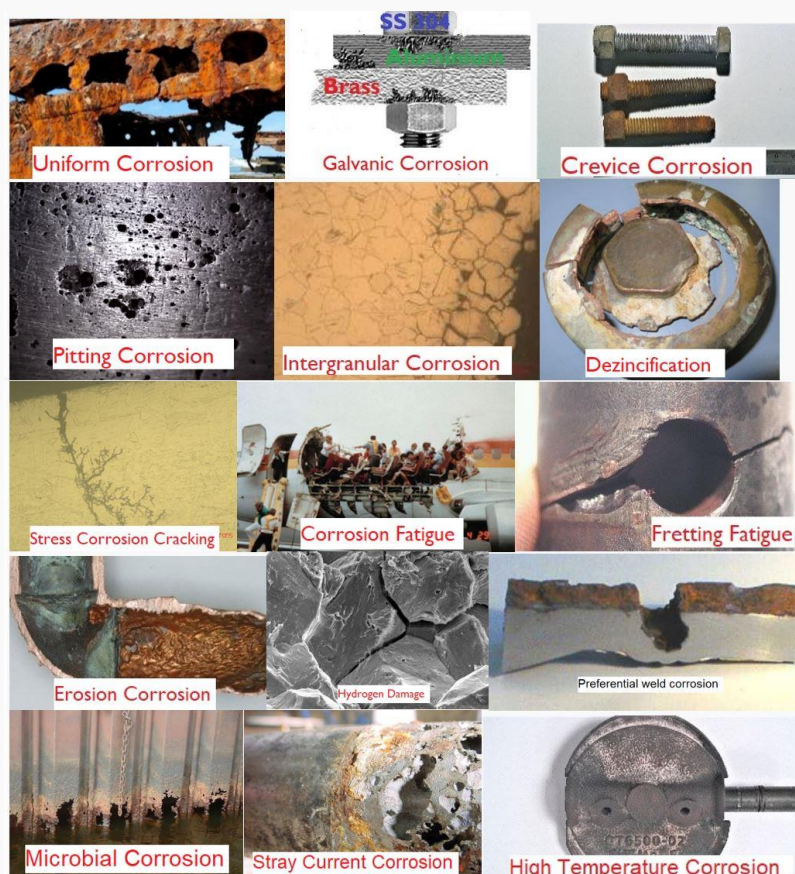

Figure 8 Examples of corrosion mechanism

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[20] Corrosion Atlas A Collection of Illustrated Case Histories Third, Expanded and revised Edition, Compiled by Evert D.D. During. 2018

[21] https://www.yubisteel.com/types-of-corrosion/

[22] API 571, Damage Mechanisms Affecting Fixed Equipment in the Refining Industry

[23] M.H. Wood et al., Corrosion-Related Accidents in Petroleum Refineries, European Commission Joint Research Centre, 2013. https://publications.jrc.ec.europa.eu/repository/handle/JRC84661
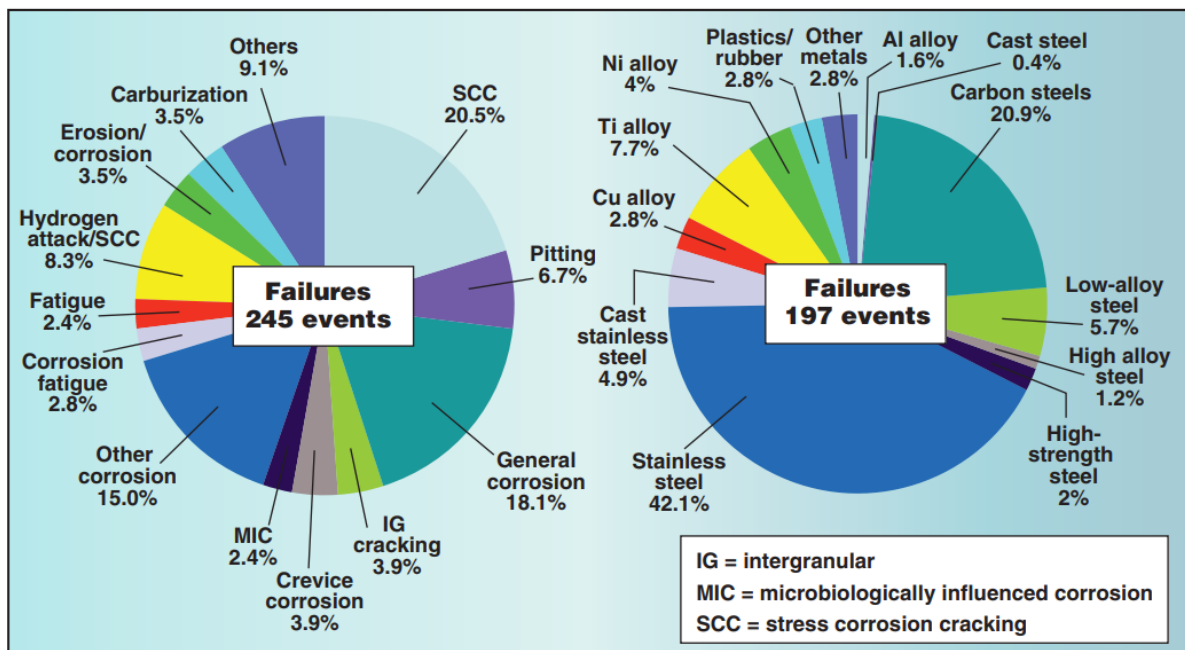
Figure 9 A 2004 survey of causes for failure in refining and petrochemical plants in Japan shows that a majority of the failures were due to corrosion (left chart). The right side shows failures by type of material of construction[24]

Examples of A 2004 survey indicates that corrosion was by far the major factor accounting for chemical plant failures. The data presented in Figure 9 shows how frequent each mechanism is identified in a large chemical facility. The RHS shows the material that were used.

4. **The Nernst Equation→ Gibb's Free Energy applied to corrosion which established the link between corrosion and the Standard Potential**

Once the early engineers, working to understand corrosion, began to apply Gibbs free energy to the corrosion reactions it resulted in better methods to quantify and understand the corrosion. (The concept of Gibbs free energy, was developed in the 1870s by the American scientist Josiah Willard Gibbs (1839-1903). Remember, the first law, also known as Law of Conservation of Energy, states that energy cannot be created or destroyed in an isolated system. The second law of thermodynamics states that the entropy of any isolated system always increases. The third law of thermodynamics states that the entropy of a system approaches a constant value as the temperature approaches absolute zero.)

At constant pressure and temperature, the Second law of thermodynamics gives the equation used to calculate the change in Gibbs free energy:
$\Delta G = \Delta H - T\Delta S$
Where ΔH = the change in enthalpy and ΔS = The change in entropy
The value of the change in ΔG determined from this equation can indicate whether a chemical reaction would proceed at constant temperature and pressure. For a reaction to proceed such as a corrosion process the change in ΔG must be negative

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[24] Russell D. Kane, A New Approach to Corrosion Monitoring, Chemical Engineering www.che.com June 2007 page 34

However, although the theory behind the statement that "a reduction in free energy of a system was essential for a reaction to proceed" was well established the application of this rule to corrosion was more difficult in practice.

The main step forward came with the insight of Walther Nernst (1864-1941) (Nobel Prise Winner 1920 for the Third Law of Thermodynamics. Walther lost his two sons in World War I and must have experienced exceptional emotional highs and lows in his life)

Since corrosion is a chemical or electrochemical reaction that obeys the conventional thermodynamic principles then the driving force behind all corrosion is the lowering of a system's Gibbs energy. This was the observation made and used by Walther Nernst to provide the famous "Nernst equation".

The important relationships/equations attributed to Walther Nernst which linked the G (Gibbs Free Energy) and E (Standard Potential):
$\Delta G = -nFE$ and $E = Eo - \dfrac{RT \ln K}{nF}$

The derivation of these equations was as follows:
For an Electrochemical Cell the change in Gibbs Energy ΔG is the maximum non-PV work that can be obtained from a chemical reaction at constant temperature and pressure.
For an electrochemical cell, $\Delta G = Wmax = Welec$

Welec the electrical work and is defined as $Welec = charge \times potential = -nFE$

where n is the number of moles of transferred electrons
        F is Faraday's constant, (96,490 Coulomb·mol^{-1})
        E is the cell potential
Therefore, $\Delta G = Wmax = Welec = -nFE$

Since ΔG bears the following relation to standard free energy change (ΔGo) and equilibrium constant(K)
$\Delta G = \Delta Go + RT \ln K$

By substituting for $\Delta G = -nFE$ into the above equation it can be written as:
$E = Eo - \dfrac{RT \ln K}{nF}$
The above equation is referred to as the **Nernst Equation**.

$$E = E^0 - \frac{RT}{zF} \ln Q$$

E = reduction potential
E^0 = standard potential
R = universal gas constant
T = temperature in kelvin
z = ion charge (moles of electrons)
F = Faraday constant
Q = reaction quotient

This allowed an electrochemical reaction to be described by the standard potential (Eo) of a cell and the reaction quotient (Q) associated with the reaction. (Q = K the equilibrium constant for a reaction that is at equilibrium) The Eo, Q or K were parameters that could be relatively easily measured and allowed greater insight into understanding corrosion.

This development allowed the electrochemical reaction to be described using standard potential (Eo) and the reaction quotient (Q) or the equilibrium constant, (K) enabling the practical application in the study of corrosion in aqueous conducting fluids.

5. The Pourbaix Diagram

The "Nernst equation" allowed the subsequent development by Marcel Pourbaix (1904-1994), of corrosion science's equivalent to the "equilibrium diagram" known as a "Pourbaix diagram" or potential/pH diagram that showed the thermodynamically equilibria and possible stable phases.
This diagram provided useful resource by providing the graphical display of applied potential and pH of a pure metal in pure water at 25°C. The diagrams are typically divided into regions of immunity, passivity and corrosion each labelled with the predominant species present. (See Figure 4)

The diagrams were first presented by Marcel Pourbaix in 1938. The chosen axes of the diagram were the two key variables that influenced the corrosion were also the two variables that the corrosion engineer could control: the applied potential and pH. The vertical axes showed the **metal-solution potential**, which can be changed by varying the oxidizer concentration in the solution or by applying an electric potential to the metal. The horizontal axis shows the pH of the solution. Figure 10. Pourbaix diagrams iron and water (LHS) and for water with a chloride content. Thus, at 25°C and a potential of 0V (SHE) iron is predicted to dissolve, (i.e. the stable species in solution is $Fe2^+$) at pH < 7, while it passivates (i.e. the stable species in solution is FeO(OH)) at pH > 7. The diagrams may be drawn at different temperature and pressure provided that a liquid aqueous phase exists to solvate the ions present in the liquid environment. Diagrams have been constructed for most metals and a few alloys There are software programs to assist in the construction of the diagrams.

Although the Pourbaix Diagrams have limitation since they represent "equilibrium condition" and do not give information on the corrosion rate or the kinetics of the corrosion reactions they have been a valuable resource during the study of the corrosion of specific metals in specific environments.
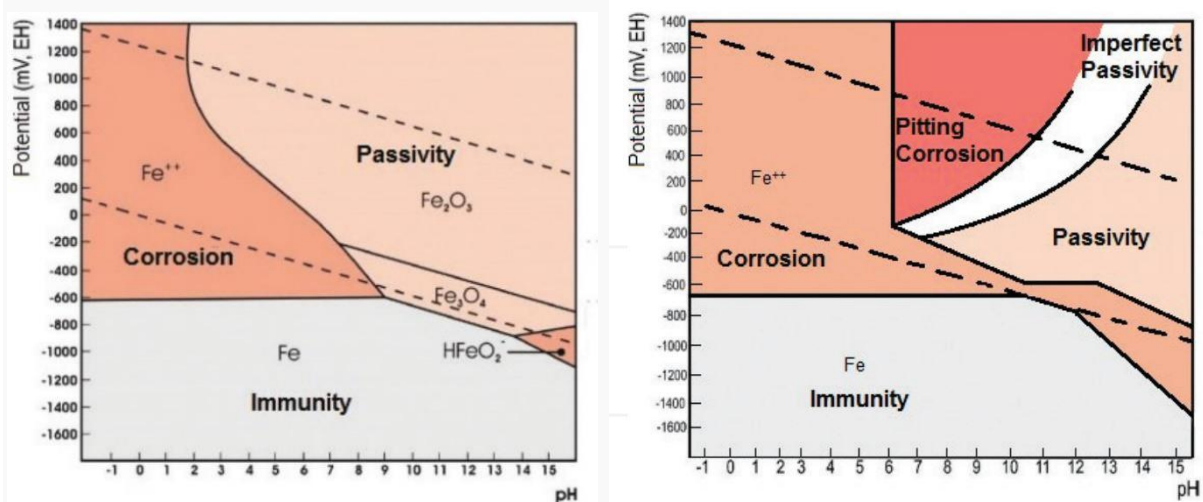

Figure 10 Iron at 25C with and without chloride

The positive uses for Pourbaix diagrams are to
- Predict whether or not corrosion can occur
- Estimate the composition of the corrosion products formed
- Predict environmental changes which will prevent or reduce corrosion attack

6. Electrochemical kinetics of corrosion

The thermodynamic approach which was shown to link the reduction in free energy (-ΔG) and the standard potential (Eo) allows the prediction of whether the corrosion reaction is permitted.

However, the metal user/designer also needs to know how fast any potential corrosion would proceed.

To accomplish the task of predicting how fast corrosion would occur we need to go back two hundred years to the discovery by Faraday of his laws of electrolysis. Around 1833 to 1834 Michael Faraday, one of the early pioneers in electrochemistry laid down two laws of electrolysis.

Faradays first law

The amount of product deposited or liberated at an electrode during electrolysis directly proportional to the charge passing through electrolyte.

The Second Law

The masses of different primary products formed by equal amounts of electricity are proportional to the ratio of molar mass to the number of electrons involved with a particular reaction.

Based on these empirical laws, a linear relationship exists between the rate of corrosion or metal dissolution and the corrosion current.

These laws can be used to determine the rate of an electrochemical corrosion penetration or the corresponding mass loss by measuring the current that flows between all the anodes and all the cathodes on the surface of a corroding metal. This would be relatively simple if we measured the current produced by anodic areas. Once we have the current flow associated with the cathodic and anodic reactions or the oxidation-reduction Faraday's law can be used to compute corrosion rates

For a detailed explanation/understanding of the procedure reference should be made to ASTM G102 "Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements"

Most control software used to carry out potentio-dynamic measurements have the determination of the corrosion rate as a standard feature.

7. Corrosion Software

It would be a major help to industry if corrosion related software could be developed that allowed corrosion engineers to relax and allow software to take over. Unfortunately, this has not occurred and it still requires highly trained corrosion engineers to run and understand the software output.

As with many areas of technology "software" assistance has developed to support corrosion technology. This includes software to predict corrosion rates, design assistance and control and monitoring of corrosion test work. The process of introducing software has probably added efficiency and allowed a more through prediction of corrosion but they have not replaced corrosion engineers

The application of computer technology in all branches of science, study and business was kindled by two events. The introduction of the personal computer in 1975, which made the computer available to individuals and the birth of the internet if January 1983.

The application to corrosion got off to a good start with a committee formed by the European Federation of Corrosion and NACE International that produced a number of Symposium Publications and Reviews. For example:

- Computers in corrosion control: proceedings of the Corrosion/86 Symposium on Computers in Corrosion Control
- Computers in Corrosion Control--Knowledge Based Systems Papers Presented at the Corrosion/94 Symposium "Computers in Corrosion Control--Knowledge Based Systems"

The work carried out during the late 1980's and the 1990's produced several databases, expert systems, neural networks, automated standards and modelling programmes that targeted common problems.

Unfortunately, these early attempts were not successful since the financial returns were also not sufficient to justify continuous software upgrades and development. In addition, the rapid development of the internet made information technology more available with relatively easy access to published literature and educational information.

The available corrosion software can be easily found by an internet search. For example, the following show software that has been developed for specific problems.

https://www.corrosionclinic.com/Recommended%20Software%20for%20Corrosion%20Prediction%20and%20Corrosion%20Modeling.htm

https://www.beasy.com/latest-news/corrosion-simulation-newsletter.html?start=6

https://www.dnv.com/services/marine-corrosion-prevention-corrosion-analysis-software-fncorrosion-103921

https://thermocalc.com/solutions/solutions-by-application/corrosion/

https://publications.jrc.ec.europa.eu/repository/handle/JRC84661

In 2007 Russel Kane, the director of corrosion services at Honeywell Process Solutions, published an article describing "A New Approach to Corrosion Monitoring" One of the main themes was to show the advance in aspects of software monitoring control the allowed systems that could monitor corrosion in real time and allow the optimisation of plant productivity. This represented a major change from the old systems that simply compiled historical data.[25] This change is shown in Figure 11.

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[25] Russell D. Kane, A New Approach to Corrosion Monitoring, Chemical Engineering www.che.com June 2007 page 34
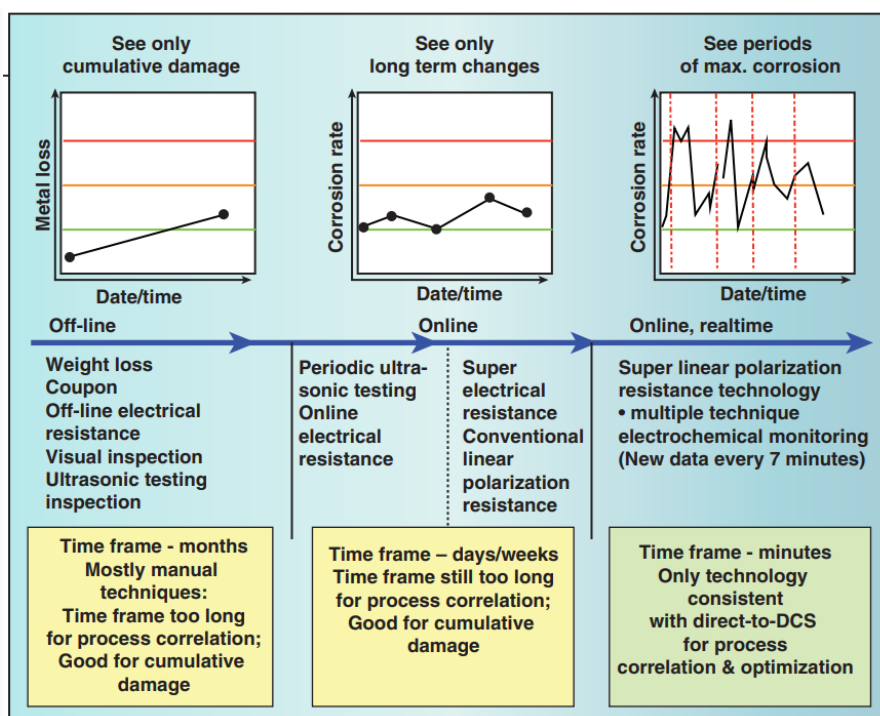
Figure 11 Corrosion monitoring has evolved from offline to online, and online, real-time measurements

The future developments in "machine learning" appears to become more complex judging by recent publications, Figure 12 shows "*the output of the main tool used for identifying relevant literature for this review was the Web of Science search engine, a large abstract/ citation database covering mainly peer-reviewed journals*"[26]

Figure 12 Visualization of the co-citation network of 'machine learning' and 'corrosion' publications

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[26] Leonardo Bertolucci Coelho et al, Reviewing machine learning of corrosion prediction in a data-oriented perspective, npj Materials Degradation (2022) 8.

8. Corrosion Testing

A good guide to laboratory corrosion tests has been prepared by Sean Brossia with the title "Laboratory Assessment of Corrosion"[27]

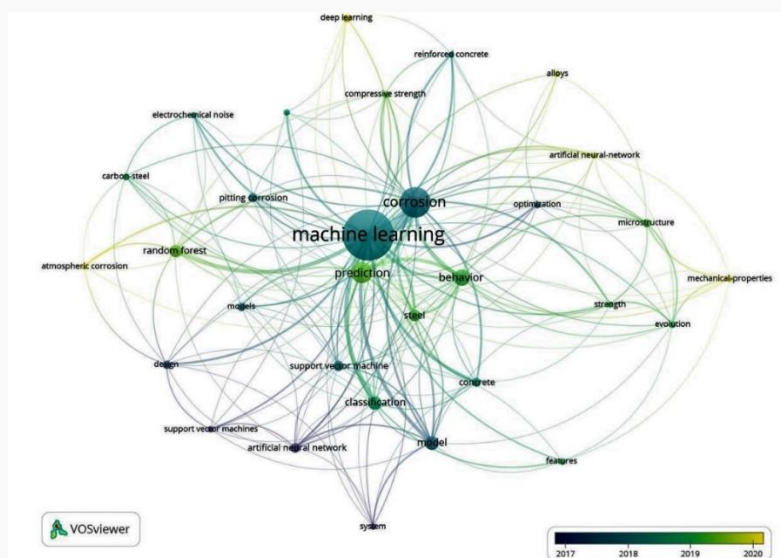Laboratory based corrosion test have been developed to carry out tests relating to a wide range of corrosive conditions and for a wide range of materials. These include tests to simulate

- atmospheric corrosion,
- corrosion during periods of wet and periods of dry conditions,
- corrosion under fully immersed conditions
- corrosion in aqueous solutions
- corrosion at high temperatures
- corrosion with water with high flow rates

When corrosion tests are used it is important to consider the service conditions are being accurately simulated. The test should also be expected to give a similar type corrosion failure mechanism that would be expected in-service

A major advantage to this test work is that specific standards that have been developed for many corrosion tests and most of these tests there are recommended standards to follow.

The test methods can be broadly grouped into three main classifications in the following sections:

- Immersion tests
- Cabinet tests (salt spray and humidity testing ASTM B117)
- Electrochemical tests such as LPR (linear polarising resistance) and the measurement of OCP (open circuit potential).

9.1. Immersion tests

Immersion tests tend to be the easiest to control and perform. As the name indicates these tests involve the immersion of a material into a solution that simulates the service environment. This type of test has been adapted to use fixture to crate artificial crevice defects. In addition, mechanical loading devices such as springs and bolts have been used to stress test pieces to simulate stress corrosion failure modes. The main advantage of immersion tests is that with minimal effort and equipment, a wide range of conditions and materials can be evaluated simultaneously. A list of tests is shown in the Table 3.1.

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[27] Sean Brossia, Laboratory Assessment of Corrosion, Handbook of Environmental Degradation of Materials By Myer Kutz Chapter 2

TABLE 3.1 Partial List of Standardized Immersion Tests

Designation	Title
ASTM G31	Standard Practice for Laboratory Immersion Corrosion Testing of Metals
ASTM G48	Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution
ASTM G36	Standard Practice for Evaluating Stress-Corrosion-Cracking Resistance of Metals and Alloys in a Boiling Magnesium Chloride Solution
ASTM G49	Standard Practice for Preparation and Use of Direct Tension Stress-Corrosion Test Specimens
ASTM G30	Standard Practice for Making and Using U-Bend Stress-Corrosion Test Specimens
ASTM G38	Standard Practice for Making and Using C-Ring Stress-Corrosion Test Specimens
ASTM G41	Standard Practice for Determining Cracking Susceptibility of Metals Exposed Under Stress to a Hot Salt Environment
ASTM G44	Standard Practice for Exposure of Metals and Alloys by Alternate Immersion in Neutral 3.5% Sodium Chloride Solution
ASTM G78	Standard Guide for Crevice Corrosion Testing of Iron-Base and Nickel-Base Stainless Alloys in Seawater and Other Chloride-Containing Aqueous Environments
ASTM G35	Standard Practice for Determining the Susceptibility of Stainless Steels and Related Nickel-Chromium-Iron Alloys to Stress-Corrosion Cracking in Polythionic Acids
NACE MR0174-95	Recommendations for Selecting Inhibitors for Use as Sucker-Rod Thread Lubricants
NACE TM0198-98	Slow strain rate test method for screening corrosion-resistant alloys for stress corrosion cracking in sour oil-field service
NACE TM0169	Laboratory Corrosion Testing of Metals
NACE TM0171	Autoclave corrosion testing in high-temperature water
USFS 5100	Standard Test Procedures For the Evaluation of Wildland Fire Chemical Products
NACE TM0177	Standard Practice for Determining the Susceptibility of Stainless Steels and Related Nickel-Chromium-Iron Alloys to Stress-Corrosion Cracking in Polythionic Acids

8.1. Cabinet testing

Cabinet testing refers to tests conducted in closed cabinets where the conditions of exposure are controlled and mostly designed to accelerate specific corrosion situations while trying to simulate the corrosion mechanisms found in service. These range from salt spray tests to humidity to full climatic chambers. A list of tests is shown in the Table 3.2

TABLE 3.2 Partial List of Standard Cabinet Test Methods

Designation	Title
ASTM B117	Standard Practice for Operating Salt Spray (Fog) Apparatus
ASTM G60	Standard Test Method for Conducting Cyclic Humidity Tests
ASTM G85	Standard Practice for Modified Salt Spray (Fog) Testing
ASTM G87	Standard Practice for Conducting Moist SO2 Tests
SAE J2334	Cosmetic Corrosion Lab Test
GM9540P	Accelerated Corrosion Test

8.2. Electrochemical corrosion testing

Electrochemical corrosion testing measures and/or controls the potential (potentiostat) or current (galvostat) and therefore the oxidation/reduction reactions. These are controlled electrochemical experimental methods and can be used to characterize the corrosion properties of metals and metal components in combination with various electrolyte solutions.

The corrosion characteristics are unique to each metal/solution system. Several types of experiments are possible by manipulating and measuring voltage and current. Most experiments impose a potential on the working electrode and measure the resulting current.

Electrochemical corrosion tests include the following techniques:

Linear polarization resistance (LPR) measurements
Potentio-dynamic polarization curves
Electrochemical potentio-kinetic reactivation (EPR) measurements for intergranular corrosion
Current vs time curves (at a given potential)
Electrochemical impedance spectroscopy (EIS)
Harmonic analysis
Electrochemical noise (EN) measurements

A list of tests and the associated standards is shown in the Table 3.3.

The effect of miniaturisation in electronic components on the size of equipment needed for potentio-dynamic testing is shown in Figure 13

TABLE 3.3 Partial Listing of Standard Electrochemical Corrosion Tests

| Test Designation	Title
ASTM G3	Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing
ASTM G5	Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements
ASTM G61	Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys
ASTM G102	Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements
ASTM G106	Standard Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements
ASTM G108	Standard Test Method for Electrochemical Reactivation (EPR) for Detecting Sensitization of AISI Type 304 and 304L Stainless Steels
ASTM G150	Standard Test Method for Electrochemical Critical Pitting Temperature Testing of Stainless Steels
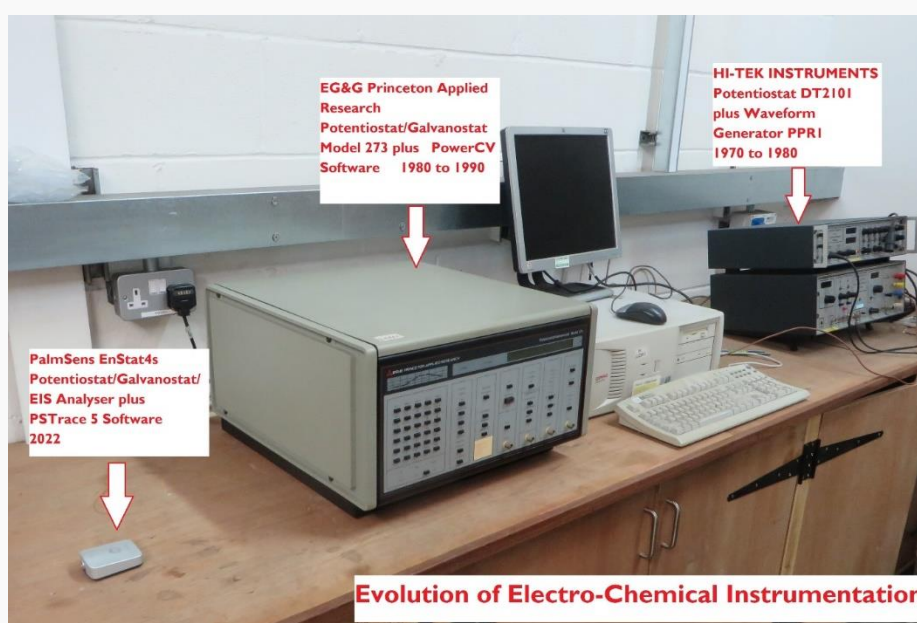
Figure 13 MSL current Potentiostat is on the LHS of the photograph

9. Corrosion of Polymers[28]

When the uniform corrosion of metallic materials takes place, it occurs at a specific corrosion rate. Therefore, the life of a metallic material in a particular corrosive environment can be accurately predicted. However, this is not the case with polymeric materials. Polymeric materials do not experience specific corrosion rates. They are usually completely resistant to a specific corrodent (within specific temperature ranges) or they deteriorate rapidly.

Polymers are attacked either by chemical reaction or solvation. Solvation is the penetration of the polymer by a corrodent that causes swelling, softening, and ultimate failure.

Corrosion of plastics can be classified in the following ways as to mechanisms:

a) Disintegration or degradation of a physical nature because of absorption, permeation, solvent action, or other factors
b) Oxidation, where chemical bonds are attacked
c) Hydrolysis, where ester linkages are attacked
d) Radiation Thermal degradation involving depolymerization and possibly repolymerization
e) Dehydration (uncommon)
f) Any combination of the above.

Results of these corrosion mechanisms will appear in the form of softening, charring, crazing, delamination, embrittlement, discoloration, dissolving, or swelling.

Polymeric materials in outdoor applications are exposed to weather extremes that can be extremely deleterious to the material. The most harmful weather component, exposure to ultraviolet (UV) radiation, can cause embrittlement fading, surface cracking, and chalking. After exposure to direct sunlight for a period of years, most polymers exhibit reduced impact resistance, lower overall mechanical performance, and a change in appearance.

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- ASM Metals Handbook, 10th Edition, Volume 13C Corrosion: Environments and Industries 2006

Appendix Useful Information

Half-Cell	Potential Ref. SHE (v)	Environment
Copper : Copper Sulfate	+0.3160	Soil
Tenth Normal Calomel	+0.3337	Laboratory
Normal Calomel	+0.2800	Laboratory
Saturated Calomel	+0.2415	Laboratory
Silver : Silver Chloride (0.1M KCl)	+0.2880	Seawater
Silver : Silver Chloride (Seawater)	+0.2222	Seawater
Silver : Silver Chloride (3.8M KCl)	+0.1990	Seawater
Hydrogen	0	Laboratory
Zinc	-0.7600	Seawater

Corrosion rate

mpy	ipy	ipm	mdd

A

C

100.0 0.10 0.009 1000
80.0 0.08 0.008 800
70.0 0.07 0.007 600
60.0 0.06 0.006 500
50.0 0.05 0.005 400
40.0 0.04 0.004

0.003 300
30.0 0.03 0.0025

0.002 200
20.0 0.02
18.0 0.018 0.0015 100
80
0.0010
10.0 0.010 0.0008 60
8.0 0.008 0.0007 50
7.0 0.007 0.0006 40
6.0 0.006 0.0005 30
5.0 0.005 0.0004
4.0 0.004 0.0003 20

3.0 0.003

0.0002 10
2.0 0.002 8
6
0.00010 5
1.0 0.0010 0.00008 4
0.8 0.0008 0.00007 3
0.7 0.0007 0.00006
0.6 0.0006 0.00005 2
0.5 0.0005 0.00004
0.4 0.0004 0.00003

0.3 0.0003 1.0
0.00002 0.8
0.2 0.0002 0.6
0.5
0.4
0.000010
0.1 0.0001 0.000008

Density

B

12.00
.50
11.00
.50
10.00
.50
9.00
.50
8.00
.50
7.00
.50
6.00

KEY
A + B = C

CORROSION RATES

mpy = Penetration in mils per year
ipy = Penetration in inches per year
ipm = Penetration in inches per month
mdd = Weight loss in milligrams per square decimeter per day

Density given in grams per cubic centimeter

Conversions between the mpy, ipy, and ipm systems
are read directly from the A scale

SHE (Standard)	AgCl (Standard)	SCE (Saturated)	$CuSO_4$ (Saturated)	Hg_2SO_4 (Saturated)	HgO (Standard)

1
1.2 1 1 0.6 0.2
0.8
1 0.8 0.8 0.6 0.4 0
0.6
0.8 0.6 0.6 0.4 0.2 −0.2
0.4
0.6 0.4 0.4 0.2 0 −0.4
0.2
0.4 0.2 0.2 0 −0.2 −0.6
0.2 0 0 −0.2 −0.4 −0.8
0 −0.2 −0.2 −0.4 −0.6 −1.0
−0.2 −0.4 −0.4 −0.6 −0.8 −1.2
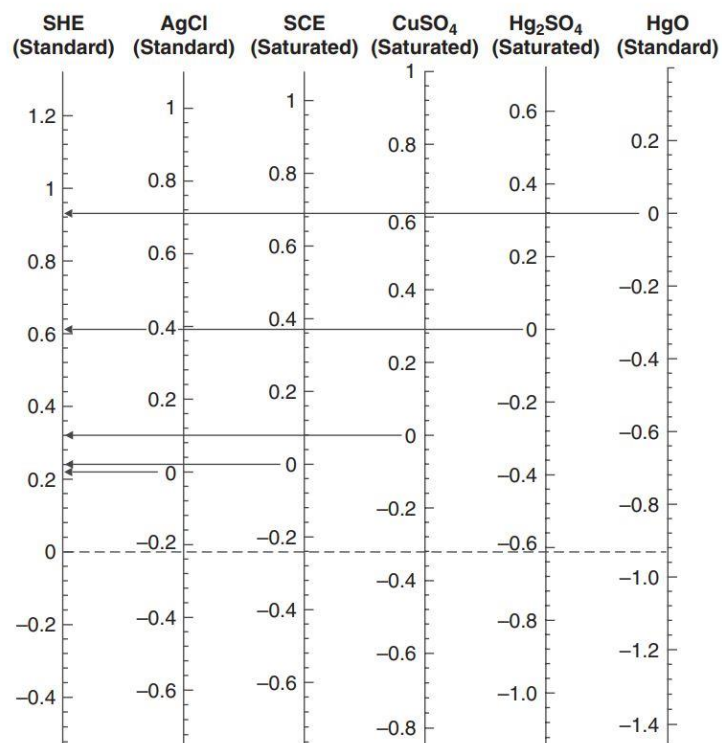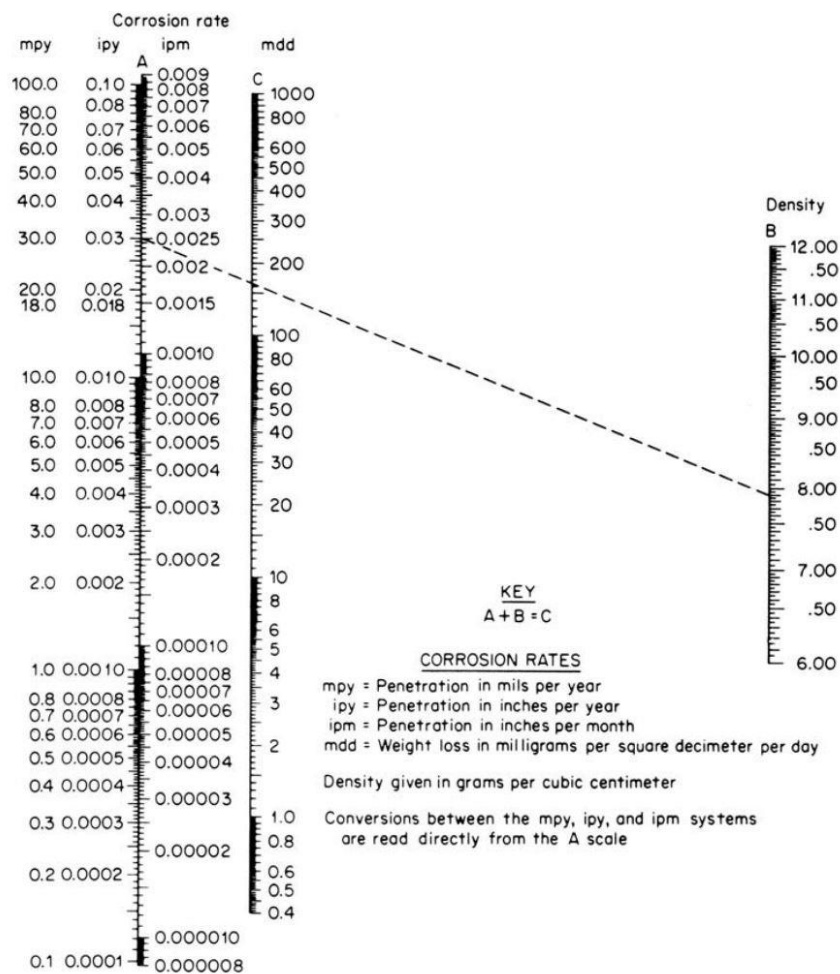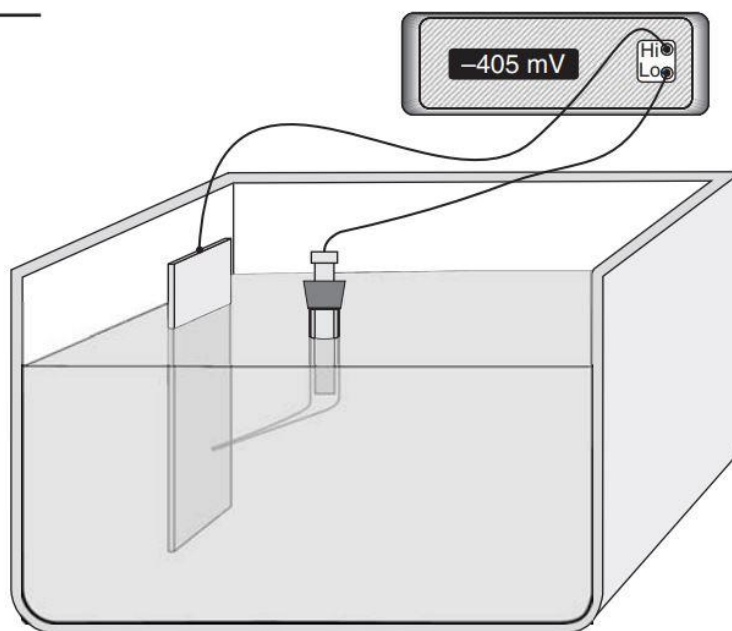−0.4 −0.6 −0.6 −0.8 −1.0 −1.4

FIGURE 4.7
Experimental
set-up to
measure the
corrosion
potential of a
specimen.

–405 mV

Hi
Lo

In measuring and reporting corrosion potentials, it is necessary to indicate the magnitude of the voltage and its sign. In the example shown in Fig. 4.7, the corrosion potential of metal M is −0.405 V. The minus sign indicates that the metal is negative with respect to the reference electrode. However, if the metal was connected to the low point (Lo) and the reference electrode to the high point (Hi) the reading would be +0.405 V. It is customary to connect the reference electrode to the low point or the instrumental ground to avoid any confusion in reporting. Nonetheless, some manufacturers of electrochemical equipment have done the opposite.

TABLE 3.1 Electrochemical and Current Density Equivalence with Corrosion Rate

Metal/Alloy	Element/ Oxidation State	Density (g/cm³)	Equivalent Weight	Penetration Rate Equivalent to 1 μA/cm² (mpy)
Pure metals				
Iron	Fe/2	7.87	27.92	0.46
Nickel	Ni/2	8.90	29.36	0.43
Copper	Cu/2	8.96	31.77	0.46
Aluminum	Al/3	2.70	8.99	0.43
Lead	Pb/2	11.34	103.59	1.12
Zinc	Zn/2	7.13	32.69	0.59
Tin	Sn/2	7.3	59.34	1.05
Titanium	Ti/2	4.51	23.95	0.69
Zirconium	Zr/4	6.5	22.80	0.75
Aluminum alloys				
AA1100	Al/3	2.71	8.99	0.43
AA2024	Al/3,Mg/2, Cu/2	2.77	9.42	0.44
AA3004	Al/3,Mg/2	2.72	9.07	0.43
AA5052	Al/3,Mg/2	2.68	9.05	0.44
AA6070	Al/3,Mg/2	2.71	8.98	0.43
AA6061	Al/3,Mg/2	2.70	9.01	0.43
AA7072	Al/3,Zn/2	2.72	9.06	0.43
AA7075	Al/3,Mg/2 Zn/2,Cu/2	2.80	9.55	0.44
Copper alloys				
CDA110	Cu/2	8.96	31.77	0.46
CDA260	Cu/2,Zn/2	8.39	32.04	0.49
CDA280	Cu/2,Zn/2	8.39	32.11	0.49
CDA444	Cu/2,Sn/4	8.52	32.00	0.48
CDA687	Cu/2,Zn/2 Al/3	8.33	30.29	0.47
CDA608	Cu/2,Al/3	8.16	27.76	0.44
CDA510	Cu/2,Sn/4	8.86	31.66	0.46
CDA524	Cu/2,Sn/4	8.86	31.55	0.46
CDA655	Cu/2,Si/4	8.52	28.51	0.43
CDA706	Cu/2,Ni/2	8.94	31.55	0.46
CDA715	Cu/2,Ni/2	8.94	30.98	0.45
CDA752	Cu/2,Ni/2 Zn/2	8.94	31.46	0.45
Stainless steels				
304	Fe/2,Cr/3 Ni/2	7.9	25.12	0.41
321	Fe/2,Cr/3 Ni/2	7.9	25.13	0.41

TABLE 3.1 (Cont.)

Metal/Alloy	Element/ Oxidation State	Density (g/cm³)	Equivalent Weight	Penetration Rate Equivalent to 1 μA/cm² (mpy)
309	Fe/2,Cr/3 Ni/2	7.9	24.62	0.41
316	Fe/2,Cr/3 Ni/2,Mo/3	8.0	25.50	0.41
430	Fe/2,Cr/3	7.7	25.30	0.42
446	Fe/2,Cr/3	7.6	24.22	0.41
20Cb3	Fe/2,Cr/3 Mo/3,Cu/1	7.97	23.98	0.39
Nickel alloys				
200	Ni/2	8.89	29.36	0.43
400	Ni/2,Cu/2	8.84	30.12	0.44
600	Ni/2,Fe/2 Cr/3	8.51	26.41	0.40
825	Ni/2,Fe/2 Cr/3,Mo/3 Cu/1	8.14	25.52	0.40
B	Ni/2,Mo/3 Fe/2	9.22	30.05	0.42
C-276	Ni/2,Fe/2 Cr/3,Mo/3 W/4	8.89	27.09	0.39
G	Ni/2,Fe/2 Cr/3,Mo/3 Cu/1,Nb/4 Mn/2	8.27	25.46	0.40

Source: Adapted from Proposed Standard, ASTM G01.11, with permission, ASTM, Philadelphia.