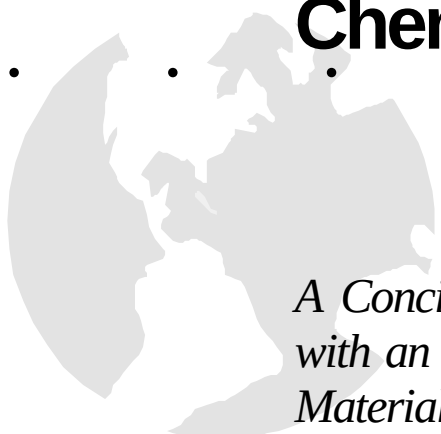


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draft 0.2 – March-May 2008

Materials Engineering for the Chemical Process Industries



*A Concise Handbook of CPI Materials –
with an Introduction to Materials Selection,
Materials Protection and Corrosion Control*

Prof.dr.ir. Walter BOGAERTS

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A. Introduction

*Lectures about Materials & Materials Performance,
and ‘good engineering practices’ for Materials
Selection and Corrosion Control in the Chemical
Process Industries ...*

Materials Engineering, Corrosion & Corrosion Control, and their Importance for the Chemical Process Industries

The approach chosen discusses attributes of common materials of construction and their corrosion characteristics, the corrosive nature of common environments, corrosion phenomena and their control, and several other aspects of corrosion control.

The book is produced with the authorization and support of both NiDI and MTI.



2. Basic Considerations

Safety, Cost, Environment and Other ...

2.1. General

The five basic considerations in corrosion control for the chemical process industries, in descending order of importance, are: safety and reliability, cost, environmental factors, energy considerations, and materials conservation.

2.2. Safety and Reliability

Safety and reliability are of primary importance. One must consider not only the immediate safety of the equipment as it relates to profitable operation, but also the short- and long-term effects upon plant personnel and even upon the local community.

The selected corrosion control measures must be considered relative to:

- ☐ Fire hazards;
- ☐ Explosion hazards;
- ☐ Brittle failures;
- ☐ Mechanical failures; and
- ☐ Release of toxic, noxious, or other hazardous materials, except with adequate safeguards (e.g., scrubbing systems).

Fire and explosion are the most dramatic incidents among corrosion failures. One should be aware of the hazards inherent not only in the leakage of process fluids because of corrosion failures, but also of the nature of some of the corrosion products themselves. Some of the problems to keep in mind are:

- ☐ Pyrophoric iron sulfides and certain sulfur-based corrosion products of zirconium become red-hot on exposure to air or oxygen;
- ☐ Explosive compounds are formed by reaction of some corrosion products (e.g., those of copper, silver, or mercury) with acetylene;

- Be aware of corrosive situations that are made worse by poor control of process variables, actual or potential. Some things to watch out for include:

- Other items which the materials or corrosion engineer should be aware of (items that might seem unrelated to corrosion inspection, control, and remedy) include:

- It is the duty of the chemical or materials (corrosion) engineer to anticipate and prevent corrosion failures related particularly to such potential dangers.

Misapplications of conventional materials also may be hazardous, for example, steel drain plugs in alloy pumps; use of the wrong welding rod (type 347 [UNS (Unified Numbering System) S34700] consumable in type 316L [S31603] equipment); failure to blank off nonresistant items during chemical cleaning (e.g., stainless steel-trimmed valves from inhibited hydrochloric acid, copper alloys from ammoniated citric acid, aluminum components from alcohol, or chlorinated solvents).

It should be evident that careful selection, design, and operation are of the utmost importance to ensure safety and reliability and that equipment must be inspected at regular intervals.

Table 2.1: Specific Hazards and Related Protective Measures

Hazard	Remedy
Localized Failures	
External corrosion of steel under wet insulation	Heavy-duty industrial coating under insulation
External corrosion of steel chlorine piping at pipe supports	Pipe slides; plastic sheathing; heavy-duty coatings
Localized corrosion of underground gas lines	Coatings plus cathodic protection
Erosion-corrosion of steel sulfuric acid piping	Reduced velocity; long-radius ells; substitute materials
Special Effects in Corrosion	
Selective dissolution of alloy constituents	Proper alloy selection
Specific hydrogen phenomena	Alloy selection; environmental control
Hot-wall effects in heat exchangers	Alloy selection; process changes
Cracking Phenomena	
<i>Mechanical</i>	
Brittle fracture (NDT of steels at low temperature, superferritic stainless steels)	Limit thickness; minimize flaws and notches
Fatigue applied stress; shot-peen; auto-fretting	Avoid sharp discontinuities; lower
<i>Corrosion-Related</i>	
Stress Corrosion Cracking (SCC)	Materials selection; stress relief
Hydrogen-Assisted Cracking (HAC)	Materials selection; hardness control
Liquid Metal Cracking (LMC)	Materials selection
Corrosion Fatigue	Avoid sharp discontinuities (as for fatigue); materials selection

2.3. Environmental Aspects

Effluent water must not only be free of biocides, carcinogens, and other objectionable species, particularly in streams which might contaminate a municipal water supply, but even "thermal pollution" may be objectionable. Thermal pollution occurs when a cooling water discharge raises the ambient temperature of the receiving body of water with possible adverse effects on commercial fishing, for example.

It is unfortunately true that many industries in developed countries grew to considerable size without adequate appreciation of the damage they were inflicting on the environment. Originally, such damage was seen by all concerned as a necessary price to pay for industrial growth and job opportunities. In today's climate, such industries must be prepared to clean up their atmospheric and aqueous effluents with all deliberate speed and with adequate consideration of the economic demands entailed. Most reputable firms today willingly embrace even multimillion-dollar environmental control programs, once the need becomes apparent, if they are permitted to do so at a rate that will not destroy them in a competitive market.

2.4. Energy Considerations

The quality and amenability to treatment of fuel and water resources has not always received proper consideration. Fuel quality considerations include inherent corrosion problems such as vanadium contamination in oil stocks, and indirect environmental effects such as sulfur dioxide emissions from high-sulfur coal, one of the causes of acid rain.

8

steam generation.

The cost of energy for a proposed plant or process must be accurately appraised, including steam losses. The mnemonic "TILT" often is used to remind one to consider traps, insulation, *leaks*, and tracing-the major sources of wastage of steam.

2.5. Materials Conservation

In some time periods, certain elements may be in critical supply; for example, chromium, nickel, and manganese.

Although such shortages may reflect only political circumstances, these are essential elements in the manufacture of corrosion-resistant and high-temperature alloys, and consideration must then be given to their possible recovery and reuse. This will not always be possible, but because the high alloys usually are used where they are in fact suitably resistant, much of the domestic usage can be recovered by adequate salvage and recycling plans.

In the past, the free enterprise system has promoted the entrepreneurial manufacture and sale of products generally without regard to the long-term needs of the economy. With present-day knowledge of the finite nature of resources, elements in critical supply should be discouraged from use unless they contribute to the real service life. For example, stainless steel in many cosmetic applications (e.g., trim on kitchen or other appliances) can be replaced with other suitable materials of equally aesthetic appearance.

3. Corrosion Mechanisms

Some Basic Understanding ...

3.1. General

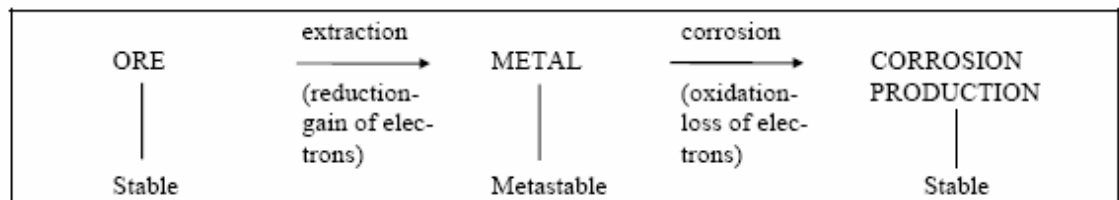
“Corrosion” is the destructive attack upon a metal by its environment and it is probably the commonest electrochemical phenomenon that is experienced in/day-to-day living.

For the practising engineer the most important aspect of corrosion science is probably “corrosion-prevention”. However before appropriate protective or preventive measures can be outlined, it is necessary to understand the basic principles ruling the corrosion phenomenon.

3.2. Basic Principles

3.2.1. Qualitative ideas

Metals occur in nature most commonly as oxide or sulphide ores in which they are in a higher oxidation state than that of the free metal. Extraction of the metal from its ore involves reduction of the oxidized form to free metal, resulting in an increase in internal free energy. Consequently the metal will try to lose its excess energy by becoming oxidized again, through loss of electrons. This oxidizing tendency of a metal is the driving force for corrosion and it is found in virtually all metals except the very noble metals such as gold or platinum.

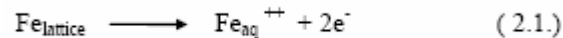


3.2.2. General classification

Corrosion is generally classified as wet or dry. In the former a corroding metal or alloy is in contact with an aqueous or organic liquid. In many practical situations the corroding liquid can also contain aggressive ions such as Cl^- , SO_4^{--} , etc.... which may accelerate the rate of corrosion. In the case of dry corrosion the environment is gaseous and often both high temperatures and reactive gases are involved.

In the case of wet corrosion (also called “electro-chemical corrosion”) the electrochemical reaction which is responsible for damage during corrosion is:

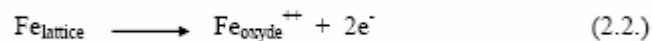
e. g. iron



Atmospheric corrosion may be considered as a special type of wet corrosion since the corrosion processes evolve in a wet film on the metal surface formed by condensation from the atmosphere

For dry corrosion (also called “chemical corrosion” or “high temperature oxidation”) the corrosion reaction is

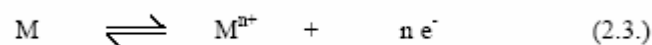
e.g. iron :



Wet corrosion is the most common type of corrosion. Therefore we will only consider this kind of corrosion in the rest of this paper.

3.2.3. Corrosion process : anodic and cathodic half cell reactions

Suppose that a metal rod (M) is placed in an aqueous solution. An equilibrium is soon set up between the solution, the metal (M) and its ions (M^{n+}) in the solution :



This is illustrated in fig. 2.1. For each ion sent into the solution, n electrons remain in the metal. The metal rod is thus negatively charged. This negative charge would quickly attract the positive ions (M^{n+}), if the conditions deviated from the equilibrium conditions. Thus, the reaction from left to right

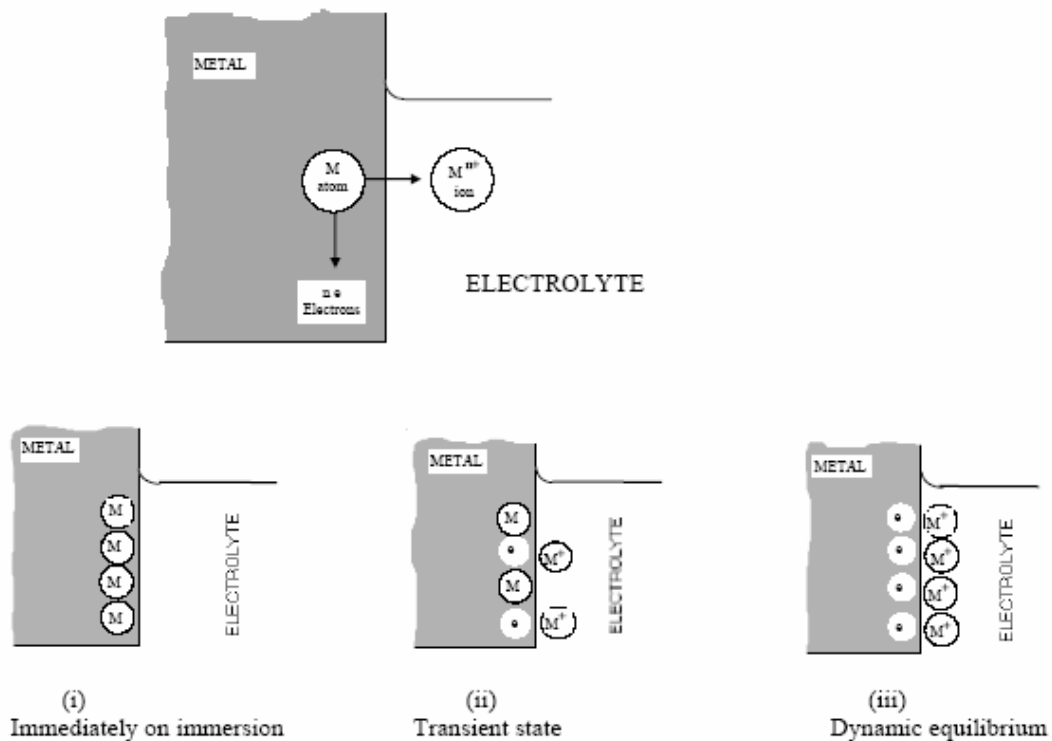
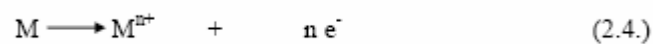


Figure 2.1 : Schematic corrosion reaction

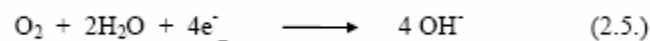
stops rapidly because otherwise the metal rod acquires too much electrical charge. Therefore : metals do not dissolve when the metal cannot get rid of the electrons left in it. This is an important conclusion. In other words the oxidation reaction (which takes place at the anodic areas or sites of the rod - anodic half cell) of the metal M



cannot go on if there isn't a reduction reaction (cathodic half cell reaction) which consumes the liberated electrons.

There are two cathodic reactions of particular importance to aqueous corrosion :

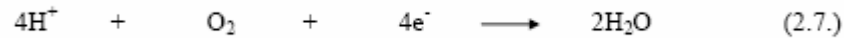
In neutral or alkaline solutions, oxygen is reduced to hydroxyl anions



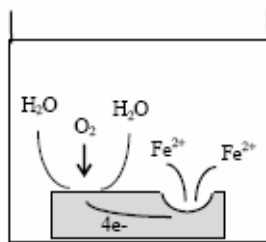
In acid solution, hydrogen ions may be reduced to hydrogen gas



In aerated acid solutions both oxygen and hydrogen ion reduction may take place in parallel (competitive reactions). The combined reaction can be represented by

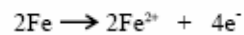


The corrosion reaction for iron is visualized in fig. 2.2.

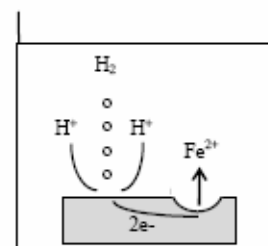
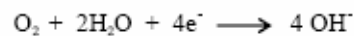


IRON CORRODING IN NEUTRAL
AERATED ELECTROLYTE

ANODE REACTION:

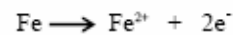


CATHODE REACTION:



IRON CORRODING IN
DEAERATED ACID SOLUTION

ANODE REACTION:



CATHODE REACTION:

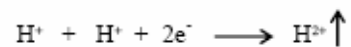


Figure 2.2 : Schematic representation of the corrosion reaction for iron. The iron atoms ionise and form Fe^{2+} ions in solution. The electrons diffuse through the metal from the anode to the cathode. At the cathode the electrons reduce oxygen to OH^- or hydrogen ions to hydrogen gas.

3.3. Corrosion Morphology

Only rarely does corrosion result in a uniform loss of section over the entire surface of engineering structures. More often corrosion results in a localised attack, producing pits, blisters, cracks and crevices which can lead to a catastrophic failure, particularly if mechanical stresses are present. They can also be extremely difficult to assess.

Fig. 3.1. shows schematically some of the more common corrosion morphologies which are encountered in practice. They range from general corrosion to pitting, intergranular attack, crack formation, exfoliation etc.

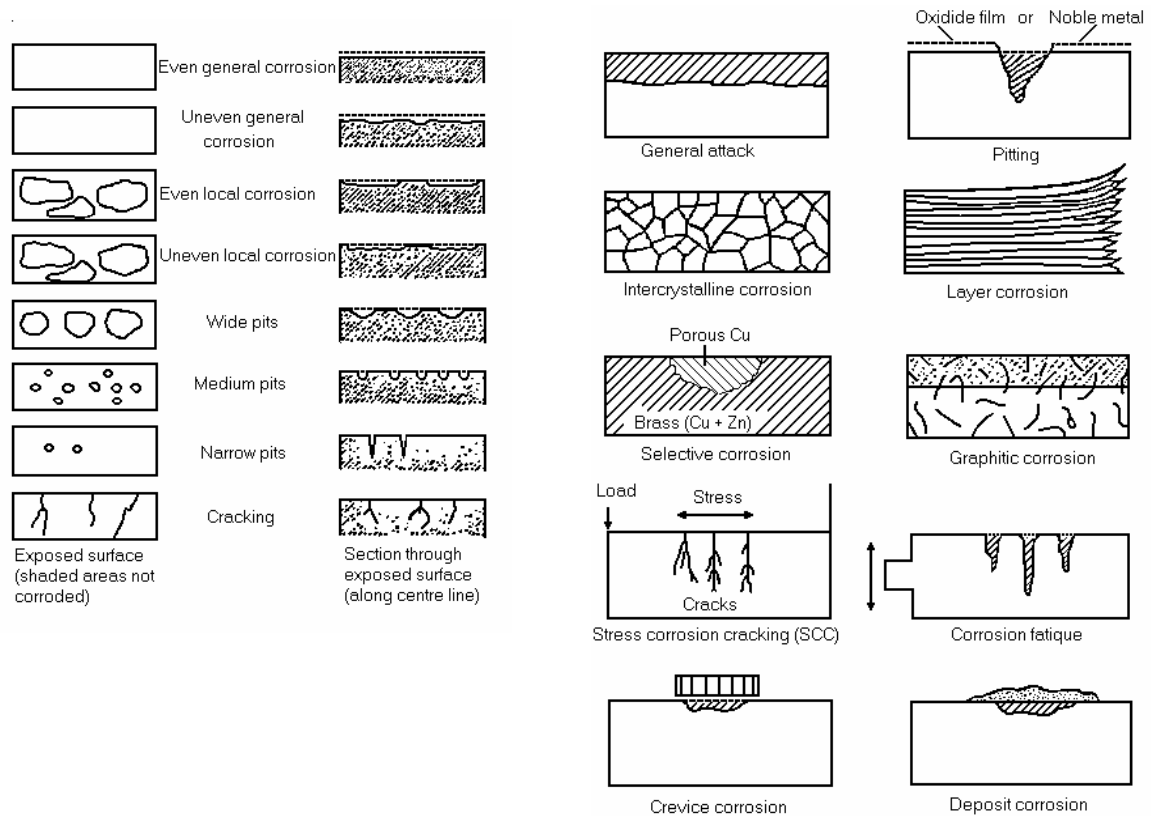


Figure 3.1 : Schematic illustration of different types of corrosion.

3.4. Energy for the reactions: *Electrochemical Thermodynamics*

3.4.1. Electromotive series of standard electrode potentials

A very important consequence of the model of corrosion as described in Chapter 2 (illustrated in fig. 2.1.) is that the interface of the metal in an electrolyte is electrified, i.e. a potential difference exists across it. Since corrosion involves -on the atomic scale- the removal of electrons from a metal atom it is also clear that the potential different across the metal - solution interface is related to the corrosion tendency of that metal.

For a metal M in a solution of its own ion (M^{n+}) of activity 1, at 25°C and atmospheric pressure this potential (difference) is well defined and is called the standard electrode potential ($E^\circ_{M/M^{n+}}$). Such potentials are often used as a guide to distinguish those metals which have a high tendency to form ions (i.e. to corrode) - having very negative potentials - from those which do not easily ionize (noble metals) - having very positive potentials. A tabulation of these potentials can be found in Ref. 1, pp. 5-7. A condensed form of it is given in Table 4.1. of this handbook.

Equilibrium reaction	E_H (Volts)
Noble	
$Au^{++} + 2e \rightleftharpoons Au$	+1.7
$\frac{1}{2}O_2 + 2H^+ + 2e \rightleftharpoons H_2O$	+1.23
$Pt^{++} + 2e \rightleftharpoons Pt$	+1.2
$Hg^{++} + 2e \rightleftharpoons Hg$	+0.85
$Ag^+ + e \rightleftharpoons Ag$	+0.80
$Cu^{++} + 2e \rightleftharpoons Cu$	+0.34
$2H^+ + 2e \rightleftharpoons H_2$	0.00 by definition

$Pb^{++} + 2e \rightleftharpoons Pb$	-0.13
$Ni^{++} + 2e \rightleftharpoons Ni$	-0.25
$Cd^{++} + 2e \rightleftharpoons Cd$	-0.40
$Fe^{++} + 2e \rightleftharpoons Fe$	-0.44
$Cr^{+++} + 3e \rightleftharpoons Cr$	-0.70
$Zn^{++} + 2e \rightleftharpoons Zn$	-0.76
$Ti^{++} + 2e \rightleftharpoons Ti$	-1.63
$Al^{+++} + 3e \rightleftharpoons Al$	-1.66
$Mg^{++} + 2e \rightleftharpoons Mg$	-2.38
Base End	

Table 4.1. The electromotive force series.

3.4.2. Empiric galvanic series

The information available in a series of standard electrode potentials will nearly never directly be applicable to practical situations. It can only directly be applied to some very selective circumstances : temperature of 25° C, atmospheric pressure and each metal is observed at equilibrium in a solution of its own ion at an active concentration of one gramme ion per litre. For other conditions, however, we have to take into account the electrode potential (E) instead of the standard electrode potential.

For a rather simple situation these electrode potentials can be calculated by means of the Nernst equation

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_{(ox)}}{a_{(red)}} \quad (4.1.)$$

For more complex systems, however, where a metal or alloy is in contact with a corrosive environment which contains a lot of different anions and cations (e.g. sea water) the electrode potential is not very well defined thermodynamically. Nevertheless, an electrode potentials does exist and can be measured. This potential can thus be used to predict the tendency (not rates) for corrosion to occur. Again the more negative the potential, the more anodic is the metal and the greater is the driving force for corrosion. The more positive the potential, the more noble is the metal or alloy and the more cathodic is its behaviour. A tabulation of some different metals and alloys, according to their corrosion tendency in sea-water, is given in table 4.2.

↑ Noble or cathodic	Platinum
	Gold
	Graphite
	Titanium
	Silver
	{Chlorimet 3 (62Ni-18Cr-18Ni)
	{Hastelloy C(62Ni-17Cr-15Mo)
	[18/8 Mo stainless steel (passive)
	[18/8 stainless steel (passive)
	[Chromium stainless steel 11-30% Cr (passive)
	{Inconel (passive) (Ni - 13Cr-7Fe)
	{Inconel (passive)
	Silver solder
	Monel (Ni- 30Cu)
	[Cupro-nickels (Cu-10 to 40Ni)
	[Bronzes (Cu-Sn)
	[Copper
	[Brasses (Cu-Zn)
	{Chlorimet 2 (66Ni-32Mo-1Fe)
	{Hastelloy B (60Ni-30Mo-6Fe-1Mn)
	}Inconel (active)
	}Nickel (active)
	Tin
	Lead
	Lead-tin solders
	{16/8 Mo stainless steel (active)
	{18/8 stainless steel (active)
	Ni-Resist (high nickel cast iron)
	Chromium stainless steel, 13% Cr (active)
	{Cast iron
	{Steel or iron
	2024 aluminium (Al-4.5Cu-1.5Mg-0.6Mn)

Table 4.2. Galvanic series of some commercial metals and alloys in seawater.

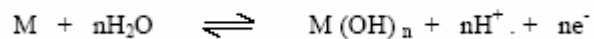
3.4.3. E-pH diagrams (Pourbaix-diagrams)

The electromotive series only takes into account those electrochemical equilibria involving metals and their simple cations (M^{n+}). In other words, the only type of reaction considered is

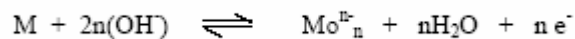


which only contains “e⁻” terms in addition to the metal (M) and metal: ion (M^{n+}) terms and so is only potential dependent.

However, there are several other relevant reactions such as

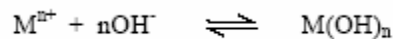


in which the metal hydroxide $M(OH)_n$ can represent a protective film if it is closely packed, tightly adherent and has a sufficiently low solubility. Another reaction is

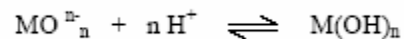


which represents corrosion of the metal in an alkaline medium. Each of these reactions contains terms in “e⁻” so that their equilibria are potential dependent, but they also contain terms in H^{+} or OH^{-} so that they are also pH dependent.

Other reactions such as



and



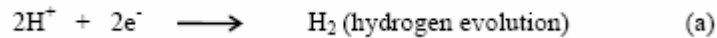
can also occur. These contain no “e⁻” terms so they are not potential dependent - but they do contain terms in H^{+} or OH^{-} so there is a dependence on pH.

It is therefore necessary to take into account considerably more data than these from the electromotive series alone in order to obtain a more complete and therefore a more useful theory of corrosion.

On the basis of the necessity to consider other equilibria a very useful form of presentation of both the potential-dependent and the pH-dependent equilibria has been evolved by M. Pourbaix in therefor, of E-pH diagrams. In these diagrams (often called Pourbaix diagrams) the two parameters E en pH are plotted for the various equilibria on normal cartesian coordinates with E as ordinate and pH as abscissa. The diagram takes account of chemical and

electrochemical equilibria for metals in conjunction with water, and since there are several such as equilibria for each metal, only one metal can be clearly represented on one diagram.

In terms of corrosion the two reduction reactions



and



are of considerable importance. Each can be seen to involve both “e” and H^+ terms so that each is both potential and pH dependent.

On the E-pH diagram these equilibria are represented by sloping lines. They are shown in fig.4.1. as the lines (a) and (b). The calculations for these equilibria have been based upon hydrogen being evolved at standard atmospheric pressure and free oxygen being available at standard atmospheric pressure. The resulting equilibrium equations are:

$$E = 0.000 - 0.059 \text{ pH} - 0.03 \log p\text{H}_2 \quad (\text{a})$$

$$E = 1.2 - 0.59 \text{ pH} + 0.015 \log p\text{O}_2$$

with $p\text{H}_2$ and $p\text{O}_2 = 1 \text{ atm}$
they become :

$$E = 0.000 - 0.059 \text{ pH} \quad (\text{a})$$

$$E = 1.2 - 0.059 \text{ pH} \quad (\text{b})$$

Hydrogen evolution is possible only at

potentials below the line (a) and only above the line (b) is oxygen evolution possible. So there is domain of the E-pH diagram in which water is thermodynamically stable.

The equilibrium diagram for H_2O (fig. 4.1.) may also be used for other diluted aqueous solutions.

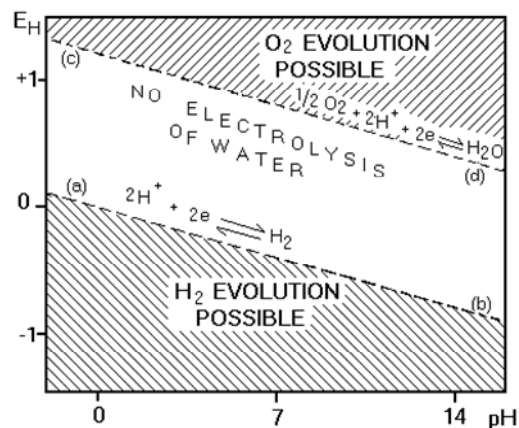
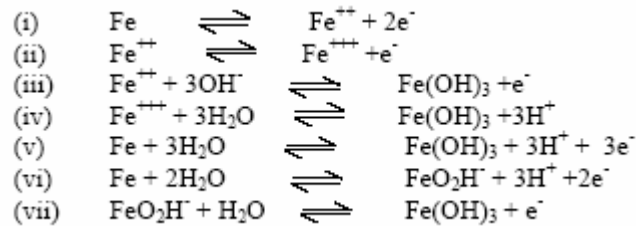


Fig. 4.1. E/pH diagram for H_2O .

In the same way that the hydrogen and the oxygen reduction reactions have the equilibria represented on the E-pH diagram, other equilibria can be represented for a metal in conjunction with water.

e.g. IRON:

The full diagram for iron is quite complex, since many equilibria are involved, but fortunately a useful simplified diagram can be obtained from a consideration of the following equilibria:



The diagram in fig. 4.2. is based upon these equilibria.

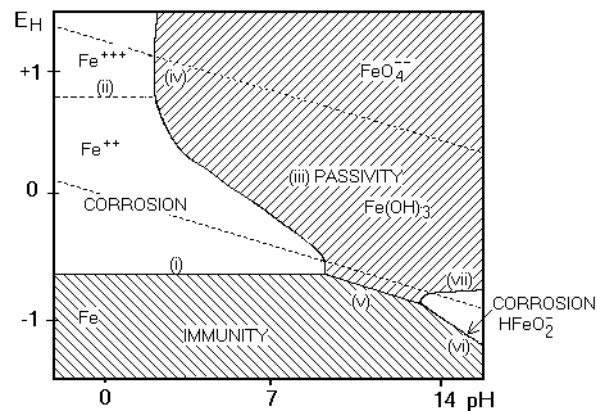


Fig. 4.2. Simplified E/pH diagram for Fe-H₂O.

3.5. Electrochemical Kinetics

3.5.1. The importance of kinetics

Thermodynamic arguments are applicable to chemical or electrochemical systems only when these are in equilibrium and can therefore only give the energetic tendencies of the reactions to proceed, that is their potential. Much more important - particularly in the case of corrosion - is a knowledge of the rates at which reactions proceed in practice, and the thermodynamic data represent only one factor affecting reaction rates.

E

E

If

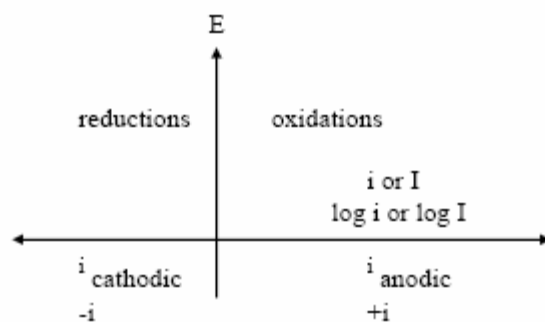
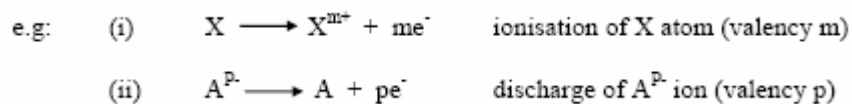


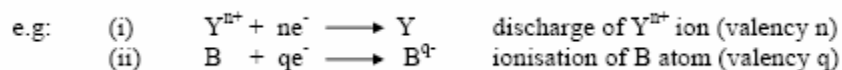
Fig. 5.1. Axes for polarisation diagrams.

There are two directions in which an electrochemical reaction can proceed, and both are important in corrosion work.

(a) Anodic - involving loss of electrons (oxidation)



(b) Cathodic - involving gain of electrons (reduction)



The rate per unit area of a typical oxidation reaction as shown in fig. 5.2 (I) and of a reduction reaction in fig. 5.2. (ii)

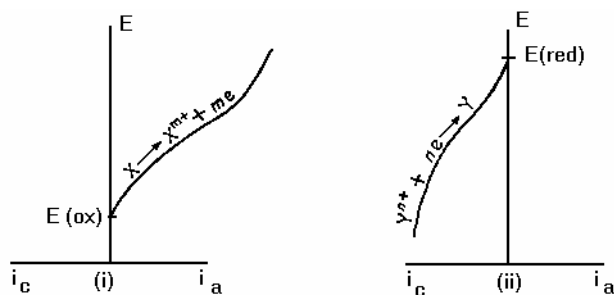


Fig. 5.2. Typical E/i curves.

3.5.3. Oxidation-Reduction balance / Real and apparent E/i curves

The rate of release of electrons by oxidation on an electrode is always exactly balanced by the rate of capture of electrons by reduction, and this balanced process comprises a continuous electron transfer.

A rate of electron transfer is, of course, a measure of electric current and this means that the total cathodic current I_c on an electrode must be exactly equal to the total anodic current I_a . By plotting on one set of axis the E/i curves for both the cathodic reaction e.g. hydrogen evolution or oxygen reduction or both of them) and for metal dissolution it is seen from fig. 5.3. and 5.4. that this balance occurs at a particular potential which is often denoted by E_{corr} . This is the rest-potential or so called corrosion-potential. It is the potential measured, for example, on a pipeline by the corrosion engineer using a reference electrode (half cell) and a voltmeter.

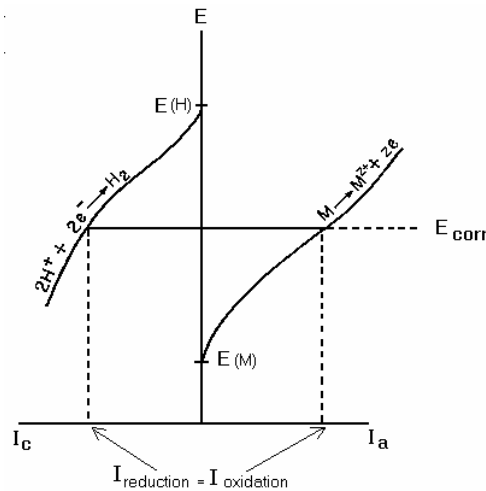


Fig. 5.3. Oxidation – Reduction balance.

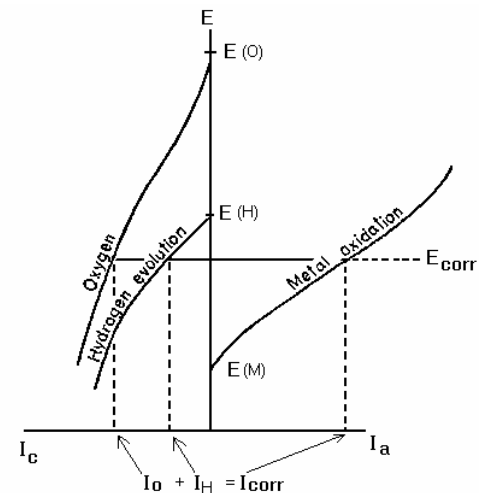


Fig. 5.4. Multi - reaction balance
(two reduction reaction + one oxidation reaction).

The magnitude of the corrosion current is, of course electrochemically equivalent to both the total rate of metal dissolution and to the rate of the reduction reaction(s), and these rate can easily be converted to mass units if required (cf. eq. 5.1.). However, the corrosion current (I_{corr}) itself can not directly be measured by means of a simple measurement with an ammeter: if an E/I curve is plotted on the basis of I being the net current as measured with an external ammeter as a function of a varying potential E , then all reactions (including reduction as well as oxidation reactions) will be included in the measurement without discrimination, to provide a compound curve. This curve will cross the vertical at E_{corr} at which the net current is zero. Such a curve is often called an apparent polarisation curve, and sometimes an electrolysis curve. The broken curve (2) in fig. 5.5. is a typical example. Another example is

represented in fig. 5.6. In this figure an apparent polarisation curve of a passivating alloy is shown. A clear explanation for the characteristic shape of this curve will be given later.

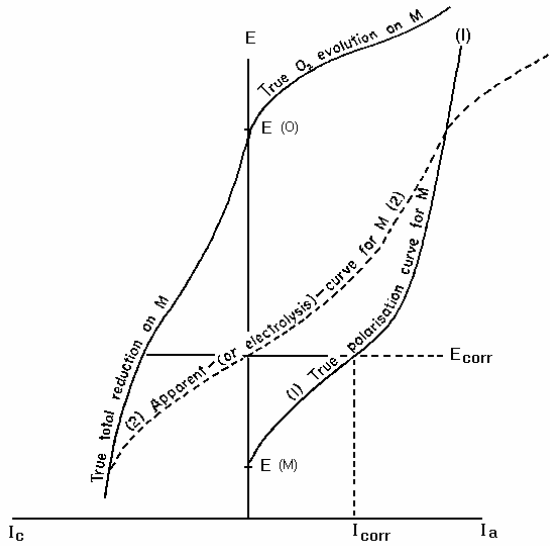


Fig. 5.5. Distinguishing true (1) and apparent (2) polarisation curves.

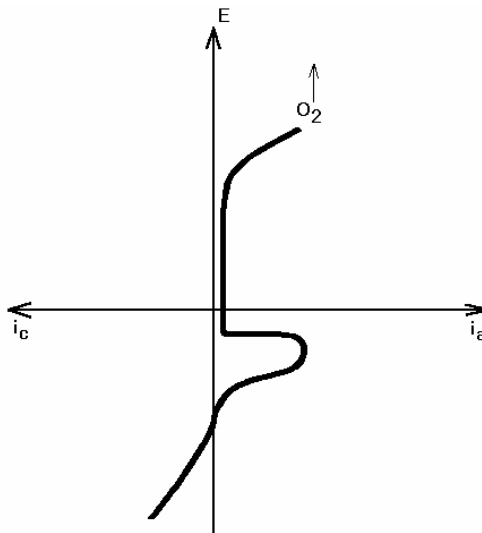


Fig. 5.6. Apparent polarisation curve for a passivating alloy.

Apparent E/I or E/i curves are most usually presented in discussions of electrode kinetics because they are obviously very much more easily produced than true polarisation curves. Therefore they must be read with an awareness of the factors causing departure from true curves.

It has already been mentioned above that I_{corr} can not directly be measured by a simple measurement with an ammeter. In a next chapter, however, we'll see how it is possible to deduce the net corrosion current from apparent polarisation curves.

3.5.4. Evans diagrams

The way of plotting E/I curves as described above is in fact a variant of the so-called “Evans diagram” where both anodic and cathodic current are drawn at the same side of the vertical axis. This is shown in fig. 5.7

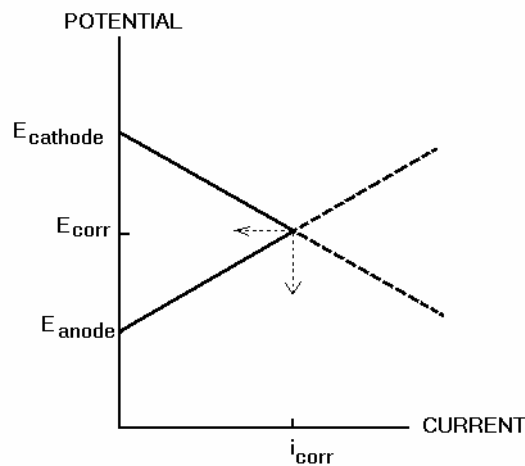


Fig. 5.7. Evans diagrams.

A more complex example of an Evans diagram for a passivating alloy is represented in fig. 5.8

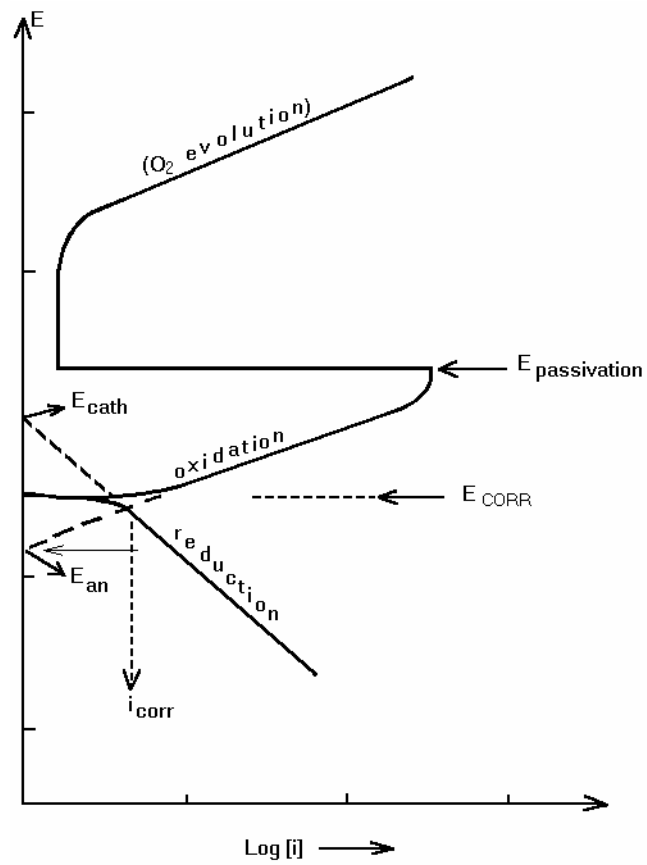


Fig. 5.8. Evans diagram for a passivating alloy.

More details about this kind of representation of E/I curves are for instance given in Ref. 1

A. Introductory:

- ### B. Rather Encyclopaedic:

- ### C. Testing:

- #### D. Data:

- More recently updated information (incl. journals) :** see overleaf –in Dutch– Annotated Corrosion Bibliography taken from: “Handboek Constructiematerialen, Corrosion & Corrosiebescherming”, Kluwer, Brussels, 1999-2003.

Literature, documentation, software & information sources

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Basic Textbooks, General Corrosion literature and Didactic Aids

Vaak wordt de vraag gesteld naar geschikte (aanvullende) literatuur omtrent corrosie en corrosiepreventieproblemen. De hiernavolgende secties proberen hierop een antwoord te geven.

Onderstaande lijst is slechts een beperkte, persoonlijke selectie van de hoofdredactie. Ze heeft enkel de bedoeling een eerste richtmaat te zijn en is (bewust) verre van volledig. Het is eerder een voorstelling van de persoonlijke handbibliotheek zoals die door leden van de redactieraad frequent wordt gebruikt in hun dagelijkse praktijk. In de toekomst zullen –mede op basis van reacties van de gebruikers van dit handboek – meer volledige overzichten worden gepubliceerd.

Handbooks

- M.G. Fontana. *Corrosion Engineering* – 3rd Ed., McGraw-Hill, New York (1986).

Hét traditionele corrosie-studieboek bij uitstek voor elke (would-be) corrosie-*expert*; oorspronkelijke edities gepubliceerd i.s.m. met N.D. Greene en algemeen internationaal gekend als (het studieboek van) "Fontana & Greene".
- H.H. Uhlig. *Corrosion Handbook*, J. Wiley, New York (1955).
- H.H. Uhlig & R.W. Revie. *Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering*, J. Wiley, New York (1985).
- U.R. Evans. *The Corrosion and Oxidation of Metals*, Edward Arnold, London (1960; supplementary volumes: 1968, 1976; 3rd revised ed. 1979).
- N.D. Tomashov. *Theory of Corrosion and Protection of Metals*, MacMillan, New York (1966).
- H. Kaesche. *Die Korrosion der Metalle* – 2nd Ed., Springer Verlag, Berlin (1979).
- F.L. LaQue & H.R. Copson. *Corrosion Resistance of Metals and Alloys*, Van Nostrand-Reinhold, New York (1963).

Enkele andere "klassiekers" uit de corrosieliteratuur; doch met een gebrekkige tot quasi onbestaande 'updating'. Sommige ook beschikbaar in verscheidene andere talen, doch niet in het Nederlands.

- D. Stuart & D. Tulloch, *Principles of Corrosion and Protection*, MacMillan, London (1986).

Eenvoudige inleiding tot het domein van de corrosie en corrosiepreventie. Aanbevelenswaardig voor een eerste kennismaking met "corrosie" tijdens een vrij week-end of verlofweek; echter niet de eerste keuze voor een gedegen en/of praktische kennis.

Andere eenvoudige inleidingen zijn:

- J.T.N. Atkinson & H. Van Droffelaar. *Corrosion and its Control: An Introduction to the Subject*, NACE International, Houston (1982).
 - L.S. Van Delinder. *Corrosion Basics*, NACE International, Houston (1984).
 - J. Bosich. *Corrosion Prevention for Practising Engineers*, Barnes and Noble, New York (1970).
 - NACE Basic Corrosion Course, NACE International, Houston (1984); nu beschikbaar in elektronische multi-media vorm (incl. video's met experimenten, interactieve zelfstudie-oefeningen, etc... - zie secties 9.7.1.2. en 9.7.4 (2000).
- J.O.M. Bockris & D.M. Drazic. *Electrochemical Science*, Taylor and Francis, London (1972).

Bockris is dé auteur voor de liefhebbers van elektrochemie. Soms visionaire inzichten en vooruitzichten omtrent de elektrochemische theorie (van corrosie).
- P.J. Gellings. *Introduction to Corrosion Prevention and Control* – 2nd Ed., Delft University Press (1985).

Eén van de preferente *inleidende* leerboeken van de hoofdredactie, geschreven door een Nederlandse auteur; echter jammer genoeg niet (meer) commercieel beschikbaar in het Nederlands. Ook internationaal een relatief ruim verspreid studieboek; tevens vertaald in het Duits (Carl Hanser Verlag, 1981) en het Vietnamees (!). Bevat wel een stevige portie elektrochemie, die misschien niet voor elke lezer even goed verteerbaar is.
- E. Mattson. *Basic Corrosion Technology for Scientists and Engineers*, The Institute of Materials, London (1996).

Als *inleidend* corrosie-studieboek een (zeer goed) alternatief voor het voorgaande; iets meer praktisch gericht, doch zonder de gedegen elektrochemische basis van het bovenstaande werk. Engelse vertaling van een uiterst succesvol Scandinavisch (Zweeds) studieboek omtrent corrosie.
- *Corrosiehandleidingen* van het Nederlands Corrosie Centrum (NCC), Bilthoven, NI. :
 - o Deel 1 : *Algemene inleiding*
 - o Deel 2 : *Materiaalkeuze en constructieve aspecten*

- o Deel 3 : Kathodische en anodische bescherming
- o Deel 4 : Corrosiebestrijding door metallische en anorganische deklagen
- o Deel 5 : Corrosiebestrijding door waterbehandeling
- o Deel 6 : Corrosiebestrijding door organische deklagen
- o Deel 7 : Onderzoek en diagnose van corrosieschade
- o Deel 8 : Corrosie van wapening en andere metalen in beton

Een unieke collectie Nederlandstalige brochures ("corrosiehandleidingen") m.b.t. diverse corrosie-bestrijdingstechnieken; startend van de basisbeginselen tot de praktische implementatie ervan – weliswaar overlappend en minder compleet dan het huidige werk, doch absoluut aangeraden literatuur voor een snelle kennismaking.

- K. Baumann, *Korrosionsschutz für Metalle*, Aufl. 2., Deutscher Verlag für Grundstoffindustrie, Leipzig - Stuttgart (1993).

Nauwelijks gekend, doch zeer goed boek(je) –215 pp.– uit de voormalige DDR; vooral gericht op de praktijkingenieur, met diverse, vaak niet elders gepubliceerde, synoptische diagramma's en beslissingstabellen.

- S.L. Chawla & R.K. Gupta. *Materials Selection for Corrosion Control*. ASM International (1993).

Een eveneens vrij onbekend werk van twee Indische auteurs, doch géén tweederangpublicatie uit een derdewereldland, maar een recent en uitstekend (studie-)boek omtrent corrosie-engineering (508 pp. – kleine druk). Een aanbevelenswaardig alternatief voor "Fontana & Greene" (cfr. supra), met Aziatisch geduld gecompileerd. Een unieke karakteristiek is zijn brede bruikbaarheid, zowel voor de (bijna) beginner als voor de meer gevorderde lezer. Bevat tevens een overzicht van moderne (elektronische) corrosie- en materialen-informatiesystemen.

- C.P. Dillon, *Corrosion control in the chemical process industries*, 2nd Ed., MTI & NACE International (1994).

Mooie inleiding voor de beginner; vooral voor degene die op zoek is naar bijkomend materiaalselectie-advies in diverse chemische milieus, eerder dan voor de volslagen corrosie-leek. Geen diepgaande beschrijvingen, doch een ganse reeks praktische beschouwingen, met interessante overzichten omtrent het gedrag van diverse materiaalengroepen in een serie belangrijke industriële chemicaliën (ca. 400 pp.).

- L.L. Shreir, R.A. Jarman & G.T. Burstein, *Corrosion*, 3rd Ed. (deel 1 & 2), Butterworth-Heinemann Ltd. (Elsevier), Oxford (1994).

Een korte titel, doch een absolute klassieker en hét referentie-handboek bij uitstek in het corrosie-vakgebied. Niet onmiddellijk een studieboek voor de beginner –21 hoofdstukken, vaak meer dan 100 pp. elk–, doch eerder een werk voor de expert die nogmaals wat wil bijstuderen, verifiëren of opfrissen. Integraal in elektronische vorm beschikbaar op "Active Library on Corrosion" CD-ROM (cfr. Sectie 9.7.4).

- In: *Chemical Engineers' Handbook* (ed. R.H. Perry & C.H. Chilton, et al.; diverse uitgaven McGraw-Hill) – "*Materials of Construction*".

Slechts een (relatief klein) hoofdstuk in een gerenommeerd handboek, doch een interessante (snelle) inleiding tot "corrosie" en het gedrag van materialen; met diverse praktische gegevens, zeker voor scheikundig ingenieurs of andere technici werkend in de chemische procestechnologie.

Encyclopaedic Works & Data books

- L.L. Shreir, R.A. Jarman & G.T. Burstein, *Corrosion*, 3rd Ed. (deel 1 & 2), Butterworth-Heinemann Ltd. (Elsevier), Oxford (1994).

Cfr. supra.

- In: *Materials Handbook* (materialen-encyclopedie — ed. G.S. Brady & H. R. Clauser, et al.; diverse uitgaven, ASM International) – Vol. 13 "*Corrosion*".

- B.J. Moniz & W.I. Pollock (Eds.). *Process Industries Corrosion – The Theory and Practice*, NACE International, Houston (1986).

Interessante poging tot inventarisatie van de corrosieproblemen en 'state-of-the-art' m.b.t. beschikbare oplossingen in de chemische procesindustrie; het belang van het boek beperkt zich echter geenszins tot deze industriesector. Meer dan 50 verschillende hoofdstukken en bijdragen van diverse gerenommeerde experts in hun vakgebied (totaal 858 pp. groot formaat, met diverse indexen). Deels in elektronische vorm terug te vinden op "Active Library on Corrosion" CD-ROM (cfr. Sectie 9.7.4).

- E. Rabald. *Corrosion Guide*, Elsevier, Amsterdam (1968).

Een magnifieke gids en uiterst belangrijke "reservoir" aan praktische corrosiekennis en -ervaring, met duizenden "materials performance case histories" en beschrijvingen voor bijna alle traditionele materiaalclassen in de meest diverse industriële chemische milieus. Bevat echter geen of weinig gegevens voor de nieuwste technische materialen (e.g. superaustenieten, -ferrieten, nieuwe generatie duplexen), doch des te meer data voor de traditionele constructiematerialen (traditionele RVS en andere staalsoorten, diverse non-ferromaterialen, etc...). Niet meer als dusdanig meer in de handel verkrijgbaar, doch integraal in elektronische vorm beschikbaar op "Active Library on Corrosion" CD-ROM (cfr. Sectie 9.7.4).

- D.J. De Renzo. *Corrosion Resistant Materials Handbook*, 4th Ed., Noyes Data Corporation (1985).
Conventionele corrosie-data selectie, met een relatief belangrijk aandeel voor data omtrent niet-metalen (inclusief cement, mortel, asfalt, ...).
- P.A. Schweitzer. *Corrosion Resistance Tables – Metals, Plastics, Nonmetallics, and Rubbers*, Marcel Dekker, New York (1976); en P.A. Schweitzer. *Corrosion Resistance of Elastomers*, Marcel Dekker, New York (1990).
Idem.
- NN., *Corrosion Handbook*. Dechema, Frankfurt (1993).
Een wat misleidende titel voor een ganse "corrosie-encyclopedie" (12 Volumes); in het Duits gepubliceerd als een losbladig aanvulwerk onder de al even misleidende naam "Dechema Werkstoff-Tabelle". Geen data-collectie in de traditionele betekenis van het woord, doch eerder een (gigantisch grote) literatuurstudie omtrent het gedrag van diverse materiaalklassen in een serie belangrijke industriële chemicaliën; vraagt interpretatie door een deskundige, doch is voor deze laatste een zeer belangrijke referentie.
- NN. *Handbook of Corrosion Data*, ASM International (1990).
Corrosie-data overzicht voor verschillende materialen in een ruime serie chemicaliën en corrosieve milieus; met diverse verwijzingen naar de primaire corrosie-literatuur waaruit de gegevens en grafieken of tabellen bekomen werden (683 pp.).
- R.S. Treseder. *NACE Corrosion Engineer's Reference Book*, NACE International, Houston (1980).
Handig naslagwerkje, oorspronkelijk bekend als (en gebaseerd op) "het corrosie-data boekje van Shell" (daterend uit de jaren '60 en stelselmatig aangevuld). De meest recente editie ("1989) is beschikbaar in elektronische vorm op "Active Library on Corrosion" CD-ROM (cfr. Sectie 9.7.4). De belangrijkste gegevens zullen finaal ook –in geupdate vorm– beschikbaar zijn in het huidige handboek.
- NN. *Corrosion Data Survey – Metals; Corrosion Data Survey – Nonmetals*, NACE International, Houston (1974 - rev. 1985; 1975).
Dé corrosie-database van NACE, oorspronkelijk in gedrukte vorm gepubliceerd, doch momenteel nog enkel beschikbaar in elektronische vorm als resp. "CORSUR" en "CORSUR 2"; integraal terug te vinden op "Active Library on Corrosion" CD-ROM (cfr. Sectie 9.7.4).
De oorsprong gaat terug tot Nelson's "Corrosion Data Survey" (Shell Development Co., San Francisco, 1969), doch de data werden zowel in de jaren '70 als '90 aangevuld en/of herzien.
- M. Pourbaix. *Atlas d'Equilibres Electrochimiques à 25°C*, Gauthier-Villars, Paris (1963).
De traditionele "Pourbaix Atlas", ook beschikbaar in Engelstalige versie (publ. NACE International, Houston), met de diverse thermodynamische evenwichten en mogelijke (elektro-)chemische reacties voor quasi alle metalen in waterige milieus bij omgevingstemperaturen.
- NN., *The Metals Black Book* (ferrous metals) / *The Metals Red Book* (nonferrous metals), Casti Publ., Edmonton (1993).
Interessante datacollectie omtrent diverse klassen metallieke materialen, doch met niet meer technische inhoud dan wat je uiteindelijk in de finale versie van het huidige handboek zal aantreffen.
- NN. *Stahlschlüssel (Key to Steel)*, 19th Edition (2001).
Hét algemene standaardwerk voor kruisreferenties (concordantietabellen) tussen materiaalspecificaties volgens normen van meer dan twintig verschillende landen of organisaties (3-talig: Engels, Duits, Frans); ca. 710 pp., ook beschikbaar in CD-ROM versie. Kruisreferenties voor veel gebruikte of belangrijke materialen zijn ook terug te vinden in sectie 8.1.2 van het huidige handboek.

Corrosion test methods & laboratory experiments

- F. Mansfeld & U. Bertocci, *Electrochemical Corrosion Testing*, ASTM, Philadelphia (1979).
- W.M. Ailor, *Handbook on Corrosion Testing and Evaluation*, J. Wiley, New York (1971).
- R. Baboian, *Electrochemical Techniques for Corrosion*, NACE International, Houston (1977); heeft diverse (losbladige) meer recente opvolgers (ed. B. Syrett et al.).
- P. McIntyre & D.J. Mills, *Corrosion Standards II*, The Institute of Materials, London (1996).
- R. Baboian, *Corrosion Tests and Standards – Application and Interpretation*, ASTM Manual MNL20, ASTM, Philadelphia (1995).

- NN., *Metal Test Methods and Analytical Procedures: Wear and Erosion; Metal Corrosion*, Annual Book of ASTM Standards Vol 03.02, ASTM, Philadelphia (jaarlijks herzien).
- E. Heitz, A. Henkhaus & A. Rahmel, *Korrosionskunde im Experiment, Untersuchungsverfahren Messtechnik*, Verlag Chemie, Weinheim (1983).
- V.E. Carter, *Corrosion Testing for Metal Finishing*, The Institute of Metal Finishing, Birmingham & Butterworth Scientific, London (1988).
- NN., *Guidelines on Electrochemical Measurements*, EFC Publication No. 4, The Institute of Materials, London (1990).
- NN., *Guidelines for Methods of Testing and Research in High Temperature Corrosion*, EFC Publication No. 14, The Institute of Materials, London (1995).

Corrosion journals

De belangrijkste hedendaagse internationale corrosietijdschriften zijn:

- *Corrosion*. NACE International, Houston.
- *Corrosion Science*. Elsevier Science, Oxford.
- *Journal of the Electrochemical Society*. The Electrochemical Society, Pennington.
- *Corrosion Abstracts* (enkel nog in elektronische vorm). Cambridge Scientific.
- *Materials Performance*. NACE International, Houston.
- *Werkstoffe und Korrosion (Materials and Corrosion)* – Tweektalig, Duits / Engels. Verlag Chemie, Weinheim.
- *British Corrosion Journal*. The Institute of Materials, London.
- *Boshoku Gijutsu* (Japan. Corrosion Engineering) – Japans, met Engelstalige Abstracts, figuren en tabellen.
- *Métaux – Corrosion – Industrie*. St. Germain-en-Laye.
- *Protection of Metals* (vertaling van het Russische Zashchita Metallov, Moscow), New York.

Daarnaast publiceren **diverse andere technische tijdschriften** (bv. Chemical Engineering, Chemical Engineering Progress, Metal Progress, ...) regelmatig interessante bijdragen omtrent allerlei corrosie- en materiaalproblemen. Een lijst van een serie "klassiekers" of belangwekkende technische artikelen en/of andere publicaties van de laatste jaren vindt u hieronder:

- Agarwal, D.C., "Defy corrosion with recent nickel alloys", Chemical Engineering Progress, vol. 94, p.62-66, 1999.
- Asphahani, A.I., "Corrosion resistance of high performance alloys," Materials Performance, vol.19, No. 12, pp. 33-42, 1980.
- Bauman, Thomas C. and Leslie T. Overstreet, "Corrosion and Piping Materials in the CPI," Chemical Engineering, pp. 59-68, 3-4-1978.
- Brown, R.S., "The three-way tradeoff in stainless steel selection," Material Engineering, vol. 96 (5), pp. 58-62, 11-1982.
- Brown, Robert S., "Selecting Stainless Steel for Pumps, Valves and Fittings," Chemical Engineering, pp. 109-112, 9-3-1981.
- Chandler, Harry E., "Ferritic Stainless Steel Combats Chloride Corrosion," Metal Progress, pp. 63-66, 10-1985.
- Cottis, R.A., "Corrosion is not a problem - but the cost of corrosion is," Metallurgia, pp. 76-80, 2-1982.
- Cowan, C.T., "Choosing Materials of Construction for Plate Heat Exchangers - Part I," Chemical Engineering, pp. 100-103, 9-6-1975.
- Cowan, C.T., "Choosing Materials of Construction for Plate Heat Exchangers - Part II," Chemical Engineering, pp. 102-104, 7-7-1975.
- Davidson, Ralph M. and Kurt H. Miska, "Stainless-Steel Heat Exchangers - Part I," Chemical Engineering, pp. 129-133, 12-2-1979.
- Davidson, Ralph M. and Kurt H. Miska, "Stainless-Steel Heat Exchangers - Part II," Chemical Engineering, pp. 111-114, 12-3-1979.
- De Clerck, Donald H. and Adam J. Patarcy, "Guidelines for Selecting Corrosion-Resistant Materials," Chemical Engineering, pp. 46-63, 24-11-1986.
- Dobson, Wilson G., "Corrosion Failure Analysis", Metal Progress, pp. 57-62, 8-1979.
- Elder, George B., "Preventing Corrosion Failures in Chemical Processing Equipment," Metal Progress, pp. 44-46, 4-1977.
- Elliot, D. and S.M. Tupholme, "An introduction to steel selection: Part 2 (Stainless steel engineering design guides)," p. 43 (boek).
- Evans, Lee, "Selecting Engineering materials for chemical and process plant", 1974 (boek).
- Evans, L.S., "Chemical and process plant: A guide to the selection of engineering materials," 1980 (boek).
- Evans, L.S., "Choosing stainless steels," Engineering, vol. 220 (8), pp. 882-883, 8-1980.
- Evans, Lee, "Materials Selection Tips for Process Plants," Chemical Engineering, pp. 99-100, 1981.
- Farag, M.M., *Materials & Process selection in engineering*, 1979 (boek).
- Fassler, K. and H. Spahn, "Materials performance and materials selection under the aspect of cooling water corrosion of heat exchangers," Zeitschrift für Werkstofftech., pp. 227-238, 7-1980.
- Flanders, Robert B., "Try tantalum for corrosion resistance," Chemical Engineering, pp. 109-110, 17-12-1979.
- Fluck, David E., Robert B. Herchenroeder, George Y. Lai, and Michael F. Rothman, "Selecting Alloys for Heat Treatment Equipment," Metal Progress, pp. 35-40, 9-1985.
- Hack, H. P., "Galvanic Corrosion", 1988 (boek).
- Hagel, W.C. and K.H. Miska, "How to select alloy steels for pressure vessels - I," Chemical Engineering, pp. 89-91, 28-7-1980.
- Hagel, W.C. and K.H. Miska, "How to select alloy steels for pressure vessels - II," Chemical Engineering, pp. 105-108, 25-8-1980.
- Hughson, Roy V., "High-nickel alloys for Corrosion Resistance," Chemical Engineering, pp. 125-136, 22-11-1976.

- Kirby, Gary N., "Corrosion performance of carbon steel," Chemical Engineering, pp. 73-84, 12-3-1979.
- Kirby, Gary N., "How to select materials," Chemical Engineering, pp. 86-131, 3-11-1980.
- Kirby, Gary N., "Selecting Alloys for chloride service - Part I," Chemical Engineering, pp. 81-83, 4-2-1985.
- Kirby, Gary N., "Selecting alloys for chloride service - Part II," Chemical Engineering, pp. 99-102, 4-3-1985.
- Klein, H. Joseph, F.G. Hodge, and A.I. Asphahani, "Corrosion Resistant Alloys for the Chemical Process Industry," Metal Progress, pp. 38-44, 2-1980.
- Knittel, Donald R., "Zirconium: A corrosion-resistant material for industrial applications," Chemical Engineering, pp. 95-97, 2-6-1980.
- Kolts, Juri, "Highly Alloyed Austenitic Materials for Corrosion Service," Metal Progress, pp. 25-36, 9-1983.
- Landrum, R. J., "Fundamentals of Designing for Corrosion Control" (NACE, Houston, 1989) (boek).
- Lee, R.P., "Tracing the causes of metal failures in process equipment," Chemical Engineering, pp. 213-220, 13-9-1976.
- Marshall, W.W., "Construction materials for C.P.I.," Chemical Engineering, pp. 221-225, 228, 5-1981.
- McClain, Gregory E. and W.A. Mueller, "Corrosion problems in Acid flow control (Sulfuric plant operations)," Chemical Engineering Progress, pp. 48-50, 2-1982.
- McDowell, David W., "Handling phosphoric acid and phosphate fertilizers - I," Chemical Engineering, pp. 119-121, 4-8-1975.
- McDowell, David W., "Handling phosphoric acids and phosphate fertilizers - II," Chemical Engineering, pp. 121-124, 1-9-1975.
- McDowell, David W., "Handling Sulfuric Acid," Chemical Engineering, pp. 118-128, 11-11-1974.
- McDowell, David W., "Handling mixed nitric and sulfuric acids," Chemical Engineering, pp. 133-135, 11-11-1974.
- McDowell, David W., "Handling Nitric acid," Chemical Engineering, pp. 129-132, 11-11-1974.
- McDowell, David W., "Choosing materials for sulfuric-acid services," Chemical Engineering, pp. 137-140, 4-7-1977.
- McIntyre, Dale R., "How to prevent stress-corrosion cracking in stainless-steels - Part I," Chemical Engineering, pp. 107-112, 7-4-1980.
- McIntyre, Dale R., "How to prevent stress-corrosion cracking in stainless-steels - Part II," Chemical Engineering, pp. 131-135, 5-5-1980.
- Minkler, Ward W., "Titanium for chemical processing equipment," Metal Progress, pp. 27-31, 2-1978.
- Moore, Robert E., "Selecting Materials to meet Environmental Conditions - Part I," Chemical Engineering, pp. 101-103, 2-7-1979.
- Moore, Robert E., "Selecting Materials to resist Corrosive Conditions - Part II," Chemical Engineering, pp. 91-94, 30-7-1979.
- Newman, Jeremy, "Fighting corrosion with titanium castings," Chemical Engineering, pp. 149-154, 4-6-1979.
- Pitcher, John H., "Stainless Steels: CPI Workhorses," Chemical Engineering, pp. 119-124, 22-11-1976.
- Pludek, V. R., "Design and Corrosion Control", 1977 (boek).
- Puyear, R.B., "Material Selection Criteria for Chemical Processing Equipment," Metal Progress, pp. 40-45, 2-1978.
- Redmond, Fairhurst, and Watanabe, "High-performance Stainless Steels (Condenser design)," Sheet Metal Industry, vol. 61, pp. 143-144, 147-148, 3-1984.
- Redmond, James D. and Kurt H. Miska, "High Performance Stainless Steels for High-chloride Service - Part I," Chemical Engineering, pp. 93-96, 25-7-1983.
- Redmond, James D. and Kurt H. Miska, "High Performance Stainless-Steels for High-chloride Service - Part II," Chemical Engineering, pp. 91-94, 22-8-1983.
- Review of technological requirements for high-temperature materials R&D, EC-Commission Report EUR 5623 en (1979, reprinted 1982) ISBN 92-825-1123-5.
- Romanoff, M., "Underground Corrosion", 1957 - original issue (boek).
- Sandstrom, R., "An approach to systematic materials selection," Materials Design, vol. 6 (6), pp. 328-338, 12-1985.
- Scarberry, R.C., Graver, and Stephens, "Alloying for corrosion control - properties and benefits of alloy materials," Materials Protection, pp. 54-57, 6-1967.
- Schillmoller, C.M., "Alloys to resist chlorine, hydroge chloride and hydrochloric acid," Chemical Engineering, pp. 161-164, 10-3-1980.
- Schillmoller, C.M. and H.P. Klein, "Selecting and Using some High Technology Stainless Steels," Metal Progress, pp. 22-29, 2-1981.
- Schott, G., "Comparison of known methods of material selection," Freiburger Forschungsh. Metall., pp. 85-91, (B221), 1981.
- Spahn, Heinz, "Performance Requirements for Stainless Steels in the Chemical Industry," Metal Progress, pp. 32-37, 2-1979.
- Streicher, Michael A., "New Stainless Steels for the Process and Power Industry," Metal Progress, pp. 29-42, 10-1985.
- Waterhouse, R. B., "Fretting Corrosion", 1972 (boek).
- Waterman, N.A., The selection of materials: Engineering Design Guides: 29, 1979 (boek).
- Wilson, C.L., Corrosion and the Engineer, 1968.
- Wilson, J., "The penalties of neglect," Consulting Engineer, vol. 46, p. 19, 9-1982.
- Yamartino, James, "Installed Cost of Corrosion-resistant Piping - 1978," Chemical Engineering, p. 138 e.v., 20-11-1978.
- Yau, Te-Lin & K.W. Bird, "Manage corrosion with zirconium", Chemical Engineering Progress, vol.91, pp. 42-46, 1995.
- Zgaga, R., "Conception of the selection of materials," Freiburger Forschungsh. Metall., pp. 9-17, (B221), 1981.

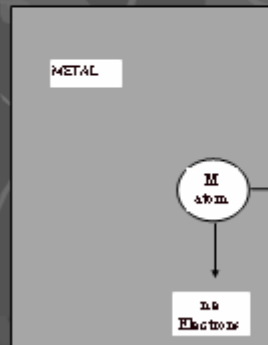
Electronic Courses, Videos & Multi-mediasystems

Dit is –vanzelfsprekend– een zeer snel evoluerend domein. Op dit ogenblik zijn volgende producten/systemen enigszins toonaangevend of ruim verspreid :

- Video's / films uitgegeven door de EFC (European Federation of Corrosion), London :
 - Corrosion Prevention by Design (25 min.)
 - Corrosion Control by Protective Coatings (21 min.)
 - Corrosion Control by Changing the Environment (27 min.)
- Marine Corrosion (video), J. Galland - Ecole Centrale, Parijs.

Additional Illustrations – Course Transparencies

Metal (in-)stability : Origin of Electrode Potential – E



Nernst :

$$E = E^0 + RT/nF * \ln [a_{ox}/a_{red}]$$

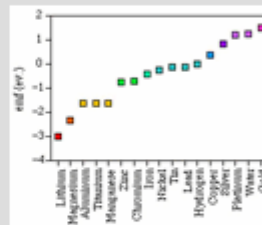
EMF Series

E^0 – Data :

Noble End (electro-positive)

	E_0 (Volts)
$Au^{3+} + 2e = Au$	+1.7
$\frac{1}{2} O_2 + 2H^+ + 2e = H_2O$	+1.23
$Pt^{2+} + 2e = Pt$	+1.2
$Hg^{2+} + 2e = Hg$	+0.85
$Ag^+ + e = Ag$	+0.80
$Fe^{3+} + e = Fe^{2+}$	+0.77
$Cu^{2+} + 2e = Cu$	+0.34
$2H^+ + 2e = H_2$	0 (def.)
$Pb^{2+} + 2e = Pb$	-0.13
$Ni^{2+} + 2e = Ni$	-0.25
$Cd^{2+} + 2e = Cd$	-0.40
$Fe^{2+} + 2e = Fe$	-0.44
$Cr^{3+} + 3e = Cr$	-0.70
$Zn^{2+} + 2e = Zn$	-0.76
$Ti^{2+} + 2e = Ti$	-1.63
$Al^{3+} + 3e = Al$	-1.66
$Mg^{2+} + 2e = Mg$	-2.38

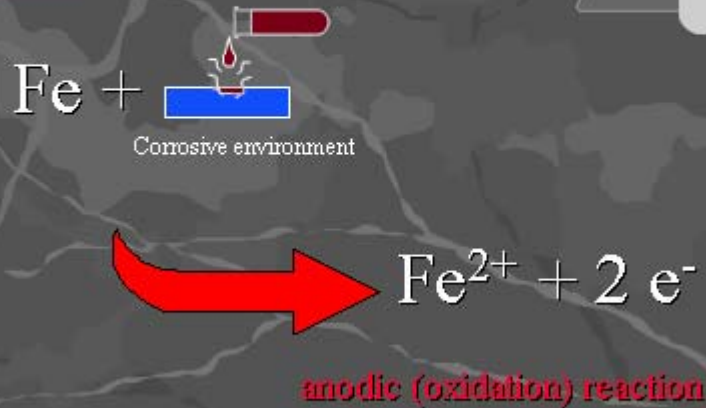
Base End (electro-negative)



Nernst :

$$E = E^0 + RT/nF * \ln [a_{ox}/a_{red}]$$

Corrosion mechanism



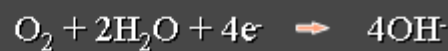
Reduction reactions

Depending on the nature & components
of the environment :

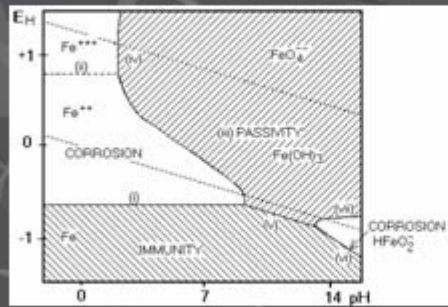
– acid environment :



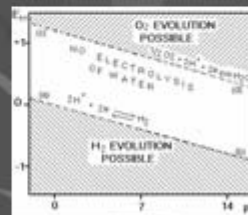
– alkaline or neutral environment :



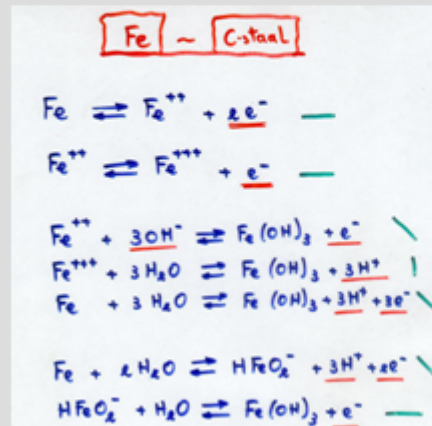
Thermodynamics: E-pH Diagrams



"Pourbaix" diagrams ...



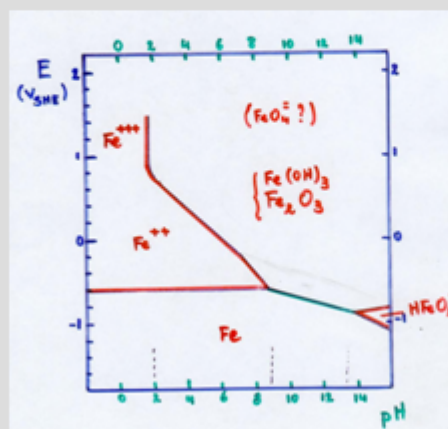
E-pH Iron/Steel



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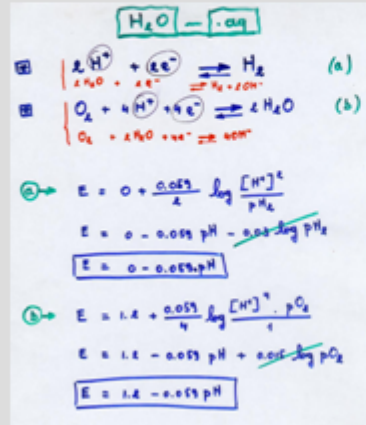
E-pH



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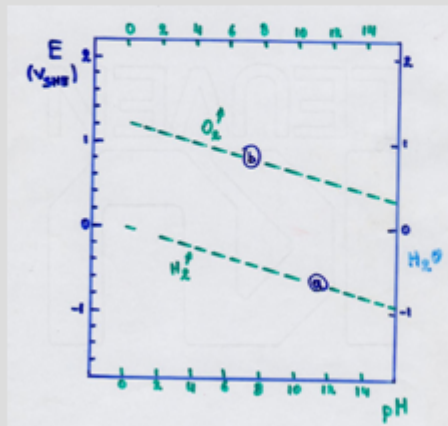
E-pH Water



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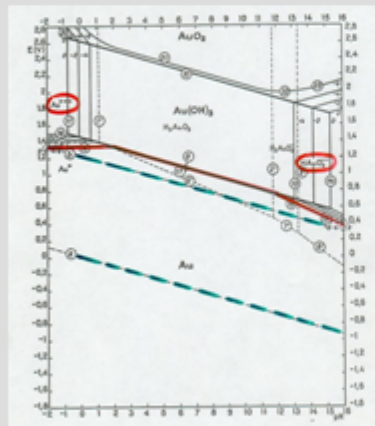
E-pH



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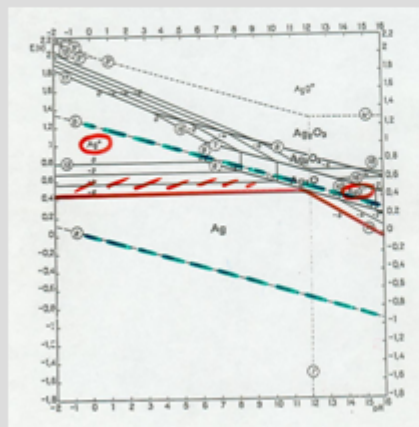
E-pH Gold



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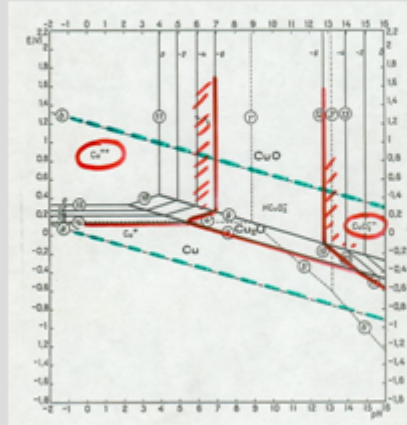
E-pH Silver



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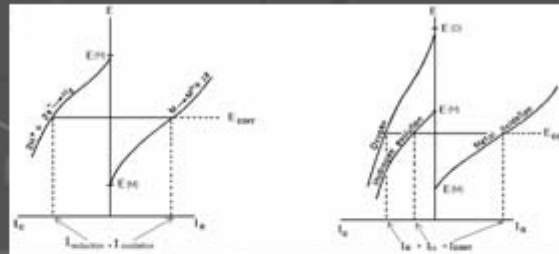
E-pH Copper



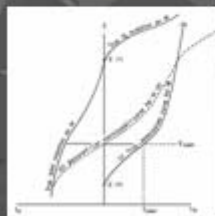
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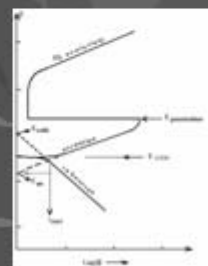
Kinetics



"Polarization curves" ...



Passivating metal



Types of Corrosion

General (uniform) corrosion

- ◆ "Rusting"
- ◆ "Wastage"
- ◆ "White Rust"

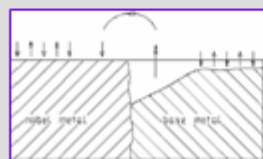


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Galvanic corrosion

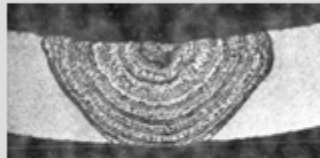
- ◆ Corrosion between a noble and less noble metal in the presence of an aggressive medium
- ◆ The more electro-positive = cathode, the least electropositive = anode



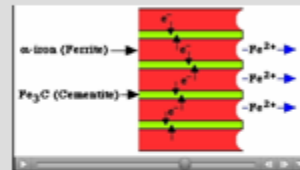
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Galvanic corrosion (2)

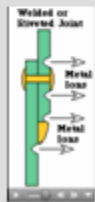


*Selective Leaching
(Dealloying)*

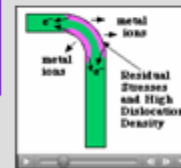


Microstructural Effects

Bimetallic Corrosion



(Oxygen) Concentration Cell



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Galvanic (3)

Galvanic series in seawater at 77°F (25°C) *

Least noble = anodic = most susceptible to corrosion

Magnesium and its alloys
Zinc
Galvanized steel or galvanized wrought iron
Aluminum alloys 3004, 3003, 1100, in this order
Cadmium
Low carbon steel
Wrought iron
Cast iron
Nickel cast irons
Stainless steel, Type 410 (active)
50-50 lead-tin solder
Stainless steel, Type 304 (active)
Stainless steel, Type 316 (active)
Lead
Tin
Muntz metal, C28000
Alloy 200 (active)
Alloy 600 (active)
Yellow brass, C27000
Aluminum bronzes, C91400
Red brass, C23000
Commercially pure copper, C11000
Silicon bronze, C65500
Alloy 200 (passive)
Alloy 600 (passive)
Alloy 400
Stainless steel, Type 410 (passive)
Stainless steel, Type 304 (passive)
Stainless steel, Type 316 (passive)
Alloy 625
Alloy 625
Alloy C
Silver
Titanium
Gold

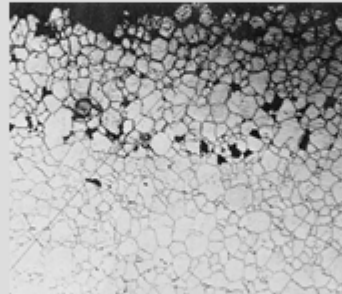
Most noble = cathodic = most corrosion-resistant

*Bimetallic corrosion :
practical ...*

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IGA & Sensitization

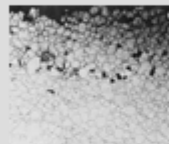


Mechanisms ...
Weld Decay .../...

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Sensitization & Weld Decay



Mechanism :
 Cr_{23}C_6

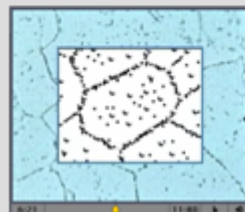


Illustration 'weld decay' ...

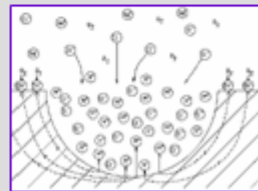
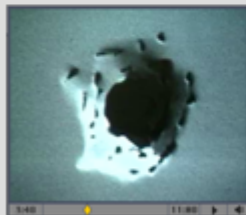


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Pitting corrosion

- ◆ Caused by Chlorides (halides)
- ◆ Passive metals & alloys = susceptible



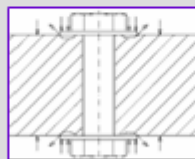
Mechanism ...

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Crevice corrosion

- ◆ Accelerated corrosion in a narrow crevice between two parts of a component, ...one of which is made from a metal ...



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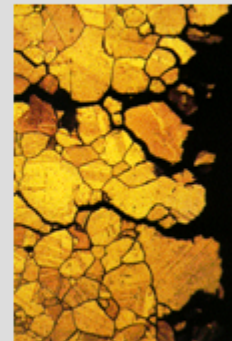
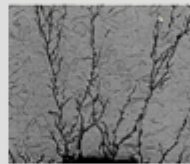
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Stress Corrosion Cracking (SCC)

(Sudden) fracture of a metal upon exposure to a corrosive environment

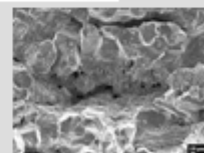
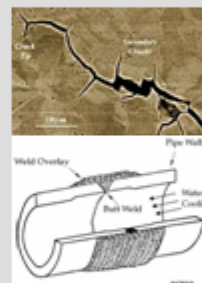
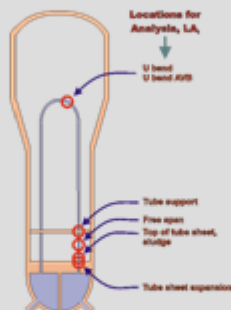
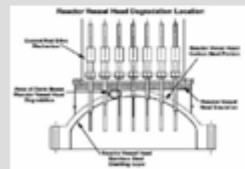
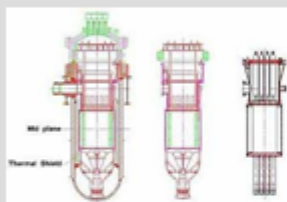
- ◆ Intergranular ...
- ◆ Transgranular ...

"season cracking"



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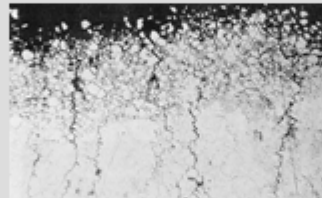
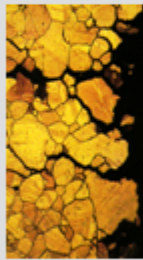
e.g. Nuclear ...



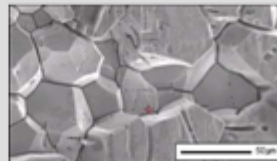
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Intergranular Stress Corrosion Cracking (IGSCC)



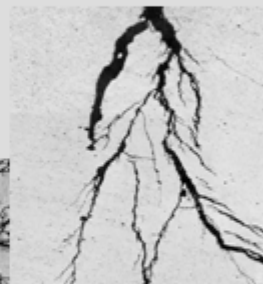
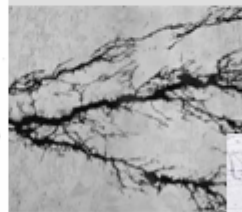
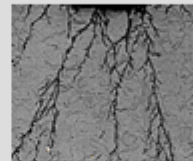
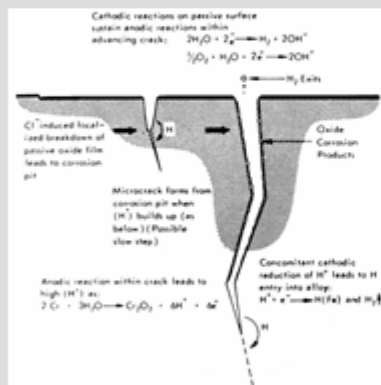
Mechanisms ...



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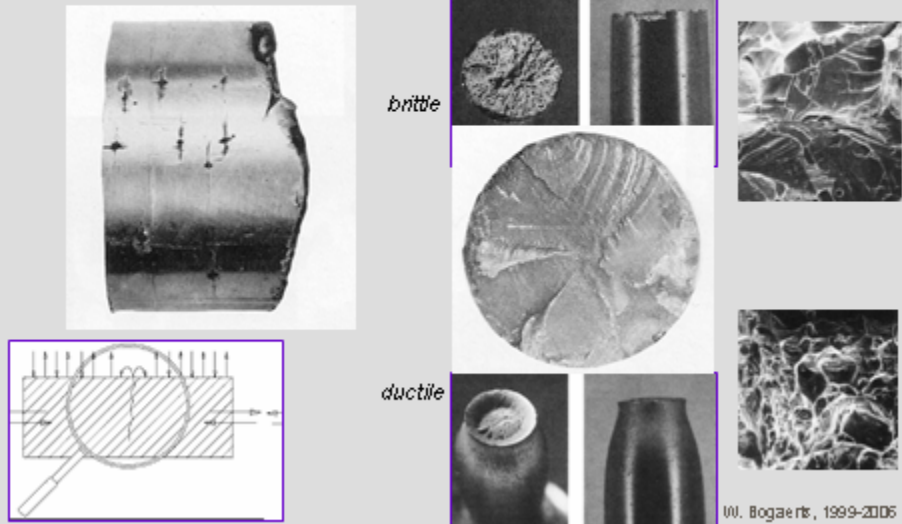
Transgranular Stress Corrosion Cracking (TGSCC)



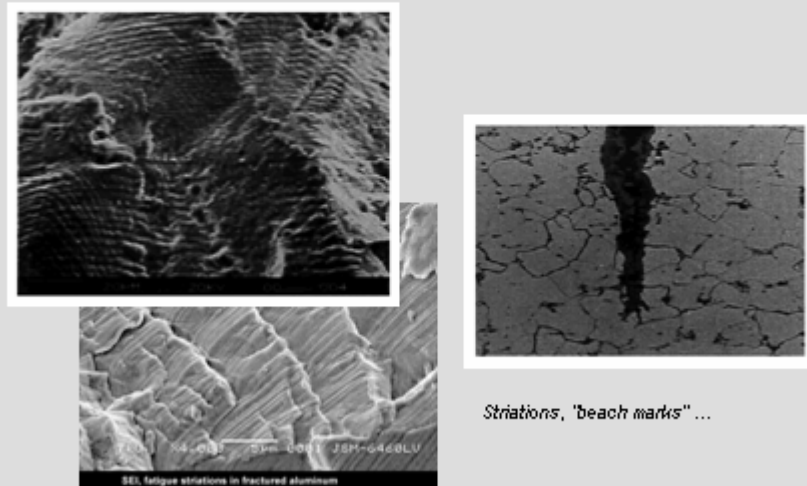
Mechanism (theories) ...

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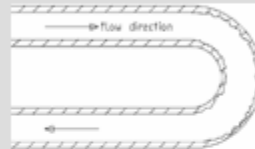
Corrosion Fatigue



Corrosion Fatigue (2)



Erosion-corrosion



Localized grooved attack ...



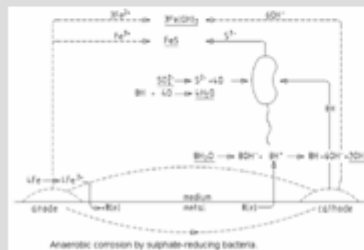
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“MIC” - Microbiologically Induced Corrosion

◆ Various ways :

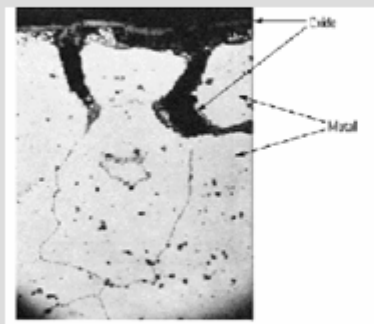
- SRBs
- Iron-oxidizing
- Etc ..., etc ...



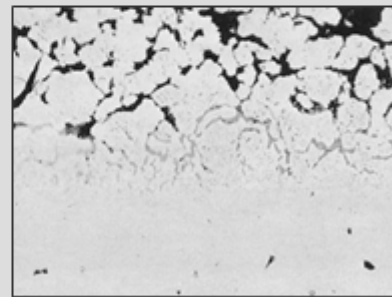
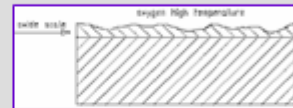
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High-Temperature Corrosion



Oxidation
Sulfidation
Carburization
....



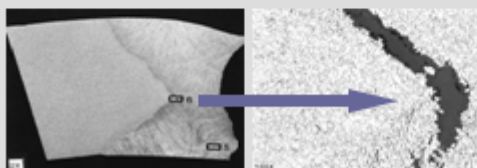
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Other ...



Hydrogen blistering



High-temperature Creep ...

*Filiform,
Cavitation,
Fretting, wear, ...*

Etc ...

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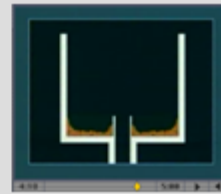
Techniques for Corrosion Mitigation

See videos ... (European Federation of Corrosion)

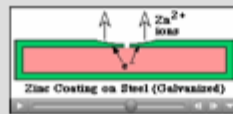
& Section E of this Handbook.

How to avoid corrosion ?...

- Design
- Material selection:
e.g. Stainless Steels, Polymers, ...
- Coatings
- Changing the environment
(incl. CP) ...



Video ...



	Weak Acid	Strong Acid	Weak Base	Strong Base	Organic Solvent	Ozone
Fluorocarbon	Resistant	Resistant	Resistant	Resistant	Resistant	Resistant
PMMA	Resistant	Attacked	Resistant	Attacked	Attacked	Resistant
Nylon	Resistant	Attacked	Resistant	Resistant	Resistant	Attacked
Low Density PE	Resistant	Attacked	Resistant	Resistant	Resistant	Attacked
High Density PE	Resistant	Attacked	Resistant	Resistant	Resistant	Attacked
Polypropylene	Resistant	Attacked	Resistant	Resistant	Resistant	Attacked
Polyethylene	Resistant	Attacked	Resistant	Resistant	Attacked	Attacked
Polyvinyl Chloride	Resistant	Resistant	Resistant	Resistant	Attacked	Resistant
Epoxy	Resistant	Attacked	Resistant	Resistant	Attacked	Attacked
Phenolics	Attacked	Attacked	Attacked	Attacked	Attacked	Attacked
Polyesters	Attacked	Attacked	Attacked	Attacked	Attacked	Attacked



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B. The CPI Materials Mosaic

*– A Panoramic Overview of Materials of
Construction –*

*The Basic Materials of Industry ...
for a Variety of Applications*

Commercial steels and cast irons are basic materials of construction for a variety of industries. We are not concerned with "pig" or ingot iron, nor with the now obsolete wrought iron (although it was once commercially important). The relatively pure low-carbon irons, such as carbonyl iron and electrolytic iron are not structural materials.

Steel is an alloy of iron and carbon, containing small amounts of other alloying elements or residual elements as well. It is the presence of carbon and its effect upon response to heat treatment that changes iron from a laboratory curiosity to an engineering material.

In the manufacture of steel, iron ore is reduced in a blast furnace to produce pig iron. Pig iron contains impurities (e.g., carbon, silicon, phosphorous, sulfur, etc.) which makes it hard and brittle. It must be refined, and the alloy content controlled, in order to obtain suitable properties. A newer method of producing steel is with the basic oxygen furnace, in which pure oxygen (rather than air) is blown through the molten metal. To prevent the reaction of residual oxygen with dissolved carbon during solidification, steel may be "killed" (i.e., made to lie quietly in the mold by the addition of deoxidants such as silicon or aluminum. Killed steels are used down to -28.9°C (-20°F), at least in thinner sections, because of their improved NDTT as compared with ordinary steels. Permissible temperatures will vary with thickness and limits of -6°C (21°F) are sometimes invoked for vessels in cold temperature service.

Carbon steels are primarily iron and carbon, with small amounts of manganese. They are the workhorse material for structural members, sheet, plate, pipe, and tubing.

Steels that have been worked or wrought while hot will be covered with a black mill-scale (i.e., magnetite, Fe_3O_4) on the surfaces, and are sometimes called black iron. Cold-rolled steels

have a bright surface, accurate cross-section, and increased yield and tensile strength. The latter are preferred for bar-stock to be used for rods, shafts, etc.

1.2.2. Principles of Heat Treatment

Carbon and low-alloy steels occupy an essential place among materials of construction, precisely because of the potential range of hardness, strength, and other mechanical properties. These are achieved primarily through heat treatment.

Iron has three allotropic crystal forms (i.e., alpha, gamma, and delta) which exist at different specific temperatures from- room temperature up to the melting point, and have different capacities for dissolving carbon.

A phase diagram (Figure below) best illustrates the following discussion. Of primary concern is the alpha (ferrite: body-centered) and gamma (austenite: face-centered) crystal forms. Ferrite converts to austenite in the vicinity of 910°C (1,670°F).

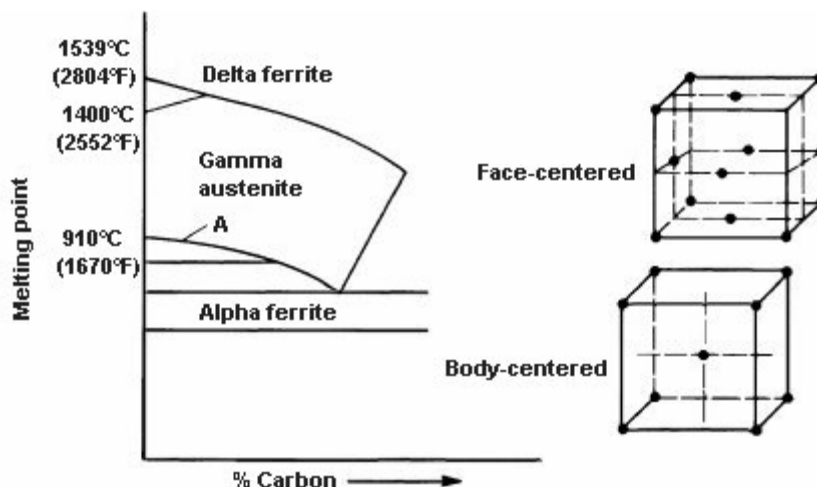


Figure Simplified iron-carbon phase diagram

The hardening of steel is due to a combination of the allotropic transformation and the different solubility of carbon in the two crystalline forms of iron. At room temperature ferrite, carbon is soluble only to approximately 0.008%, any excess being in the form of iron carbides (i.e., cementite). On the other hand, the austenite which is formed at high temperatures can dissolve up to approximately 2% carbon.

A typical carbon steel might contain approximately 0.30% carbon. At room temperature, approximately 0.29% of the carbon is dispersed in the ferrite structure as alternate platelets of cementite. The mixture of ferrite and cementite is called pearlite, because it has the appearance under the microscope of mother-of-pearl.

When such a steel is heated to the transformation temperature (point A in Figure 11.3), the austenite phase is formed and all of the 0.30% carbon dissolves. If the alloy is slowly cooled, the austenite reverts to ferrite and the pearlite is also reformed. The process of heating and slow cooling is called annealing (or normalizing, at a somewhat lower temperature). There is little, if any, change in mechanical properties under these conditions.

However, if the heated steel in its austenite form is rapidly cooled (i.e., quenched), the reversion to ferrite is very rapid while the precipitation of carbon is much slower. The carbon atoms then become entrapped in the ferrite lattice, stretching and distorting the structure. This gives a distorted, acicular structure called martensite (Figure below), which is very hard and brittle. In this quenched condition, the material is both at maximum hardness and strength and minimum ductility or toughness. In most engineering applications, a combination of toughness and strength is desired, so some compromise must be effected.

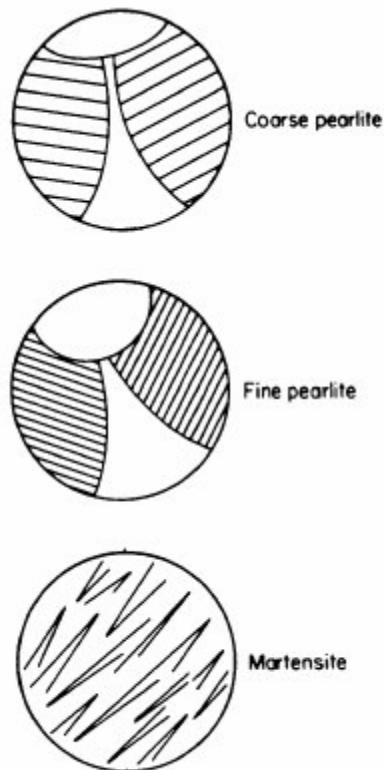


Figure Microstructures of steel.

This compromise is attained by reheating the hardened steel to some temperature below the lower critical temperature of approximately 720°C (1,330°F). This procedure is known as tempering or drawing, and allows the "logjam" of iron and carbon atoms to sort itself out. The higher the temperature and the longer the time, the more the iron and carbon revert from the martensite to the ferrite-pearlite structure. A quenched and tempered steel will have much

higher strength and less ductility than an annealed or normalized steel, but lower strength and more ductility than the same material in the fully hardened condition.

In hardening a steel, the rate of cooling is critical. For a given composition, it is easier to completely harden (i.e., "through-harden") a smaller diameter piece than a thicker one. The latter may retain a softer core than the outside surface, giving a hardness profile across the diameter (Figure below), which may or may not be desirable for the intended end use.

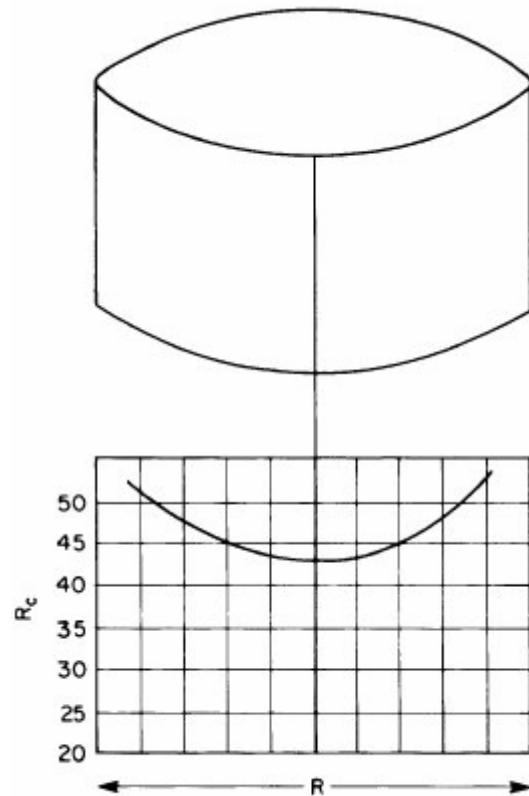


Figure Hardness profile of steel bar.

1.2.3. Alloy Steels

Alloying elements, in small amounts, affect primarily the rate of cooling required to harden the steel. For example, with small additions of chromium, nickel and molybdenum, heavier sections can be through-hardened. By the same token, a less drastic quenching medium (e.g., oil instead of water) can be used. More highly alloyed steels can be "quenched" in still air. Also, it should be remembered that, in welding, the weld proper and adjacent areas will be quenched by the mass of cold metal surrounding the joint, causing hardening and leaving high residual stresses.

As a general rule, the dividing line between low-alloy and high- alloy steels is approximately 5% total alloying elements. Low-alloy steels were developed primarily to control response to

heat treatment and extend mechanical properties. Their corrosion resistance is usually not significantly different from that of carbon steel, although some chromium-molybdenum grades have improved resistance to hydrogen effects (Chapter 30) at elevated temperatures and graphitization (Chapter 31). High-alloy steels are more often made for improved corrosion resistance, with the exception of a few specialty steels (e.g., Hadfield's manganese steel for abrasion resistance). The effects of the individual alloying elements are as follows:

Carbon

Carbon is the principal hardening element. In fact, the percentage of carbon can be estimated from the maximum hardness induced by heat treatment.

Manganese

Manganese is a deoxidizer and desulfurizer which also contributes to strength and hardness. A major purpose of desulfurizing steel is to improve hot-workability, since iron sulfides cause cracking (i.e., hot-shortness) during hot-working. Further, a manganese-to-carbon ratio of not less than 3:1 is beneficial for impact strength and nil ductility transition temperature (NDTT).

Silicon

Silicon is a principal deoxidizer. The amount of retained silicon will vary with deoxidation practices. A "killed" steel may contain as much as 0.6%, although structural steels usually have a range of 0.15 to 0.30% silicon.

Aluminum

Aluminum is used to complete the deoxidation practice; and, silicon-killed and aluminum-finished steels are used at moderately low temperatures.

Phosphorus

Phosphorus is primarily an impurity, decreasing ductility, and toughness. A maximum phosphorus content of 0.04% or less is commonly specified.

Sulfur

Sulfur is likewise undesirable, except where improved machinability is required. Manganese sulfides break up the chips during machining, but they have an adverse effect upon ductility and impact strength. Sulfur content is usually held to 0.05% or less, except in resulfurized free-cutting grades (which may contain from 0.1 to 0.3% sulfur).

Copper

Copper is added only to improve resistance to atmospheric corrosion, which it probably does by scavenging sulfur. Only small concentrations of copper can be tolerated (not more than 0.2 to 0.3%) because of its low solubility, and hot-short or LMC effects.

The major alloying elements that affect corrosion as well as metallurgical characteristics and response to heat treatment, are:

Chromium

Chromium is added to increase the depth to which thick sections can be hardened; to provide abrasion resistance; to provide higher hardness of carburized or carbonitrided surfaces; to improve corrosion and oxidation resistance; to improve resistance to high-temperature, high-pressure hydrogen; and to improve resistance to high-temperature graphitization.

Molybdenum

Molybdenum is added to prevent graphitization and give close control of hardenability, while increasing high temperature tensile and creep strength. It is used at approximately 0.5% concentration in conjunction with chromium and also is effective in preventing temper embrittlement.

Nickel

Nickel is added to improve toughness (particularly NDT~), response to heat treatment, and corrosion resistance.

Vanadium

Vanadium is added to refine grain size and improve mechanical properties, as well as to increase the hardenability of medium-carbon steels.

A combination of two or more alloying elements usually imparts some of the characteristic good properties of each. Chromium-nickel steels develop good hardening properties with excellent ductility, while chromium-nickel-molybdenum steels develop even better hardenability with only a slight reduction in ductility. The carbide-forming elements (e.g., chromium, molybdenum, vanadium) also increase resistance to hydrogen attack at elevated temperatures and pressures, under conditions which lead to embrittlement, blistering, or methanation of carbon steels.

1.3. Cast Irons

Various types of cast irons are used widely, especially for pipes, valves, pumps, and certain mechanical parts. Cast iron is an alloy of iron, silicon, and carbon. The carbon content varies from approximately 1.7 to 4.5%, most of which is present in insoluble form (e.g., graphite) in this range. This definition adequately covers the unalloyed gray irons, white irons, malleable irons and ductile irons.

1.3.1. Unalloyed Cast Irons

The most common form of unalloyed cast irons is gray cast iron, although the process industries today use ductile cast iron (DCI) almost exclusively (see further below). When the casting is allowed to cool slowly, the insoluble carbon precipitates as flakes of graphite, which are the outstanding feature of this material and cause its typically brittle behavior (because the material fractures along the graphite flakes). Gray irons are quite soft and readily machinable. A typical microstructure is shown in Figure 11.1.

White iron is produced by rapid cooling of a gray cast iron of controlled composition, that low silicon, high manganese, to produce an alloy that is hard, brittle, and practically un-

A relatively ductile material called malleable iron can be produced by prolonged heat treatment of white iron. A 30-hour treatment at 925°C (1,700°F), followed by an equivalent period of slow cooling, allows the graphite to precipitate as nodules rather than flakes. Ductility is therefore much less impaired, compared to gray cast iron. Malleable irons have been used in fittings, machinery, tools, and automotive parts.

The best modern form of cast iron, having superior mechanical properties and equivalent corrosion resistance, is ductile cast iron (DCI). The addition of a small amount of nickel-magnesium alloy to cast iron causes the graphite to precipitate as spheroids rather than as flakes (Figure 11.2). This results in a ductility approaching that of steel. Ductile iron can be produced to have as much as 18% elongation, while some wrought carbon steels have no more than 20%. Ductile iron castings also can be produced to have improved low-temperature impact properties (i.e., low ductility transition temperature, NDTT) by control of the phosphorous, silicon, and alloy content, as well as the thermal treatment.

Molybdenum

Silicon

Nickel

Copper

Copper is a mild strengthener, increasing resistance to wear and to certain types of corrosion.

Chromium

Chromium is added to cast irons in amounts varying from 0.15 to 1%, in order to improve resistance to graphitic corrosion. In amounts from 1 to 1.5%, it is added to increase high temperature oxidation resistance. In special alloys, up to 35%, chromium may be added for resistance, both to corrosion and high temperature oxidation.

1.4. Numbering

The traditional numbering system for steels was developed by Society of Automotive Engineers (SAE). A similar system was that of the American Iron and Steel Institute (AISI). Together with the numbering system for other alloys, these have been assimilated into the UNS (Unified Numbering System).

Each steel is assigned an identifying number consisting of a letter (usually "G" or "K" for carbon and low alloy steels) and a five-digit number. The first two digits codify the major alloy additions, and the next two the carbon content (expressed in hundredths of a percent). The final digit encodes any special requirements. For example, a plain carbon steel of 0.20% carbon (SAE [AISI] 1020) is numbered UNS G10200. G31300 is a nickel-chromium steel of 0.30% carbon, while G43xx0 is chromium-nickel-molybdenum, and G6 lxx0 is a chromium-vanadium steel of a specific carbon content xx.

1.5. Suggested Resource Information

- ☐ ASM Handbook, Vol. 1, Properties and Selection-Iron, Steels, and High-Performance Alloys (Materials Park, OH: ASM International, 1990).
- ☐ R. M. Davison, J. D. Redmond, "Practical Guide to Using Duplex Stainless Steels," Materials Performance 21, 1 (1990): p. 57.
- ☐ G. Krauss, Principles of Heat Treatment of Steel (Materials Park, OH: ASM International, 1980).
- ☐ W. T. Lankford, Jr., N. L. Samways, R. F. Craven, H. E. McGannon, The Making, Shaping, and Treatment of Steel (Pittsburgh, PA: Association of Iron and Steel Engineers, 1985); available from ASM International.
- ☐ Metals and Alloys in the Unified Numbering System, (Warrendale, PA: SAE).
- ☐ The Metals Black Book, Vol. 1, ferrous Metals (Edmonton, Alberta, CAN: CASTI Publishing, 1992); available from NACE International.
- ☐ B. J. Moniz, W. I. Pollock, eds., Process Industries Corrosion-The Theory and Practice (Houston, TX: NACE International, 1988), p. 373.

2. Stainless Steels

The CPI ‘Workhorses’ ...

2.1. Introduction

The addition of chromium to an ordinary steel (with a minimum of approximately 11%) produces a “*stainless steel*” (D: “rostfreies Stahl” / F: “acier inoxydable” / NL: “roestvast staal”).

This phenomenon was first discovered by *Henry Brearly* in Sheffield (1913), soon followed by Krupp in Germany, who produced the first *austenitic* stainless steel, V2A, which had a composition of about 0.3% C, 20% Cr and 7% Ni. This was the forerunner to the 18Cr-8Ni stainless steels most known as Type 304. Important commercial production of this type of austenitic steels did not start until after World War 1 – around 1920-24.

The evolution of austenitic stainless steels followed different paths depending on the various applications. Additions of Mo and Si were used at an early stage to improve the corrosion resistance to acids, one important industry being the pulp and paper industry (sulfite industry). Increased Cr levels were used to get a better high temperature oxidation resistance. Type 310, with about 25% Cr and 20% Ni, was produced already in the 1930s.

The driving force for development of the austenitic stainless steels has been the need from the end-user side for materials that are resistant to increasingly harsh environments. Stainless steels are used in a variety of applications ranging from simple protection from iron contamination (e.g., of pure water, foodstuffs, or refined chemicals) to the most demanding corrosive chemical services.

Nowadays, there are many compositions of stainless steel belonging to different "families", from the basic 11 to 13% chromium steel to complex alloys containing chromium, nickel, molybdenum, copper, etc.

2.2. Nature of Stainless Steel

The addition of about 12% chromium to steel produces a synthetic "noble metal" (D: “Edelstahl”), with little tendency to react with most natural environments. The difference between stainless steels and the true noble metals of silver, gold, and platinum is that the

nobility or *passivity* as it is commonly called, of the stainless steel, can be induced, reinforced, or removed by chemical or electrochemical reactions.

Passivity is a surface phenomenon, associated primarily with an oxide film or with adsorbed oxygen. Depending upon the stability, reactivity, and solubility of the film in a given environment, the stainless steels may be either *passive* or *active*. In the active condition, they may be less resistant than ordinary steel in hot caustic, molten salts, and reducing acids, for example.

The *passive protective film* on stainless steels is formed by reaction with oxygen (which is why it resists most natural environments) or with oxidizing agents (e.g., nitric acid). The film is removed by reaction with hydrogen or reducing agents. The film is penetrated by some species, notably chloride ions. Stainless steels tend to be rapidly attacked by reducing acids or hot caustic, for example, and pitted (or cracked) by chloride environments, but tend to resist nitric acid, other oxidizing acids, peroxides, etc. The film can also be removed mechanically, as by abrasion, wear, or erosion, but re-forms readily on exposure to air or aerated water.

Passivity is the normal state of existence for stainless steels, and they are usually several tenths of a volt cathodic to carbon steel in natural waters and aqueous solutions. Only under special conditions will they become active, in which case they are anodic to steel.

Passivation treatments are chemical treatments used both to remove iron contamination and provide a more homogeneous surface to corrosive environments. Typically, dilute nitric acid is used, but hydrogen peroxide, ammonium persulfate, and similar oxidizing solutions may also be employed, as can electrochemical passivation. Such treatment slightly thickens the protective oxide film. Non-oxidizing solutions do not passivate, nor do nitric-hydrofluoric pastes or solutions. However, a simple water rinse after non-passivating chemical cleaning will restore normal passivation.

2.3. Types of Stainless Steel

2.3.1. Overview

Chapter 1 discussed the ferrite/austenite/martensite transformation in steel and alloy steels, based on the iron-carbon phase diagram. A similar diagram (Figure 2.1) is used to explain the phase transformations in iron-chromium and related alloys.

When chromium is the only major alloying element, and carbon is held essentially constant at a moderate value, the conditions under which martensitic and ferritic stainless steels are formed is explained by "the gamma loop." (Note: Greek letter used to denote the austenite phase.) An increase in temperature takes the alloy through the gamma loop up to approximately 12% chromium content. Because they undergo the ferrite/austenite transformation, these 11 to 13% stainless alloys can be hardened to a *martensitic* structure by cooling from above the transformation temperature. Above approximately this chromium content (the next level of alloying is usually around 17%), the alloy never passes through the gamma loop, and therefore, remains *ferritic* and of its original hardness, regardless of heat treatment.

If the chromium is in the 16 to 19% range and approximately 8 to 14% nickel is added, the phase diagram would show the gamma loop expanded to fill the diagram. Such type 300 series alloys are *austenitic* over the normal range of temperature, rather than ferritic or martensitic.

Nominal compositions of typical wrought stainless steels are given in Table 2.1.

Figure 2.1 : The gamma loop

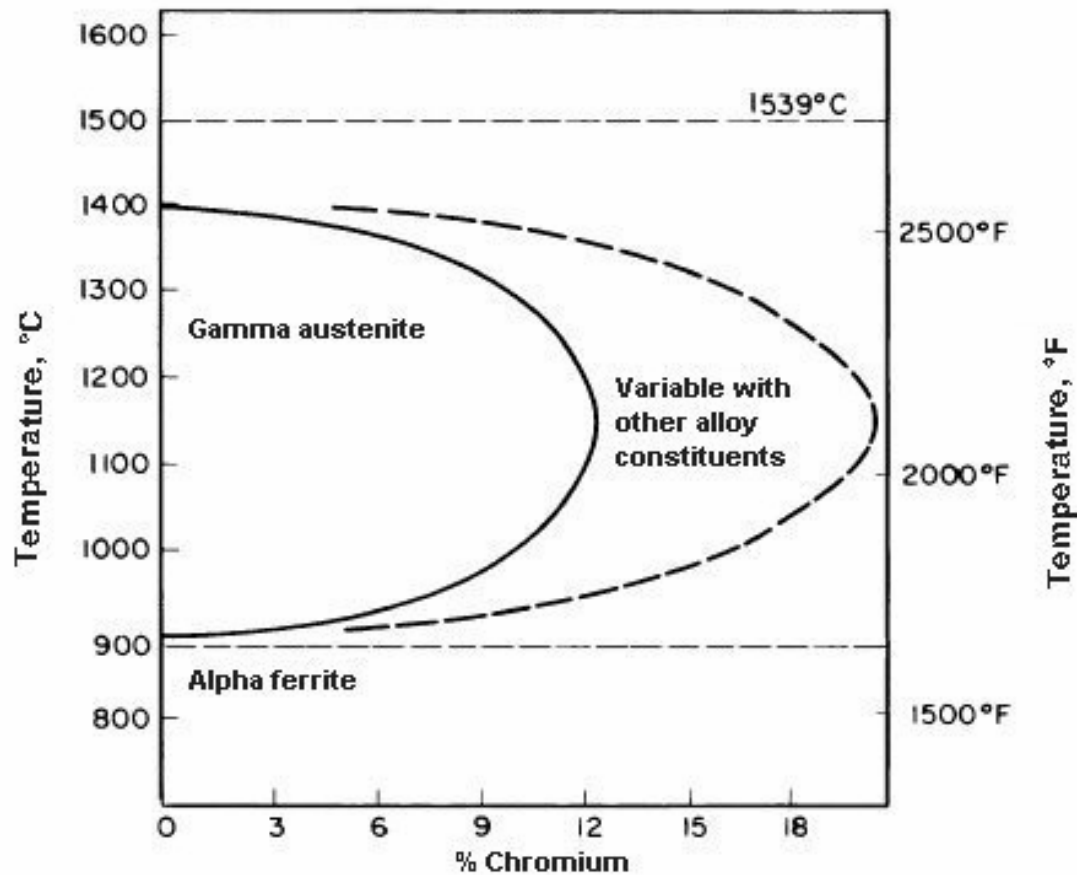


Table 2.1 : Wrought Stainless Steels, nominal wt.%

Name	UNS	Cr	Ni	C (max)	Other
Type 410	S41000	11.5	-	0.15	-
Type 430	S43000	16	-	0.12	-
Type 446	S44600	23	-	0.20	-
Type 304	S30400	18	8	0.08	-
Type 304L	S30403	18	8	0.03	-
Type 321	S32100	17	9	0.08	Ti 5 x C min
Type 347	S34700	17	9	0.08	Nb 10 x C min
Type 316	S31600	16	10	0.08	Mo 2
Type 316L	S31603	16	10	0.03	Mo 2
Type 317	S31700	18	11	0.08	Mo 3
Type 317L	S31703	18	11	0.03	Mo 3
Type 309	S30900	22	12	0.20	-
Type 310	S31000	24	19	0.25	-
Alloy 20Cb-3	N08020	19	32	0.07	Mo 2, Cu 3, Nb 8 x C

The several types and grades of stainless steels tend to resist corrosion by water or other natural environments by virtue, primarily, of a passive oxide film promoted by the presence of >11% chromium. Other alloying elements have significant effects on the protective properties of this film and, therefore, on the resistance to initiation of corrosion on these alloys in the presence of common contaminants.

An element's influence on the resistance to *initiation* of attack is not necessarily the same as its influence on *propagation*. Where appropriate, these differences are further noted below.

ELEMENT	EFFECT
Chromium	Enhances passivity and, therefore, tends to improve resistance to initiation of attack. Once corrosion starts, it aggravates acidity and results in rapid propagation.
Molybdenum	Enhances passivity and improves pitting and crevice corrosion resistance.
Nickel	Balances austenite structure and has a small positive effect in enhancing resistance to crevice corrosion initiation. If corrosion starts, it significantly reduces the rate of attack.
Copper	Correct levels of copper (approx. 1% or less) improve resistance to crevice corrosion initiation. Other levels, particularly higher levels, reduce resistance to initiation of corrosion, although higher levels reduce the rate of attack.
Silicon	High levels (>4%) improve pitting resistance. Otherwise, negligible influence except in conjunction with Mo.
Manganese	Reacts with sulfur to form MnS, which act as sites for initiation of pitting and crevice corrosion. At relatively high sulfur levels (0.02 to 0.03%), reducing Mn from 1.5% to 0.5% or less improves resistance. At lower sulfur levels (<0.01%), resistance is already high and lowering manganese levels has only a small effect.
Nitrogen	Balances austenite and strengthens. At levels above 0.15%, it significantly improves resistance to initiation of pitting and crevice corrosion.

2.3.2. Ferritic Stainless Steels

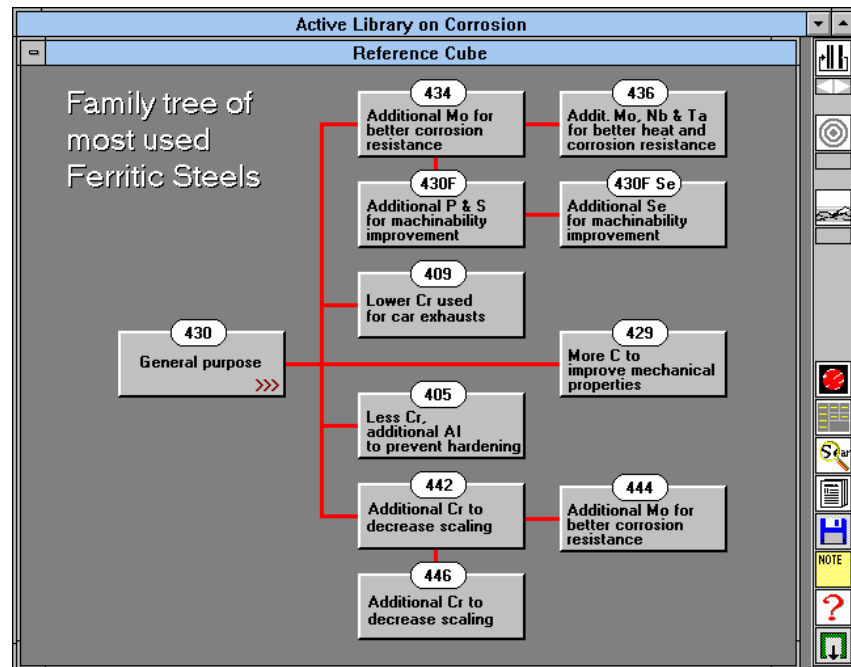
The ferritic stainless steel class of alloys starts in the 15 to 18 % chromium range, although they can go up to approximately 30%. Well outside the gamma loop, they are wholly ferritic. Note that both martensitic and ferritic grades are ferromagnetic, regardless of heat treatment.

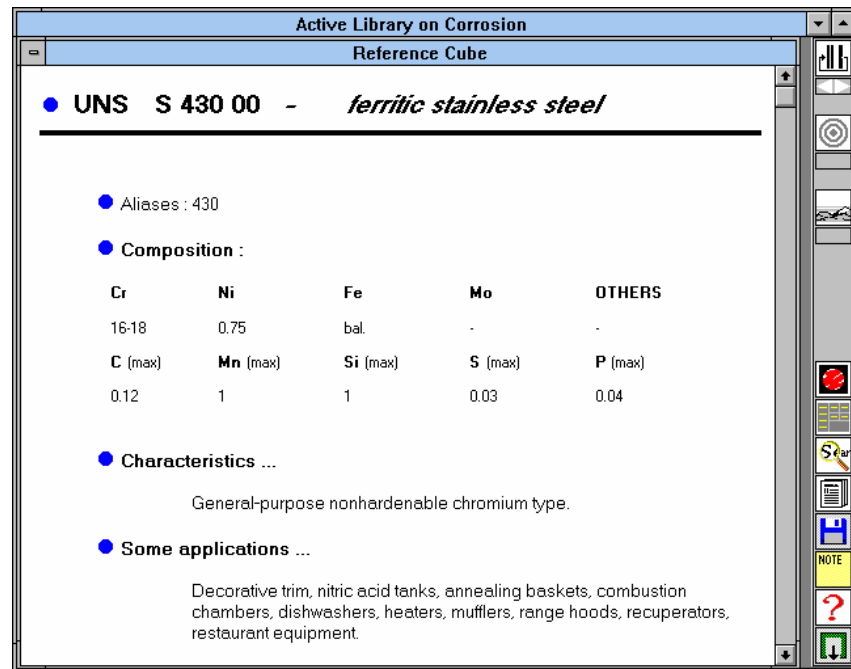
The ferritic grades, exemplified by Type 430 (UNS S43000), have corrosion resistance superior to the martensitic grades, by virtue primarily of their higher chromium content. They are commonly used for nitric acid services, water, food processing, automobile trim, and architectural applications. Their high temperature oxidation resistance is also good, and they are used for furnace and turbine parts. Their impact resistance and weldability are rather poor, even though they are not hardenable by heat treatment.

Welding may result in brittleness and/or diminished corrosion resistance, unless proper pre- and post-weld heat treatment are employed. For example, fast cooling can result in IGA (the reverse of the situation for the austenitic type 304, for example).

Ferritic stainless steels have poor impact resistance at low temperatures, sometimes even at relatively warm temperatures, as discussed further below. They are not susceptible to hydrogen attack, but can suffer SCC in caustic environments, and to a much lesser extent, in chlorides. On heating, as by welding, grain growth can occur, with attendant embrittlement.

Modern controlled-melting and other improved practices have permitted development of a new group of "**superferritic stainless steels**." These are molybdenum-bearing variants with very low contents of carbon, nitrogen, and other interstitial elements. Such superferritic grades (e.g., alloys 26Cr-1Mo [26-1, S44627], 29-4 [S44735], and Sea-Cure [S44660]) have improved resistance to chloride pitting and SCC and improved general corrosion resistance in some environments, but have some deficiencies in impact strength (e.g., high Nil Ductility Transition Temperature [NDTT] even above 40°C [104°F]) and weldability.



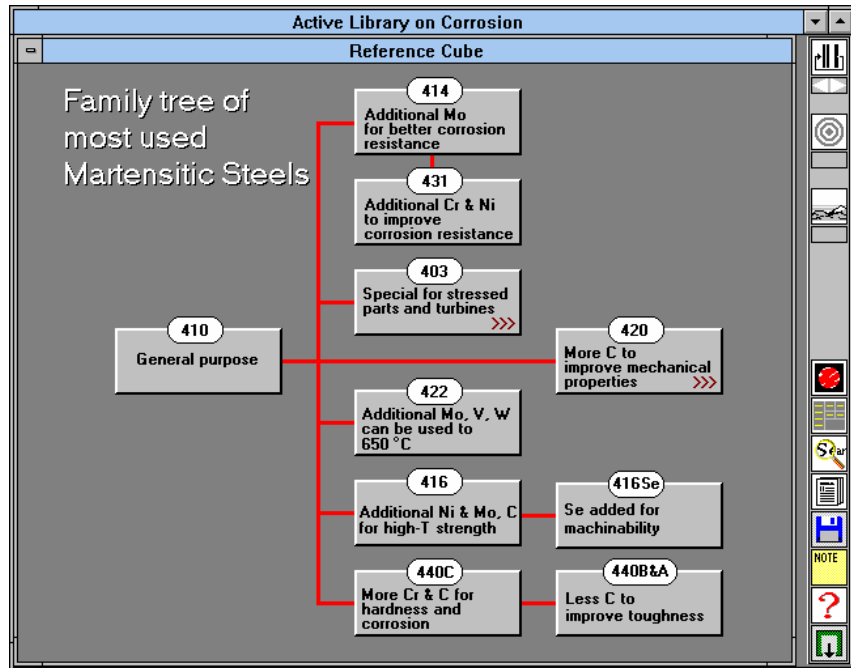


2.3.3. Martensitic Stainless Steels

Because of the combination of *hardenability* with *stainless* properties, the martensitic grades are of interest for cutlery, turbine blades, and high temperature parts. Their high order of resistance to atmospheric corrosion, compared with steel, places them into the stainless category. They are, however, of limited usefulness in process exposures compared with the more highly alloyed grades. The martensitic grades are exemplified by Type 410 (UNS S41000) and Type 420 (UNS S42000).

These and related alloys are somewhat difficult to fabricate by **welding**, as they require extensive pre- and post-weld heat treatment, because of their air-hardening characteristic. Their transformation rate is so sluggish that a quench in oil or water is not required for hardening, as a slow air cool suffices to effect the martensite transformation.

The greatest weakness of the martensitic grades is a susceptibility to absorption of atomic hydrogen, resulting in *hydrogen-assisted corrosion* (HAC), notably in sulfide environments. Their low-temperature impact resistance is also poor and when cooled rapidly from elevated temperature they are susceptible to IGA.



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● MARTENSITIC STAINLESS STEELS

- **General :**

With lower Cr and higher C content, it is possible to produce stainless steels that are hardenable by heat treatment. These steels are usually selected when their excellent strength is required.

AISI Type 410 is the most widely used of the martensitic grades. It is occasionally used in the handling of chemicals, but because of its lower Cr and higher C content, its corrosion resistance is substantially less than that of, for example, Type 304 (austenitic) stainless steel.

The straight-chromium martensitic stainless steels may be resistant to chloride stress corrosion cracking but are susceptible when fully hardened.
- *Family Tree >>>*
- *Type 403 >>>, Type 420 >>>*
- **See also ...**

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● **UNS S 403 00 - *martensitic stainless steel***

● Aliases : 403

● **Composition :**

Cr	Ni	Fe	Mo	OTHERS
11.5-13	-	bal.	-	-
C	Mn	Si	S (max)	P (max)
0.15	1.0	0.5	0.03	0.04

● **Characteristics ...**

"Turbine-quality" grade (special for stressed parts and turbines).

● **Some applications ...**

Steam turbine blading and other highly stressed parts including jet engine rings.

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● **UNS S 420 00 - *martensitic stainless steel***

● Aliases : 420

● **Composition :**

Cr	Ni	Fe	Mo	OTHERS
12-14	-	bal.	-	-
C (min)	Mn	Si	S (max)	P (max)
0.15	1.0	1.0	0.03	0.04

● **Characteristics ...**

Higher carbon modification of Type 410.

● **Some applications ...**

Cutlery, surgical instruments, valves, wear-resisting parts, glass molds, hand tools, vegetable choppers.

2.3.4. Austenitic Stainless Steels

The group, austenitic stainless steels, characteristically non-magnetic, is the most important for process industry — and many other — applications. By virtue of their austenite-forming alloy additions, notably *nickel* and *manganese*, these stainless steels have the face-centered austenite structure from far below zero up to near melting temperatures. They are not hardenable by heat treatment, but can be strain-hardened by cold-work. This also induces a small amount of ferromagnetism. (Note: In the cast varieties, a small amount of magnetism is induced deliberately through an imbalance in austenite-forming vs ferrite-forming elements in order to improve casting characteristics.)

The "garden-variety"-type 300 series austenitic stainless steels are exemplified by Type 304 (UNS S30400). Such alloys have a rare combination of corrosion resistance, high-temperature strength and oxidation resistance, ease of fabrication and weldability, and good ductility and impact resistance down to at least -183°C (-216°F). Their mechanical properties, in general, are excellent. Improved chemical resistance is obtained by molybdenum additions (e.g., Type 316), and resistance to IGA by stabilization (e.g., Type 347 with Nb and Type 321 with Ti), or low carbon content (e.g., Types 304L and 316L).

Today, both base metal and surface chemistries are improved by argon-oxidation-decarburization (AOD) and other mill practices, and the former differences in mechanical properties between regular- and low-carbon grades largely may be eliminated. Such products may be dual labeled as 304/304L, for example, because they meet all ASTM requirements or both grades due to pin-point control of alloying elements.

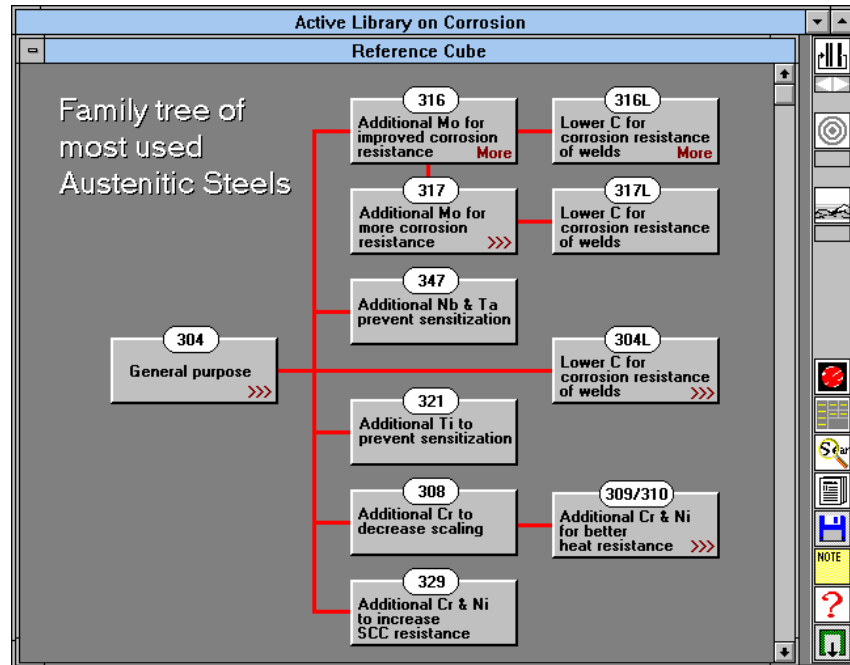
The most highly alloyed of this group is Type 317L (UNS S31703) with a nominal composition of 18%Cr-11%Ni-3%Mo-0.03%C, which has been used widely in the pulp and paper industry. Modern variants have somewhat higher molybdenum content and are strengthened with *nitrogen*, e.g., types 317LN (UNS S31753), 317LM (UNS S31725), and 317L4 (UNS S31726). Nitrogen is also an austenitizing constituent which can replace nickel to a certain extent.

When substantial amounts of nickel are replaced by *manganese*, an analogous group of alloys is formed, exemplified by the 8%Mn-4%Ni alloy (UNS S20200).

Other grades can be *precipitation-hardened* (e.g., alloys 17-4 PH [S17400] and PH 15-7Mo [S15700]) while retaining corrosion resistance similar to that of Type 304 or 316.

Higher austenitic alloys, such as Type 309 (22Cr-12Ni, UNS S30900) and Type 310 (25Cr-20Ni, UNS S31000), are used for high-temperature applications and for welding type 300 series to steel.

There are also duplex alloys (i.e., mixed ferrite-austenite structure) for improved corrosion resistance, although at some cost in fabricability; an example is Type 329 (UNS S32900) - (See Section 2.5.3.a).



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● UNS S 317 00 - molybdenum *austenitic stainless steel*

● Aliases : AISI 317

● Composition :

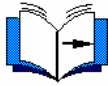
Cr	Ni	Fe	Mo	OTHERS
18-20	11-15	bal.	3-4	-
C (max)	Mn (max)	Si (max)	S (max)	P (max)
0.08	2	1	0.03	0.045

● Characteristics ...

● Some applications ...

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• **UNS S 310 08 - *austenitic stainless steel***



• Aliases : 310, 310S

• **Composition :**

Cr	Ni	Fe	Mo	OTHERS
24-26	19-22	bal.	-	-
C (max)	Mn (max)	Si (max)	S (max)	P (max)
0.08	2	1.5	0.03	0.045

• **Characteristics ...**

Higher elevated temperature strength and scale resistance than *Type 309*.

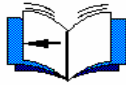
A 25/20 stainless steel with similar oxidation resistance to Type 309 but less liability to embrittlement due to sigma phase formation if used for long periods in the range 425 to 815 C.

• **Some applications ...**

Furnace parts, combustion chambers, gas turbine parts, incinerators, heat exchangers, recuperators, welding filler metals.

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• **UNS S 310 40 - *austenitic stainless steel***



• Aliases : 310, 310Nb, 310 Cb

• **Composition :**

Cr	Ni	Fe	Mo	OTHERS
24-26	19-22	bal.	-	Nb (Cb) + Ta = 10x %C (1.1 max)
C (max)	Mn (max)	Si (max)	S (max)	P (max)
0.08	2	1.5	0.03	0.045

• **Characteristics ...**

• **Some applications ...**

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● **UNS S 309 08 - *austenitic stainless steel***



● Aliases : 309, 309S

● Composition :

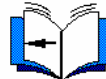
Cr	Ni	Fe	Mo	OTHERS
22-24	12-15	bal.	-	-
C (max)	Mn (max)	Si (max)	S (max)	P (max)
0.08	2	1	0.03	0.045

● Characteristics ...

A 23/14 steel with greater oxidation or heat resistance than the 18/10 varieties (e.g., *Type 304*) because of its higher chromium content.

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● **UNS S 309 40 - *austenitic stainless steel***



● Aliases : 309, 309Nb, 309Cb

● Composition :

Cr	Ni	Fe	Mo	OTHERS
22-24	12-16	bal.	-	Nb (Cb) + Ta = 10x %C (1.1 max)
C (max)	Mn (max)	Si (max)	S (max)	P (max)
0.08	2	1.5	0.03	0.045

● Characteristics ...

Higher chromium and nickel content than *Type 304* for better heat resistance. Stabilized with niobium (columbium) for restriction of carbide precipitation.

● Some applications ...

2.3.5. High-Performance Stainless Steels

In order to truly meet the definition of a stainless steel, the material must be a ferrous alloy and must contain more than 50% iron. Those special alloys which are strictly neither iron-based nor nickel-based are covered in Chapter 5. Like the type 300 series varieties, the high-performance stainless steels are usually made by the argon-oxygen-decarburization (AOD) process, which gives very low carbon content, while nitrogen is often added to increase strength and improve pitting resistance of higher grades.

The several types and grades of high-performance alloys (see also Chapter 5) tend to resist corrosion (e.g. chloride environments) by virtue of their higher chromium and molybdenum content.

ELEMENT	EFFECT
Chromium	Enhances passivity; used in 20 to 30% range, depending on the alloy grouping.
Molybdenum	Enhances passivity and improves pitting and crevice corrosion resistance. Used from 2% (in duplex stainless steels) to 6% in the nickel-rich grades.
Nickel	Balances austenite structure as needed; improves Nil-Ductility Transition Temperature (NDTT) of ferritic alloys and enhances resistance to crevice corrosion in nickel-rich grades.
Copper	Sometimes used in conjunction with 4% Mo; improves resistance to crevice corrosion and reduces rate of pit propagation.
Nitrogen	Balances austenite and strengthens. Improves resistance to pitting corrosion.

The high-performance stainless steels, other than the extra-low interstitial or superferritic grades discussed above, fall into both *duplex* and *austenitic* categories.

The latter are upgrades of Type 316L (UNS S31603) and 317L (UNS S31703), having increased chromium, nickel, and molybdenum contents and developed to have a higher chloride pitting resistance than e.g. Alloy 20Cb-3 (UNS N08020; cf. *infra*) at a lower cost.

The duplex grades are used for lower cost due to lower nickel content, and a lower coefficient of thermal expansion plus chloride resistance and mechanical strength.

Both types of alloys are often categorized by a *pitting resistance equivalent* (PRE), which is intended to reflect chloride pitting and crevice corrosion resistance (and Cl⁻-induced SCC).

The PRE for austenitic grades is calculated as follows:

The PRE calculation for duplex stainless steels is slightly different:

2.3.5.a. Duplex Grades

It should be noted that the ferrite is not an unmixed blessing. Ferrite may be attacked selectively in reducing acids, sometimes aggravated by a galvanic influence of the austenite phase, while the sigma phase produced by thermal transformation (as by the heat of welding) is susceptible to attack by strongly oxidizing acids. The duplex structure is subject to so-called “475°C (885°F) embrittlement”, and has poor NDTT properties. Except for the temper embrittlement, these problems can be minimized through corrosion qualification tests and impact testing.

Today, the basic duplex steels are Alloy 2205 (UNS S31803) and Alloy 255 (Ferralium 255, UNS S32550). Alloy 2205 has excellent stress corrosion cracking resistance, pitting, and crevice corrosion resistance exceeding Type 317L in most environments, and more than twice the strength of Type 316L. Alloy 2507 (UNS S32750), with high nickel, molybdenum and nitrogen contents, has corrosion resistance similar to that of the 6% Mo austenitic stainless steels (see below), and with approximately three-times the strength of Type 316L. The compositions of some widely used duplex grades are shown in Table 2.2.

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Table 2.2 : Duplex Stainless Steels, nominal wt. %, and typical PRE of some alloys

Name	UNS	Cr	Ni	Mo	Cu	C (max)	N	Other	PRE
Alloy 2304	S32304	23	4	-	-	0.02	0.10	-	
Type 329	S32900	26	3.5	1.5	-	0.20	-	-	
Alloy 3RE60	S31500	19	4.5	2.5	-	0.03	-	Si 1.5	
Ferrallium 255 ^(A) (Alloy 255)	S32550	26	6	3.0	1.5-2.5	0.04	0.15	-	38
Alloy 2205 ^(B)	S31803	22	5.5	3.0	-	0.03	0.18	-	34
Zeron 100 ^(C)	S32760	25	7.5	3.8	0.7	0.03	0.25	W 0.75	>40
Alloy 2507	S32750	25	7	4.0	-	0.03	0.25	-	>40
Alloy 47N	S31260	25	6	3.0	< 0.5	0.03	0.20	-	
Alloy 7-MoPLUS	S32950	28	4.5	2.0	-	0.03	0.20	-	

^(A) Available in cast form.

^(B) UNS J92205 in cast form.

^(C) UNS J99380 in cast form.

(Note: A similar family of 6%Mo superaustenitic alloys have different UNS designations — namely, alloys AL-6XN is N08367 and alloys 1925hMo (also named alloy 926) and 25-6Mo are N08926; see Chapter 5.)

2.3.5.b. Austenitic Grades

Since the first commercial production of stainless steels in the beginning of this century the austenitic family of stainless steels has been the totally dominating type. The main reasons for this are superior properties combined with the comparable ease of production and of fabrication, and, not the least, their excellent weldability. Over the years there has been a continuous development and improvement of the austenitic grades frequently resulting in higher alloyed variants. The evolution has been driven by the increased requirements from users and fulfilled by producers through R&D efforts and improved steelmaking capabilities. This has resulted in several high performance stainless steels providing many special property profiles.

Alloy 22-13-5 (22%Cr-13%Ni-5Mn-2%Mo-0.06C, UNS S20910) has chemical resistance equivalent to Type 316L, better resistance to SCC, and much higher strength. It is useful for pump shafts, for example, to minimize corrosion fatigue in services where Type 316L otherwise is used.

Alloy 254 SMO (UNS S31254), referred to as a "superaustenitic" stainless steel, contains nominally 20%Cr-18%Ni-**6%Mo**-1%Cu-0.02%C. It is superior to the duplex grades in seawater (certainly to duplex alloys of PRE <40) and is used in applications requiring both resistance to general corrosion and to chloride pitting and SCC.

2.4. Welding of (austenitic) Stainless Steels

One classical problem is that of weld decay due to carbide precipitation followed by susceptibility to intergranular corrosion of the heat affected zone. This problem is today eliminated by control of the carbon levels in the steels.

2.5. Stainless Castings

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Table 2.3 : Designations for Stainless Steel Castings, nominal wt. %

ACI	UNS	Cr	Ni (max)	Other
CA- <i>nn</i> ^(A)	-	12	1	C
CB- <i>nn</i>	-	19	2	C
CD-4MCu ^(B)	J93370	26	6	C 0.04 max., Mo 2, Cu 3
CF-8	J92600	19	11	C 0.08 max
CF-3	J92500	18	12	C 0.03 max
CF-8M	J92900	19	12	C 0.08 max, Mo 2
CF-3M	J92800	18	13	C 0.03 max, Mo 2
CH-20	J93402	23	15	C 0.20 max
CK-20	J94202	24	22	C 0.20 max
CN-7M	N08007	20	31	C 0.07 max., Mo 2, Cu 3
HK- <i>nn</i> ^(C)	-	24	20	C 0.60 max

^(A) C indicates Corrosion-Resistant; nn is maximum carbon.

^(B) Duplex alloy.

^(C) H indicates Heat-Resistant; nn is middle +/- 0.05% carbon.

2.6. Suggested Resource Information

- ☐ NN, *ASM Handbook, Vol. 1, Properties and Selection: Irons, Steels, and High-Performance Alloys* (Materials Park, OH: ASM International 1990).
- ☐ NN, *ASM Handbook, Vol. 13, Corrosion* (Materials Park, OH: ASM International, 1987).
- ☐ J. Frick, ed., *Woldman's Engineering Alloys*, 7th Ed. (Materials Park, OH: ASM International, 1990).

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3. “Superaustenitic Stainless Steels” or High-Performance Ni-rich Alloys

For demanding applications ...

3.1. Definition

The evolution of austenitic stainless steels started more than eighty years ago. Early, it involved also *high-alloy grades* today often called “*super-austenitic*” or *high-performance grades*. This Chapter tries to describe this important part of the development: characteristic properties of superaustenitic stainless steels are described, particularly corrosion resistance, mechanical properties, and weldability.

The concept Superaustenitic Stainless Steel has not been clearly defined and depending on the definition, the time of the first superaustenitic steel can be between the 1930s and the 1970s. The term has probably been formed analogous to nickel-base superalloys, used for highly alloyed nickel-base alloys. A current interpretation of superaustenitic stainless steel is an austenitic steel composition with high amounts of chromium, nickel, molybdenum and nitrogen (Cr, Ni, Mo and N) resulting in an iron content close to or less than 50%. Typical examples are the so called 6% Mo steels that will be discussed to some extent in this Chapter. However, other highly alloyed austenitic steels for both aqueous corrosion resistance and high temperature service should be included in this group.

Important prerequisites for the development of these materials have been improved steel production processes, better tools for assessing properties and simulation or modeling techniques for production and use of the alloys.

3.2. History

The driving force for development of the austenitic stainless steels has been the need from the end user side for materials that are resistant to increasingly harsh environments. A particular medium that gave rise to development of special stainless steel alloys already in the 1930s is sulfuric acid. In Europe (France) “*Uranus B6*”, with approximately 20% Cr, 25% Ni, 4.5% Mo and 1.5% Cu was developed and in USA, “*Alloy 20*”, containing 20% Cr, 30% Ni, 2.5% Mo and 3.5% Cu, was developed. Alloy 20 had, due to the high alloy content, poor hot workability and therefore limited availability in wrought form. This was later remedied by the addition of various trace elements and the alloy is still used extensively for sulfuric acid service (Carpenter 20Cb-3; cf. infra), see Table 5.1. Alloy B6, more known today as “*904L*”, came to a very widespread use starting from the 1970s in applications such as pulp and paper and also chemical industry. One reason for the increased use was improved production capability through the introduction of new refining technologies, such as AOD (Argon Oxygen Decarburization) in the early 1970s. These technologies allowed a better control of alloy additions and improved the removal of detrimental tramp elements considerably. Thus, the possibility to produce extra low carbon (ELC) steels was improved drastically.

In the 1970s a special high-alloy austenitic stainless steel was developed for phosphoric acid service. The grade, *Sanicro 28*, contained high Cr and Ni amounts (Table 5.1) and showed also a high resistance to stress corrosion cracking as did 904L and Alloy 20. This alloy has been used extensively in the form of pipes and tubes in phosphoric and sulfuric acid environments but also as casing and liners in deep sour gas wells.

Alloy 20 and 904L formed a base for further development of *super-austenitic steels*. In the 1960s, an alloy that showed high resistance to e.g. seawater with a Mo content above 5%, NSCD, was introduced by Ugine. In 1967, INCO applied for a patent of an alloy containing 14-21% Cr, 20-40% Ni and 6-12% Mo with enhanced resistance to corrosion in chloride media such as seawater. A steel according to this patent, introduced in the early 1970s, was AL-6X with 20% Cr, 25% Ni and 6% Mo. In 1975 Allegheny Ludlum made a patent application on the same alloy ranges in the INCO patent but claimed improved hot workability through controlled additions of Ce. AL-6X was mainly used in thin walled condenser tubing for seawater cooled power plants. The high alloy content made the steel prone to precipitation of intermetallic phases preventing fabrication in heavier sections.

In the late 1960s it was shown that *N addition* retards both carbide and intermetallic phase precipitation in austenitic steels. The German grade 1.4439 (~317 LMN) with minimum 4% Mo and 0.15% N was an example of a steel where this knowledge was used. This grade has since been used in many applications with severe corrosion environments such as heat exchangers, flue gas desulfurization (FGD) and pulp and paper bleach plants. A further development of 1.4439 was Bohler Antinit ASN 7W with as high as 7% Mo, see Table 5.1. This alloy did for some reason not see any important commercial use and a successor with lower molybdenum content, VEW A963 (Table 5.1), was presented later. Also, other higher alloyed austenitic steels were developed where the strong austenitizing effect of N was utilized to an even greater extent. To achieve higher N solubility and thereby even higher N levels, Mn alloying was practiced. This resulted in highly alloyed austenitic grades with high corrosion resistance as well as a much improved strength. One example was Amaganit 3974 with the composition as shown in Table 5.1. The grade was used in non-magnetic submarines as one example.

Another development in the early 1970s using N addition was an alloy intended for urea production. The alloy, 2RE69 (Table 5.1), with high Cr and Ni levels, showed excellent corrosion resistance also in nitric acid and chloride environments.

In 1976 Avesta Jernverks AB patented and introduced 254 SMO, a 6Mo superaustenitic stainless steel with a balanced composition containing 20% Cr, 18% Ni, 6% Mo, 0.7% Cu and 0.2% N. The addition of N made the precipitation of intermetallic phases more sluggish, facilitating production of heavier gauges. It also improved the mechanical and corrosion properties. Later, other 6% Mo steels followed this N alloying approach. Examples include *AL-6XN* and *Cronifer 1925hMo*, see Table 5.1. Common for this family of so-called *6Mo super austenitic steels* is a very high resistance to pitting and crevice corrosion. Therefore, they have been used extensively in the offshore and desalination industries for seawater handling, in chlorine and chlorine dioxide stages in bleach plants, and in flue gas desulfurization plants.

A special development in the 1970s was a *high Si* austenitic stainless steel for use in sulfuric acid at high temperature and concentrations and highly concentrated nitric acid. Avesta Jernverk and Sandvik Steel jointly developed and patented this alloy. It was later denominated SX and contains as high as 5% Si and 2% Cu; cf. supra: par. 4.3.5 (see also: Table 5.1) providing the steel excellent properties for those special environments.

Further developments in the 1980s have been to use the Sanicro 28 base and add more alloying elements. *Alloy 31* is one example where the Mo content has been increased and N addition has been practiced, see Table 5.1. This grade has, due to its very high Cr level, a higher pitting resistance than the current 6Mo grades.

The concept of N alloying austenitic grades has been used for decades and *very high N* levels, up to about 1%, have been achieved. Well-known commercial grades are for example the Nitronic series from Armco. The positive influence of Mn on N solubility has been used in many developments but *chromium* and *molybdenum* have similar and maybe synergetic effects. In the 1980s alloys, high in these three elements, and with very high N levels were developed in Sweden and Germany. Both grades, 934LN and 1.4565, contained about 0.4% N, as seen in Table 5.1. These grades show similar corrosion resistance but superior strength compared to the 6Mo steels. The use of thermodynamic databases to predict the N solubility in high alloy austenitic steels has resulted in further development. If the alloying levels of Cr and Mo are further increased, even higher N contents can be reached yet with quite low Mn addition. This was utilized in the development of 654 SMO, with just 3% Mn and still 0.5% N as listed in Table 5.1. 654 SMO is one of the most highly alloyed superaustenitic stainless steels produced to date and as a consequence, it has a corrosion resistance on level with the best nickel-base alloys (cf. infra).

Table 5.1 : Modern superaustenitics, nominal wt. %, typical PRE, applicable standards and producers

Alloy	C _{max}	Mn	Cr	Ni	Mo	Cu	N	Other	PRE	EN	UNS	Trademark
304	0.08		18	9					18	1.4301	S30400	
316L	0.03		17	12	2				24	1.4404	S31603	
Alloy 20	0.05		20	30	2.5	3.5			32	-	-	
20 Cb-3	0.06		20	34	2.5	3.5		Nb,Ta	32	-	N08020	Carpenter Technology
B6, 904L	0.02		20	25	4.5	1.5			35	1.4539	N08904	
Sanicro 28	0.02		27	31	3.5	1			39	1.4563	N08028	Sandvik
NSCD	0.03		17	16	5.5	2.5			35	-	-	Ugine
AL-6X	0.03		20	25	6				40	-	N08366	Allegheny Ludlum
AL-6XN	0.03		20.5	24	6.3		0.22		45	-	N08367	Allegheny Ludlum
1.4439	0.03		17	14	4		0.15		33	1.4439	S31726	
2RE69	0.02		25	22	2		0.12		37	1.4466	S31050	Sandvik
ASN 7W	0.04		18	16	7	2	0.15		43	-	-	Böhler
VEW 963	0.03		17	16	6.3	1.6	0.15		40	-	-	VEW
Antinit 3974	0.03	6	23	17	3		0.40	0.2Nb	39	-	-	Thyssen
254 SMO	0.02		20	18	6.1	0.7	0.2		43	1.4547	S31254	Avesta Sheffield
1925hMo	0.02		20	25	6.2	0.7	0.2		44	1.4529	N08925	VDM
SX	0.02		17.5	20	1	2		5 Si	21	-	S32615	Sandvik
Alloy 31	0.02		27	31	6.5	1.2	0.2		52	1.4562	N08031	VDM
934LN	0.02	10	20	15	4.5		0.4		41	-	-	
1.4565	0.03	6	24	18	4.5		0.4		45	1.4565	S34565	
654 SMO	0.02	3	24	22	7.3	0.5	0.5		56	1.4652	S32654	Avesta Sheffield

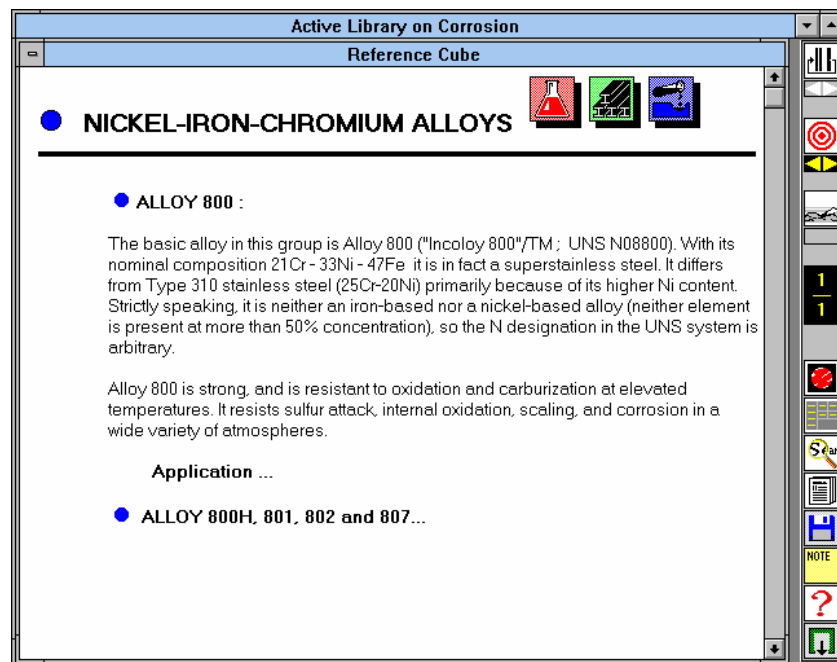
3.3. Superaustenitics

3.3.1. Iron-Nickel-Chromium Alloys

The basic alloy in the group of high-performance nickel rich alloys is Alloy 800 (UNS N08800). This is a nickel-chromium-iron alloy, nominally 30%Ni-20%Cr-balance Fe. Strictly neither an iron-based nor a nickel-based alloy (because neither element is present at more than 50% concentration), the UNS "N" designation is arbitrary, as explained below.

Alloy 800 has much better resistance to corrosion, oxidation, and chloride-induced attack than does Type 304L, for example. However, it is not better than the type 300 series in resisting caustic cracking. A variant for high-temperature services is Alloy 800H (N08810). The place of Alloy 800 in the market for chloride environments is being taken over almost completely by molybdenum-bearing grades.

Because this alloy could be classified as neither iron based nor nickel based, ASTM elected arbitrarily to assign it to the nonferrous category and assign a UNS number in the Nxxxxx listing. This policy continued and other related or somewhat similar alloys were assigned to the nonferrous category and given UNS "N" designations e.g., alloy 825 with 38%Ni-20%Cr-3%Mo-2%Cu (UNS N08825). These alloys characteristically have chromium, nickel, molybdenum (and sometimes copper) totaling in excess of 50%, and are stabilized with columbium (niobium) or titanium, or in more modern developments made with very low carbon (or with both low carbon and stabilized), to resist IGA. (Note: There is a movement afoot in ASTM to categorize an alloy by its predominant alloying element even if it is less than 50% concentration. This may result in some high-performance alloys [such as alloy 904L(N08904)] being included in the ASTM ferrous category with their UNS "N" designations retained.)



3.3.2. Iron-Nickel-Chromium-Molybdenum-(Copper) Alloys

This category embraces a number of alloys, somewhat similar to austenitic stainless steels, that contain chromium, nickel, and molybdenum as the main alloying elements.

The original such alloy was a casting of approximately 20%Cr - 29%Ni - 3%Mo - 2%Cu, developed primarily for intermediate concentrations of sulfuric acid. This material, as first developed, could not be obtained in wrought form (cf. supra). Eventually, the addition of small amounts of rare earth alloying elements resulted in a wrought material for sheet, plate, strip, pipe, and tubing. Somewhat later, in order to improve resistance to chloride-induced SCC, the nickel was increased and the alloy became known as Alloy 20Cb-3 (N08020), sometimes referred to generically as "Alloy 20."

An important group of "*4 Mo*" alloys were developed with 4 to 5% molybdenum content (thereby improving resistance to localized corrosion) and lower nickel content (still yet sufficient to prevent SCC). The Fe-Ni-Cr-Mo Alloy 700 (N08700) and the Fe-Ni-Cr-Mo-Cu Alloy 904L (N08904) are among the prototypical compositions in this group. The 1 to 2% copper addition with molybdenum (e.g., in Alloy 904L) is almost as effective as a somewhat higher molybdenum content in alloys without copper.

While Alloy 20(Cb-3) (N08020) was primarily intended for sulfuric acid, the Ni-Fe-Cr-Mo-Cu Alloy 825 (N08825) is sometimes as good or better, depending upon specific contaminants in intermediate strengths of sulfuric acid. On the other hand, attempts to provide increased resistance to chloride pitting and crevice corrosion prompted the development of the 25%Ni-20%Cr + Mo alloys.

Table 3.3 compares Fe-Ni-Cr-Mo-Cu alloys with Alloy 20Cb-3, arranged in increasing molybdenum content. The lower carbon contents result from AOD processing and other improvements in melting practices.

Table 3.3 : Fe-Ni-Cr-Mo-Cu Alloys, nominal wt. %, and typical PRE of some alloys

Alloy	UNS	Fe	Ni	Cr	Mo	Cu	C (max)	Other	PRE
20Cb-3	N08020	40	33	20	2.5	3	0.07	Nb (Cb)	
28	N08028	35	31	27	3.5	1	0.03	—	36.9-41.2
904L	N08904	45	26	21	4.5	2	0.02	—	32.2-37.9
925	N08925	46	25	20	6	1	0.02	—	

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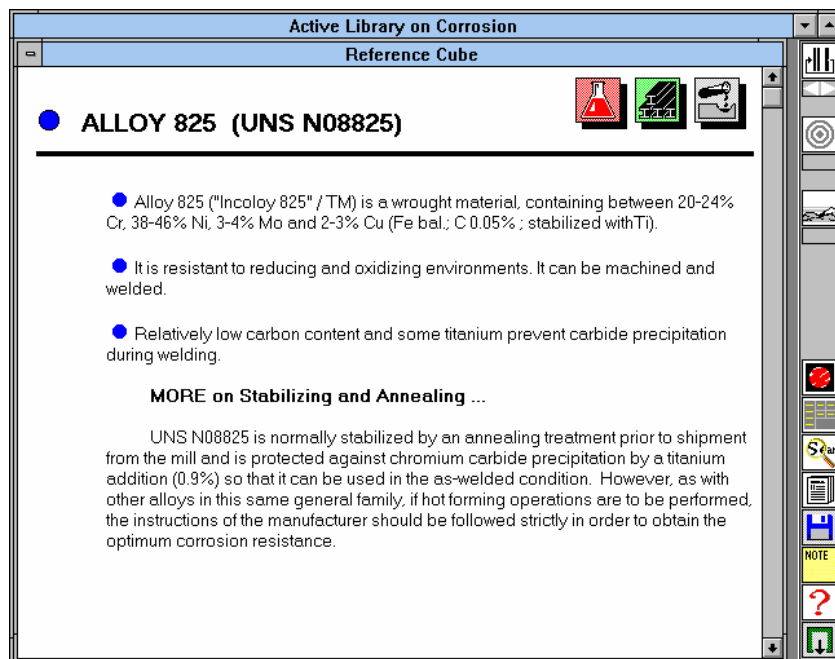
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ALLOY 20 variations and Highly Alloyed Austenitic Stainless Steels (Nickel alloys)

Austenitic Stainless Steels with very high alloy contents

Table 101

Composition %				Examples of steels commercially available
Cr	Ni	Mo	Cu	
20	25	4	1.5	Avesta 254 SLX Nyby 20-25 UMoCu Sandvik 2RR65 Uddeholm 904L Uranus B6
20	18	6	0.7	Avesta 254 SMO
20	24	6	—	Allegheny A1 6X
21	35	3	3	Carpenter 20Cb-3
21	40	3	2	Incoloy 825



3.3.3. Iron-Nickel-Chromium-6%Molybdenum Alloys

More recently, because of some corrosion-related problems with the "4% Mo" grades in severe chloride services, a newer group of "6% Mo" *superaustenitic alloys* with very-low carbon contents became available with improved chloride resistance to both pitting and SCC. The *nitrogen* additions result in high strengths.

Table 3.4 lists "6% Mo" superaustenitic alloys. They comprise Alloys 254 SMO, AL-6XN, 1925hMo (also called alloy 926), 25-6MO, and 31. The higher molybdenum level of Alloy 31 gives excellent resistance to fretting and crevice corrosion in neutral and aqueous acid solutions. Also included is Alloy 654 SMO, a new 7+% Mo alloy, with corrosion resistance associated with nickel-based alloys and with about double the strength of Type 316L. (*Note*: some alloys have UNS "S" designations and others "N" designations).

Table 3.4 : Fe-Ni-Cr-Mo Alloys (6% Mo Superaustenitics), nom. wt %, and typical PRE of some alloys

Alloy	UNS	Fe	Ni	Cr	Mo	Cu	C (max)	Other	PRE
254 SMO	S31254	54	18	20	6.1	0.7	0.020	N 0.20 ^(A)	44.7-48.6
AL-6XN	N08367	48	24	20	6	-	0.030	N 0.20 ^(A)	39.8-45.1
1925hMo (Alloy 926)	N08926	46	25	20	6.2	1	0.030	N 0.20 ^(A)	>40
25-6MO (Alloy 31)	N08031	33	31	27	6.5	1	0.020	N 0.20 ^(A)	
654 SMO	S32654	42	22	24	7.3	0.5	0.020	N 0.50 ^(A)	

^(A) Nitrogen added for increased strength

3.4. High-Nickel Austenitics

3.4.1. Nickel-Iron-Chromium-Molybdenum-Copper-Alloys

A number of these alloys are apparently compromises, more costly than those alloys with iron as the predominant alloying element, intended to resist sulfuric acid and SCC, while simultaneously showing improved resistance to pitting and crevice corrosion.

Table 3.5 gives compositions of two Ni-Fe-Cr-Mo-Cu alloys, with Alloy 825 included for comparison.

Table 3.5 : Ni-Fe-Cr-Mo-Cu Alloys, nominal wt. %, and typical PRE

Alloy	UNS	Ni	Fe	Cr	Mo	Cu	C (max)	Other	PRE
825	N08825	42	30	22	3	2	0.05	Ti	
20Mo-4	N08024	38	33	23	4	1	0.03	Nb	

20Mo-6	N08026	35	31	24	6	3	0.03	—	41.5-51.1
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3.4.2. Nickel-Chromium-Iron-Molybdenum-Copper Alloys

Among the high-performance alloys, one was developed years ago with the specific purpose of resisting the wet phosphoric acid process. The original Alloy F evolved successively into niobium-containing Alloy G (UNS N06007), then to a low-carbon and columbium-stabilized variant Alloy G-3 (UNS N06985), and ultimately to the current chromium-enriched Alloy G-30 (N06030). (See also Table 3.6).

Table 3.6 : Ni-Cr-Fe-Mo-Cu Alloys, nominal wt. %

Alloy	UNS	Cr	Ni	Fe	Mo	Cu	C (max)	Other
G	N06007	22	45	20	6.5	2	0.05	Nb 2.0
G-3	N06985	22	48	18	7.2	2	0.015	Nb 0.3
G-30	N06030	30	45	15	5.5	2	0.03	Nb 0.7, W 2.5

3.5. Mechanical Properties

The prime target for superaustenitic stainless steel has been to achieve high corrosion performance by certain alloying additions and not to develop or establish specific mechanical properties. Resulting mechanical properties have therefore been of secondary importance also bearing in mind the fact that austenitic steels seldom display any dramatic effects.

Characteristic for the austenitic stainless steels is a moderate strength combined with a high ductility. Incidental to the improvements achieved in corrosion resistance, the *high nitrogen* superaustenitic stainless steel may show increases of 50-100% in *yield strength* while retaining the superb ductility and toughness that characterize austenitic stainless steels. This is illustrated in Table XX, where typical mechanical data for several superaustenitic steels are listed. It can be seen that the alloys with high contents of N show the highest strengths, in some cases on level with those of duplex stainless steels. Despite the high strength, the *elongation* is considerable and even superior to that of many lower alloyed grades.

This is explained by another feature pertinent to high N; a high work hardening rate. Thus, very high strengths can be obtained in cold worked components. Applications where this property can be used are for tubulars in deep sour wells and for bolts etc.

Table XX

not yet available ...

3.6. Corrosion Resistance

Many years ago, if Type 316L or 317L was not suitable for an oxidizing chemical service, only the early or later versions of "Alloy 20" (N08020) were available before having to use the nickel-based Alloy C (N10002) or C-276 (N10276). (Nickel-based alloys are discussed in Chapter 6.) When the corrosion problems were related to chloride, especially as regards pitting and crevice corrosion rather than SCC, however, N08020 was not really superior to Type 316L or analogous stainless steels.

corrosion types of great importance for the high performance steels, namely *uniform corrosion*, *pitting*, *crevice corrosion* and *stress corrosion cracking*.

3.6.1. Uniform corrosion

Uniform corrosion on stainless steels occurs mainly in acids and hot alkaline solutions that are able to destroy the passive layer. The most important alloying additions to increase the passivity of a stainless steel are Cr and Mo. Thus, the alloys very high in these elements show excellent corrosion resistance in many solutions. Ni increases the resistance in some non-oxidizing acids and in certain environments additions such as Si, Cu and W give increased resistance.

Corrosion data for various steels could be presented as corrosion rates in mm/year or in **iso-corrosion diagrams** covering different concentrations and temperatures of a certain chemical. In Figure 5.1, an iso-corrosion diagram for a number of austenitic stainless steels in sulfuric acid is shown. The higher alloyed steels show a superior resistance in a wide range of concentrations than the standard grades 304 and 316. The diagram also shows that the high-silicon steel, SX, has a very high resistance to concentrated sulfuric acid. The iso-corrosion diagram in hydrochloric acid is shown in Figure 5.2. Also here, the great advantage of using a high alloy superaustenitic grade is apparent. In sulfuric and hydrochloric acid the very high alloyed grade 654 SMO shows superior corrosion resistance at most concentrations.

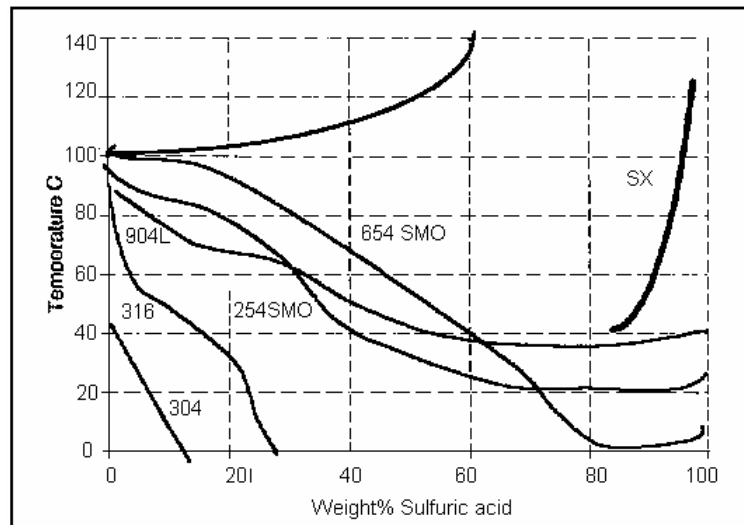


Figure 5.1: Iso-corrosion diagram, 0.1 mm/year, in sulfuric acid

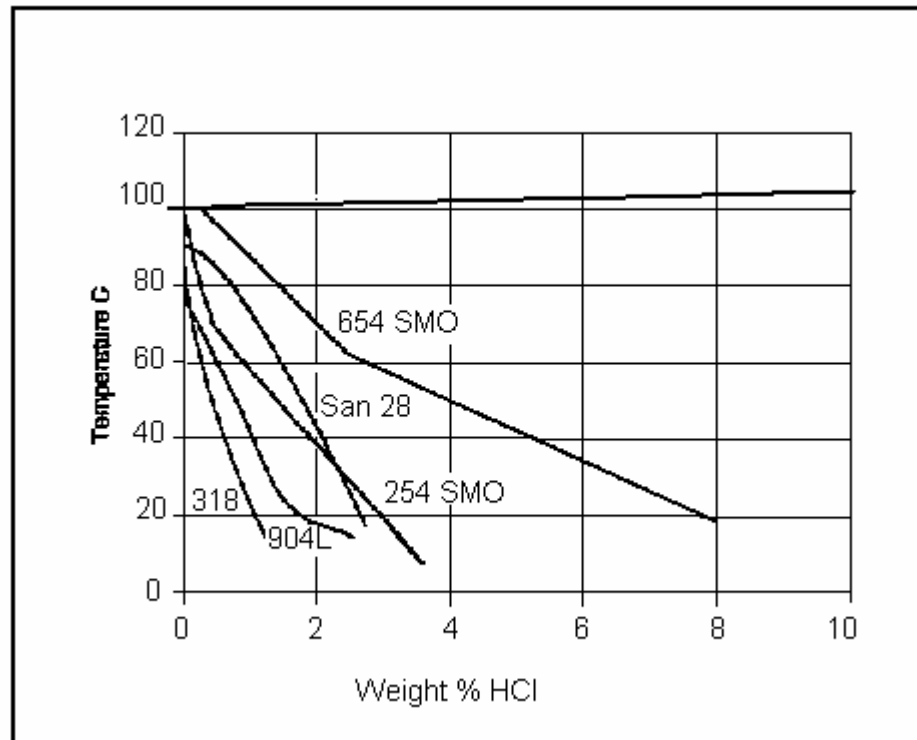


Figure 5.2: Iso-corrosion diagram, 0.1 mm/year, in hydrochloric acid

3.6.2. Pitting and crevice corrosion

Pitting and crevice corrosion are two closely related types of corrosion that regularly cause failures on stainless steels exposed to chloride containing environments. It is also a well known fact that increased contents of Cr and Mo enhance the pitting corrosion resistance. By adopting a **pitting index** or **pitting resistance equivalent** (PRE - cf. Section 4.3.5) the influence of various elements on the chloride pitting corrosion resistance can be estimated. The PRE is the result of application of linear regression mathematics to the values of a particular corrosion result as a function of the composition of the grades tested. The most current PRE expression involves Cr, Mo and N, as shown below, but also other elements could have some effect on pitting resistance.

$$\text{PRE} = \% \text{Cr} + 3.3 \times \% \text{Mo} + k \times \% \text{N}$$

where k is reported as between 13 and 30 (cf. supra).

A positive factor has been proposed for W and a strong negative factor has been reported for S. The pitting indices, using a factor for N of 16, are listed in Table 5.1.

A common laboratory test method for ranking different alloys is a modified ASTM G48 test where a **critical pitting temperature** (CPT) can be assessed in a ferric chloride solution. The CPT is normally defined as the lowest temperature where a pitting attack occurs. In Figure 5.3 the CPT values for a number of austenitic stainless steels are plotted against the PRE value using a factor for N of 16. The 6Mo steels, represented by 254 SMO, show quite high PRE numbers and CPT values. This family of superaustenitic stainless steels has also been used extensively in applications where a high pitting resistance is required. The highest PRE values are reached in Alloy 31 and, particularly, in 654 SMO. With these high values the pitting resistance is on the level with many high performance nickel-base alloys. The ranking of the crevice corrosion resistance is largely similar as that of pitting resistance.

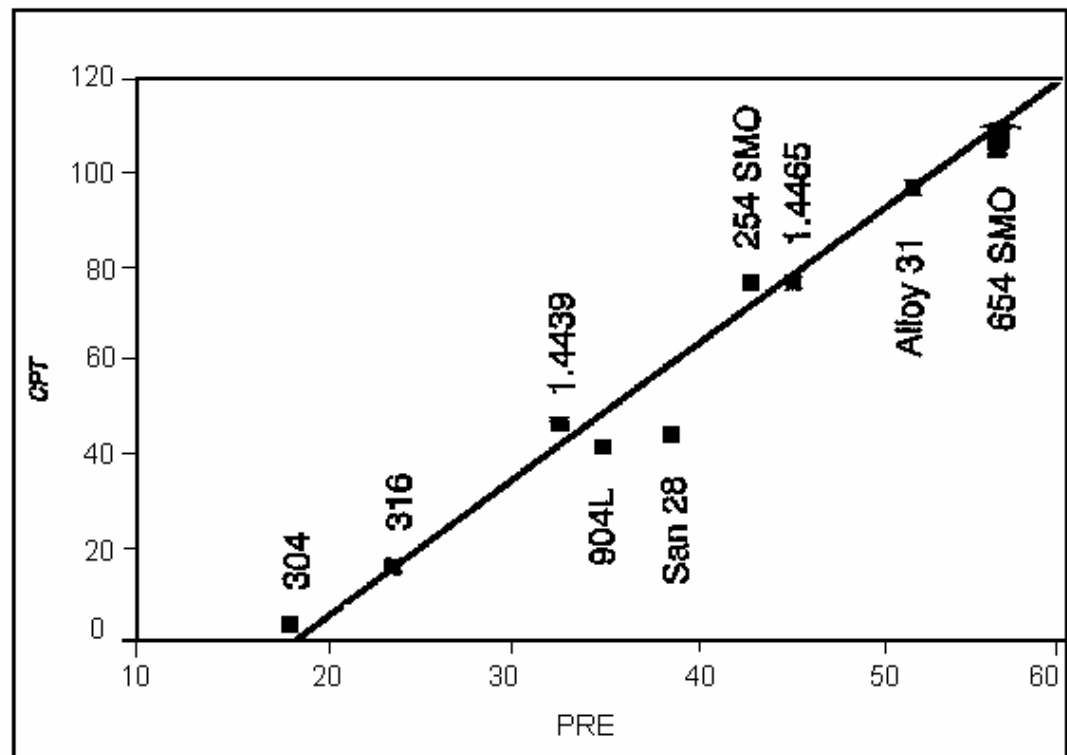


Figure 5.3: Plot of CPT in Ferric chloride versus PRE for several austenitic grades

3.6.3. Stress corrosion cracking (SCC)

Stress corrosion cracking is caused by a combination of tensile stresses and corrosive environment. For stainless steels, SCC occurs mainly in chloride environments above about 50°C. The standard austenitic stainless steels are more prone to SCC than ferritic and duplex

stainless steels. However, when it comes to superaustenitic stainless steels, very high resistance can be obtained, in many instances superior to the duplex grades.

This is illustrated in Figure 5.4 (where the **threshold stresses** for SCC, under severe evaporative conditions, determined by the drop evaporation test are shown). Increased risk of attack is encountered if hydrogen sulphide (H_2S) is present, as common in oil and gas wells. Such wells are currently called sour wells. Superaustenitic stainless steels show high resistance in sour environments while the duplex stainless steels are more prone to cracking due to hydrogen embrittlement of the ferrite phase. In the most severe oil and gas environments with high hydrogen sulfide contents, austenitic alloys are the optimal choice of material.

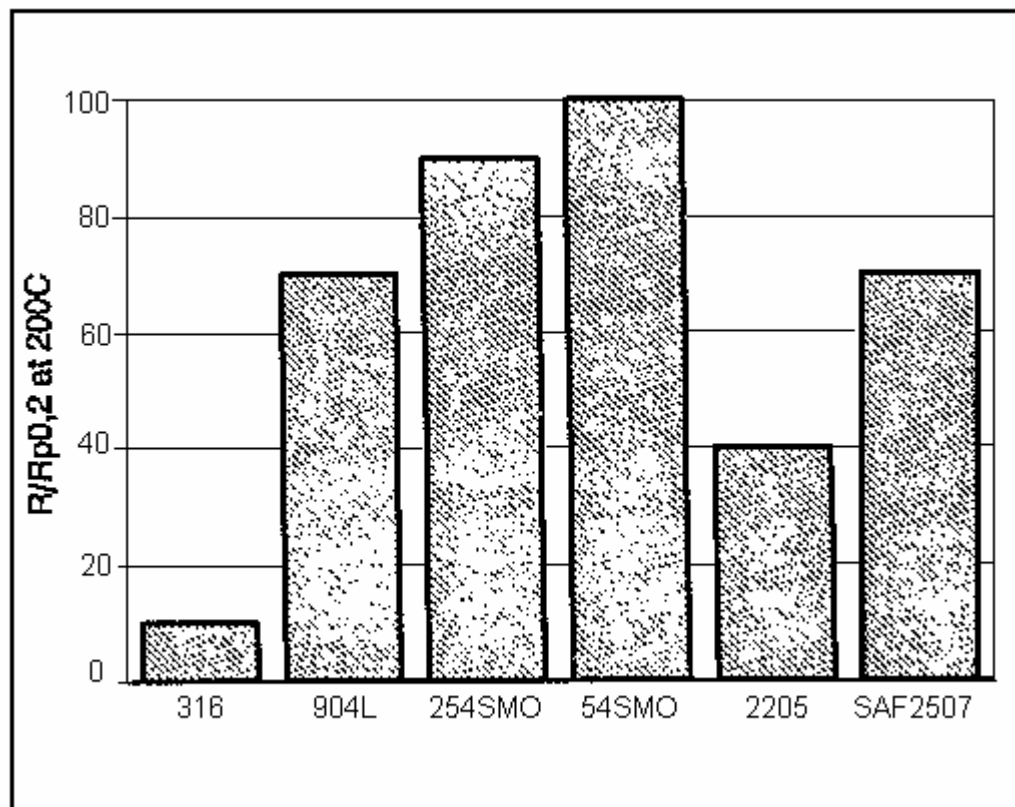


Figure 5-4: Threshold stresses determined by the drop evaporation test.

3.6.4. Conclusion

The general observation is that the high-alloy superaustenitic steels show superior resistance to all four corrosion types described above. Therefore a single alloy can be used in many harsh environments which is of great importance in some industries. The evolution has been

that super-austenitic grades can serve as multipurpose grades similarly to the role of 316L for less severe conditions. Thus 317L and 904L have been multipurpose grades for the pulp and paper industry for many years. This role has today been overtaken by the 6Mo grades.

3.6.5. Ranking Alloys

Although some semi-empirical parameters — such as the PRE value — can be a useful indication, it must be emphasized, that one alloy cannot be ranked over another until the conditions and chemistry of exposure are fully defined.

For example, Type 316L is the optimum alloy in production of ethylene diamine by the ethylene dichloride route, since Type 317L offers no better corrosion resistance and Alloy 20Cb-3 shows less resistance by virtue of its high nickel content which can be complexed by hot amines. Furthermore, Alloy G-30 resists nitric-hydrofluoric acid mixtures better than the Ni-Cr-Mo alloy C-276 (N10276). The relative resistance of Alloy G-30 and Alloy 28 (N08028) in wet process phosphoric acid varies with the chemical composition of the raw phosphate rock (especially as to contaminants) at various geographical locations.

On-going alloy developments can be expected and one must try to remain abreast through the available manufacturers' and technical literature.

3.7. Alloys for High-Temperature Resistance

An evolution has also occurred during the years of heat resisting austenitic stainless steels. A determining factor for this field of application is the fact that the austenitic structure implies a high creep strength. Types 309 and 310 were thus used early for high temperature service due to both high oxidation resistance and creep strength. For more critical applications nickel-base alloys with ~20% Cr and up to ~70% Ni were used. They contained various other additions for improved high temperature performance. Austenitic stainless steel grades with ~20% Cr and 30-40% Ni have also been available since the early 1920s as oxidation resistant alloys for use in furnace parts and heating elements. Due to nickel shortage in the early 1950s, INCO introduced Incoloy 800, containing about 20% Cr and 30-35% Ni. The alloy also contained Al and Ti additions that were found to improve the high temperature properties considerably. Later, several modified versions have resulted in Alloy 800 representing a family of materials with a range of properties.

Minor alloy additions to the high temperature materials have been used to improve the scaling resistance and creep strength. Elements most commonly used to reduce the scale formation are Al and Si but trace additions of Th, Y, Zr and REM (Rare Earth Metal) can have drastic effects. Elements that enhance creep properties are e.g. C, N, Mo, Al+Ti. Different alloying philosophies have been used during the years resulting in a great variety of heat resisting superaustenitic grades. Some producers have successfully used a combination of Si, N and REM to achieve superior high temperature properties of a 21% Cr, 11% Ni steel, 253 MA. Recently, Avesta Sheffield introduced a high temperature grade containing 25% Cr, 35% Ni utilizing this combination of additions. This superaustenitic steel, 353 MA, shows superior oxidation resistance and excellent creep strength (Table XX). Silicon and REM additions in combination with a high chromium content, give the good oxidation resistance. The high solidus temperature compared to nickel-base alloys, 1360°C for 353 MA, is also an advantage

3.8. Welding

For the more highly alloyed superaustenitic grades, particular concern has to be paid to two phenomena related to the solidification, namely those of *hot cracking* and *elemental segregation*.

Hot cracking occurs either directly during the solidification, and is referred to as solidification cracking, or upon reheating of successive weld runs and is then consequently called reheat cracking. Both types of cracking are related to the solidification mode of the weld deposit and presence of certain impurities such as sulfur and phosphorous. A primary ferritic solidification as is the case in standard austenitic grades such as 304 and most 316 gives high crack resistance. Superaustenitic stainless steels that normally have fully austenitic solidification are therefore more prone to both types of cracking. A classical case is grade 310 showing a wellknown susceptibility to hot cracking. Some of the highly alloyed, heat resistant grades have a similar susceptibility. Although having an austenitic solidification, 6Mo grades exhibit less sensitivity. However, the nickel-base fillers that are normally used for this group of steels may bring the deposit to a more susceptible composition. To avoid or reduce the hot cracking, welding should be done with low arc energy and with joints giving low restraints.

One alloying element in steels with a high tendency to segregate during solidification is molybdenum. Accordingly, superaustenitic grades with high molybdenum levels such as the 6Mo steels show large molybdenum microsegregations in autogenous weld metals. The areas depleted in molybdenum have a lower local pitting index and are thus less resistant to chloride pitting corrosion. To overcome this reduction in corrosion resistance, *fillers* overalloyed with molybdenum, preferably nickel-base alloys, are used. Alternatively, a post weld solution heat treatment can restore the pitting resistance of autogenous welds. Another possibility is welding with nitrogen addition to the shielding gas that enhances the nitrogen level in the weld to such a degree that improved pitting resistance is achieved. This, however, may not be fully sufficient to restore the pitting resistance.

3.9. Applications

Some examples of applications for the superaustenitic stainless steels were described already above. Due to their good combination of corrosion resistance, many superaustenitic grades are used under a great variety of conditions. The 6Mo grades were originally and are still used much in the pulp and paper industry in so-called C- and D-stage bleach washers and in flue gas scrubbers. In these applications the 6Mo grades replaced other stainless steels such as 317L and 904L that suffered pitting corrosion. The largest single field of application for the 6Mo steels is the North Sea offshore industry where large quantities are being used in the seawater systems, mainly in the form of pipes and fittings. Other important applications where seawater or saline water is the environment are condensers, heat exchangers and piping in

desalination plants. Due to the good combination of pitting and uniform corrosion resistance of the 6Mo steels, many installations in chemical and pharmaceutical industry have been made.

The most highly alloyed super-austenitic steel, 654 SMO, has found applications where the 6Mo steels are not sufficiently resistant and takes up the competition with nickel-base alloys and titanium. Examples of this are plate heat exchangers and flanges for seawater at higher temperatures, D-stage bleach washers and condenser tubing.

Superaustenitic heat resistant grades, like 353 MA, show excellent high temperature properties that bring them on level with certain nickel-base alloys, particularly concerning oxidation, carbon and nitrogen pick-up and creep resistance. Important areas of application are equipment for heat treatment, power industry, thermal destruction-incineration units and cement industry.

3.10. Conclusion

The development of superaustenitic stainless steels has been guided by new demands and made possible through new or improved production processes. However, a deep understanding of the correlations between properties and structure has been crucial for the development. Today, the highest alloyed superaustenitic stainless steels exhibit characteristics that make them on the level with some of the nickel-base alloys. Certainly, the evolution has not ceased. Due to even more advanced or new process techniques and better simulation and modeling capabilities there are great potentials also for further evolution.

3.11. Suggested Resource Information

- ☐ NN, *ASM Handbook, Vol. 13, Corrosion* (Materials Park, OH: ASM International 1987).
- ☐ R. M. Davison, J. D. Redmond, "Practical Guide to Using 6 Mo Austenitic Stainless Steels," *Materials Performance* 27, 12 (December, 1988), p. 39.
- ☐ NN, *The Metals Red Book, Vol. 2, Nonferrous Metals* (Edmonton, Alberta, CAN: CASTI Publishing, 1993).
- ☐ B. J. Moniz, W. I. Pollock, eds., *Process Industries Corrosion — The Theory and Practice* (Houston, TX: NACE International, 1983, p. 427.

'Though' and Ductile ...

4.1. Introduction

Parallel to the evolution of austenitic stainless steels there was also an early development of austenitic nickel-base alloys for corrosive environments. Thus for example various “*Hastelloys*” (cf. *infra*) were developed already in the 1920s and 1930s.

The production was made in quite a small scale during the first decades. As with the austenitic stainless steels, however, the introduction of new refining technologies such as electroslag remelting (ESR), vacuum arc remelting (VAR) and AOD resulted in increased yields and improved production economy.

The family of nickel alloys is among the most important because they resist corrosion in a wide variety of environments, but salts and other contaminants have specific effects on particular alloy compositions.

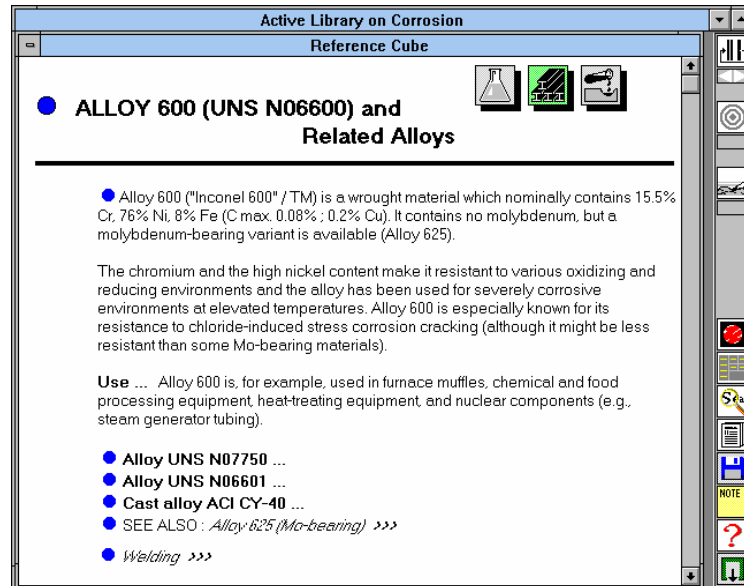
The alloys can be divided into two groups:

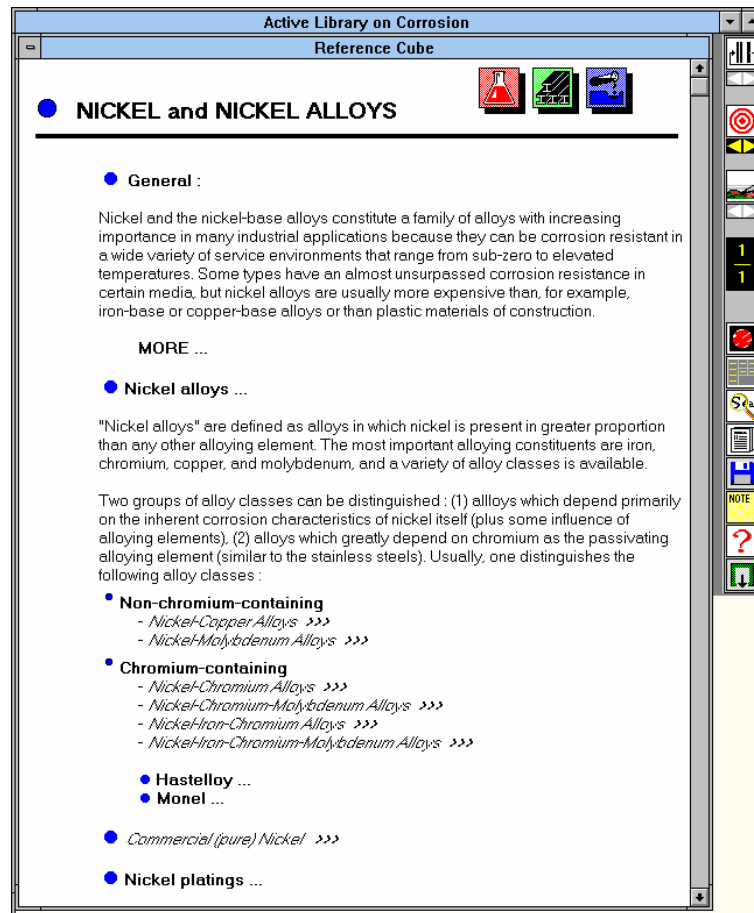
- (1) those which depend primarily on the inherent characteristics of nickel itself (plus the influence of certain alloying additions); and
- (2) those which employ chromium as a major element to develop a passive film analogous to that which forms on iron-chromium alloys such as stainless steels.

The alloys of primary interest are listed in Table 6.1. These, and other related alloy variations, are discussed below.

Table 6.1 : Nickel-based Alloys, nominal wt. %

Alloy	UNS	Cr	Cu	Mo	Fe	Ni	C	Other
<i>CHROMIUM-FREE</i>								
200	N02200	—	—	—	—	99.5	0.01	
400	N04400	—	31	—	0.1	66	0.1	Mn 1
500	N05500	—	26	—	0.1	67	0.1	Mn, Al, Ti
B-2	N10665	—	—	28	0.002	71	0.002	Mn 1
<i>CHROMIUM-BEARING</i>								
600	N06600	16	—	—	8	72	0.05	Mn 1
625	N06625	22	—	9	4	61	0.05	Nb 3.5
C-276	N10276	16	—	16	5.5	57	0.005	W 4





4.2. Nickel Alloys

4.2.1. Nickel

Commercially pure nickel (e.g., Alloy 200; UNS N02200), is a white, magnetic metal very similar to copper in its other physical and mechanical properties. The Curie point, i.e., the temperature at which it loses its magnetism, fluctuates with the nature and extent of alloy additions, rising with increased iron and cobalt concentrations, falling with addition of copper, silicon and most other elements. Nickel is also, of course, an important alloying element in other families of corrosion-resistant alloys (e.g., alloy cast irons, cupronickels, stainless steels).

Nickel is used by itself as a *material of construction*, as a *cladding* on a steel substrate, and as a *plating* on steel or other less noble metals. The plating may be deposited either by electrochemical techniques or as electroless nickel plating (ENP) deposited by a chemical reduction process.

In addition to Alloy 200, there are a number of alloy modifications developed for increased strength, hardness, resistance to galling, and improved corrosion resistance. The several variants of nickel are substantially equivalent in corrosion resistance, but the *low-carbon Alloy 201* (0.02% carbon maximum, N02201) is preferred for service above 300°C (570°F), as in caustic evaporators.

A major application of nickel is in the production of high-purity *caustic* in the 50 to 75% concentration range. The sodium hydroxide is produced in nickel or nickel-clad evaporators to meet the rigorous requirements of the rayon, soap, and other manufacturing industries for iron-free, copper-free caustic.

Nickel, like copper, is not resistant to *ammonia* or its derivatives in the simultaneous presence of air, oxygen, other oxidants. This is due to the formation of soluble complex ions, similar to the copper-ammonium complex.

Nickel is moderately resistant to *acids* (since it does not liberate hydrogen), except under oxidizing conditions. Oxidizing cations (e.g., ferric or cupric ions) or anions (e.g., nitrates, nitrites) cause rapid attack.

Nickel-plated steel, particularly of the electroless variety (actually a nickel/nickel phosphide alloy), is used for the shipment and storage of many chemicals which require protection against iron contamination. Electroless nickel plating can be hardened by heat treatment for wear resistance approaching Cr-plate.

4.2.2. Alloy 400 (Monel)

“*Monel*”, or Alloy 400 (UNS N04400), is a well-known and widely used alloy containing approximately 30% copper and up to 2.5% iron. Alloy 400 is readily forged, worked, cast, and welded (or brazed), and has approximately the same machinability as steel. Its Curie point is very close to room temperature, hence it can lose its magnetism when merely warmed by the sun, only to recover it upon slight cooling. (Cast Monel has a higher Curie point because of increased silicon content.)

There are a number of variants (e.g., precipitation-hardened Alloy 500 — UNS N05500) for improved strength, hardness, machinability or resistance to galling.

Corrosion resistance is good in many (although not all) *natural waters*, including seawater. Both Alloys 200 and 400 can be attacked in soft waters, having critical ratios of oxygen to carbon dioxide. Alloy 400, however, is the standard material of construction for water meter parts, pumps, valves, strainers, etc. A substantial amount is used in fabrication of hot-water tanks. It should be noted, however, that under hot-wall conditions (i.e., in coolers or condensers), some fresh waters will cause pitting, even though otherwise non-corrosive.

Alloy 400 and its variants will resist both acids and alkalis, in the absence of oxidizing agents. As one would expect, these nickel-copper alloys are subject to corrosion by ammonia and its derivatives in the presence of oxygen or oxidants.

These alloys are subject to environmental cracking under some conditions (e.g., SCC by hydrofluoric acid vapors plus air due to the influence of cupric fluoride, and by hot concentrated caustic, HAC by atomic hydrogen, in the cold-worked condition; LMC by

mercury or its salts). For HF SCC of Alloy 400 by cupric fluoride, thermal stress relief is only partially effective.

4.2.3. Nickel-Molybdenum Alloys

Alloy B (UNS N10001) is an alloy of nickel with approximately 28 % molybdenum, developed to resist *hydrochloric acid* up to the atmospheric boiling point. This resistance is, however, severely impaired by the presence of oxidizing contaminants (e.g., ferric ions in muriatic acid).

As one would expect, the alloy resists *reducing* acids quite well, and oxidizing acids not at all.

Alkali resistance is also good, but use of such an expensive alloy is not warranted. Like other high-nickel alloys, it is susceptible to attack by amines, in the presence of air or oxidants, due to the nickel-ammonium type complex.

Because of susceptibility to IGA in the HAZ after welding in some environments, a *low-carbon variant* has been developed. Alloy B-2 (UNS N10665) is replacing alloy B in most applications. An improved version, alloy B-3 (UNS N10675), has been introduced. It is specially formulated to achieve a level of thermal stability superior to alloy B-2. Improved thermal stability provides superior fabricability, e.g., ease of heat treatment procedures. Alloy B-4 (N 10629), also recently introduced, has high resistance to SCC in the aged condition and no embrittlement during thermal-mechanical processing.

4.3. Chromium-Bearing Alloys

4.3.1. Nickel-Chromium Alloys

The prototype alloy in this category is Alloy 600 (UNS N06600), often called just “*Inconel*”- with no designation following the trade name, which contains approximately 76% nickel, 16% chromium, and 8% iron. The presence of chromium gives it a passive film and corrosion characteristics analogous to those of stainless steels. A variant is Alloy 601 (N06601), with a somewhat lower carbon content and a somewhat higher chromium content.

Alloy 600 is used as a heating coil in caustic evaporators, unless traces of Cr(VI) ions are objectionable in the product. Nevertheless, at high stress levels, it is subject to SCC in strong caustic on prolonged exposure above approximately 300°C (570°F).

Alloy 600 can replace austenitic stainless steel in some chloride environments, but it can be pitted (although not cracked) under severe conditions. It is at least an order of magnitude better than Type 300 series stainless steels in steam contaminated with both chlorides and caustic, and has been widely used to replace Type 321 (S32100) stainless steel for corrugated expansion joints in such service.

Alloy 600 has excellent resistance to halogens and halogen acid anhydrides at elevated temperatures. However, as with all nickel alloys, it is subject to LMC by sulfur contamination at elevated temperatures (e.g., in welding, where the materials must be scrupulously clean and

5

A

W

A

Table 6.2 : Nickel-Chromium-Molybdenum Alloys, nominal wt. %

Alloy	UNS	Ni	Cr	Mo	W	Fe	C(max)	Other
C-276	N10276	57	16	16	4	5	0.01	—
C-4	N06455	65	16	16	—	2	0.01	—
C-22	N06022	56	22	13	3	3	0.01	—
59	N06059	59	23	16	—	1	0.01	—
625	N06625	61	21	8	—	4	0.10	Nb 3.5

These alloys are outstanding in resistance to hot seawater, aggressive organic acids (e.g., boiling formic or acetic acid mixtures) and hot oxidizing acids (e.g., mixtures of nitric with hydrochloric) . Alloy 625 is usually, although not always, somewhat less resistant than the 15-16% molybdenum grades in chemical services. Ni-Cr-Mo alloys are also sometimes employed for severe SCC environments (e.g., centrifuges for high-chloride resin or polymer mixtures, such as polyvinyl chloride [PVC]) where the super-stainless steels or high-performance nickel-rich alloys might be suspect or of too low a mechanical strength.

Again, it should be noted that superiority cannot be claimed for one Ni-Cr-Mo alloy over another (nor even over alloys of lesser content of elements conveying or enhancing corrosion resistance) without reference to specific chemical environments.

Active Library on Corrosion
Reference Cube

**● ALLOY C-276 (UNS N10276)
and ALLOY C-4 (UNS N06455)**

● Introduction

Welded structures made from the basic Alloy C material require annealing to overcome carbide precipitation in the heat-affected zone.

Considerable research resulted in the development of an alloy that was more resistant than N10002 to the formation of precipitates in the grain boundaries that robbed the adjacent areas of chromium, nickel and molybdenum.

● Alloy C-276 ...

The first improved alloy, Alloy C-276 (UNS N10276), has a low C content (0.02%) and a low Si content (0.05%) and does not require stress relieving heat treatment. It is usually suitable for weld fabricated chemical process equipment where the heat affected zones are held in the sensitizing range of about 1200-2000 F (650-1090 C) for five minutes or less.

Alloy C-276 is known for its outstanding resistance to pitting and stress corrosion cracking, and for its good performance in oxidizing atmospheres to 1900 F.

● Alloy C-4 ...

● Cast Versions of Alloy C >>>

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● ALLOY 625 (UNS N06625)

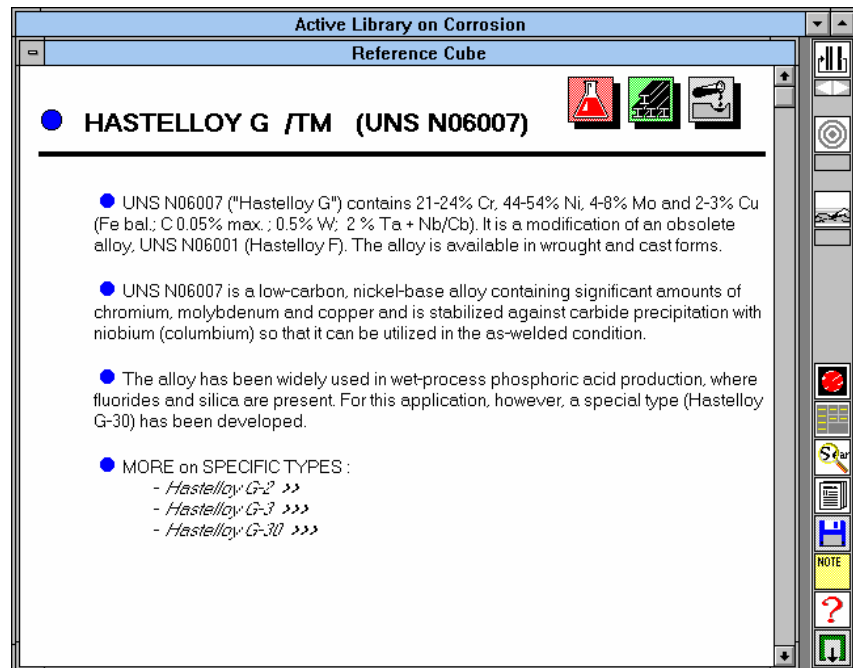
● Alloy 625 could be considered a Mo-containing variant of Alloy 600, although it also contains more chromium (and less nickel). Its nominal composition is 61% Ni, 21.5% Cr and 9% Mo (Fe max. 5%, C max. 0.1%). It also contains tantalum and niobium/columbium (Ta+Nb 3.6%).

● Alloy 625 ("Inconel 625"), by virtue of the matrix strengthening effect of niobium (columbium) and molybdenum, has good mechanical properties at elevated temperatures, in addition to corrosion resistance in numerous environments.

● The presence of about 3.65% Nb (Cb) plus tantalum stabilizes this alloy against the formation of carbides in the heat affected zones of welds. However, heating for about one hour at 760 C will produce intergranular chromium carbide precipitation.

● Alloy 625 has excellent resistance to seawater corrosion, and combines excellent resistance to oxidizing acids with good resistance to reducing acids.

● There is a cast version of N06625 with similar corrosion resistance. The cast version of the alloy is included in ASTM specification A494/A494M alloy CW-6MC.



4.4. Suggested Resource Information

- ☐ NN, *ASM Handbook, Vol. 13, Corrosion* (Materials Park, OH: ASM International, 1987).
- ☐ W. Z. Friend, *Corrosion of Nickel and Nickel-Base Alloys* (New York, NY: Wiley-Interscience, 1980).
- ☐ NN, *The Metals Red Book, Vol. 2, Nonferrous Metals* (Edmonton, Alberta. CAN: CASTI Publishing, 1993).
- ☐ B. J. Moniz, W. I. Pollock, eds., *Process Industries Corrosion — The Theory and Practice* (Houston, TX: NACE International, 1988), p. 461.

5. Copper and Its Alloys

Materials with a long tradition, not always the CPI's 'materials of choice' and nowadays fairly expensive, but with a range of interesting properties ...

5.1. Introduction

Copper and its alloys have been known and utilized for more than 6,000 years. The Bronze Age antedates the Iron Age by approximately 1,500 years. The corrosion resistance of copper alloys was recognized almost from the beginning, as evidenced by their use in containers for food and drink and for long-lasting statuary. Apparently, initial workings of hammered copper were followed by crude castings of lean bronze from impure copper ores. Finally, true bronzes, e.g., tin ~phosphor) bronzes, appeared. In modern times, highly purified coppers, free of all but traces of other elements, as well as copper alloys compounded for specific properties, are widely used in industry. Table 8.1 lists the nomenclature and approximate compositions of some of the more important wrought and cast copper alloys.

Table 8.1: Copper Alloys, nominal wt. %

Name	UNS	Cu	Zn	Sn	Al	Ni	Other
<u>Wrought</u>							
Copper	C11000	99.9	-	-	-	-	
Red Brass	C23000	85	15	-	-	-	
Yellow Brass	C27000	69	31	-	-	-	
Admiralty B	C44300	72	27	1	-	-	As 0.1
Phosphor Bronze	C52400	90	-	10	-	-	P 0.3
Al Bronze D	C61400	90	0.2	-	7	-	Fe 3
High Si Bronze	C65500	95	1.5	-	-	0.6	Si 3
90-10 Cu-Ni	C70600	86	1.0	-	-	10	Fe 1.5
70-30 Cu-Ni	C71500	68	1.0	-	-	30	Fe 1
85-15 Cu-Ni	C72200	83	1.0	-	-	15	Cr, Fe
<u>Castings</u>							
Ounce Metal	C83600	85	5	5	-	-	Pb 5

Mn Bronze	C86500	57	40	1	-	1	Mn 1
G Bronze	C90500	87	2	10	-	1	-

Active Library on Corrosion

Reference Cube

Compositions and standard designations of Copper Alloy Families - Wrought

Table 112

UNS Number *	Description	Major Constituents
C10100-C15000	Coppers	Cu
C16200-C19500	High-copper alloys	Cu plus Cd, Be, Cr/Fe
C20500-C28200	Brasses	Cu, Zn
C31400-C38600	Leaded brasses	Cu, Zn, Pb
C40500-C48500	Tin brasses	Cu, Sn, Zn
C50100-C52400	Phosphor bronzes	Cu, Sn
C53400-C54800	Leaded Phosphor bronzes	Cu, Sn, Pb
C60600-C64200	Aluminium bronzes	Cu, Al
C64700-C66100	Silicon bronzes	Cu, Si
C66400-C69800	Special brasses	Cu, Zn plus Mn, Si, Al
C70100-C72500	Copper Nickels	Cu, Ni
C73200-C79900	Nickel silvers	Cu, Ni, Zn

To table for Cast Alloy Families >>>

Active Library on Corrosion

Reference Cube

Compositions and standard designations of Copper Alloy Families - Cast

Table 112B

UNS Number	Description	Major Constituents
C80100-C81100	Copper	Cu
C81300-C82800	High-copper alloys	Cu + Cr, Be, Co, Ni, Si
C83300-C83800	Red brasses,	Cu, Sn, Zn, Pb
	Leaded red brasses	
C84200-C84800	Semi-red brasses,	Cu, Sn, Zn, Pb
	Leaded semi-red brasses	
C85200-C85800	Yellow brasses,	Cu, Sn, Wn, Pb
	Leaded yellow brasses	
C86100-C86800	Manganese bronzes,	Cu, Zn, Al, Mn, Pb
	Leaded manganese bronzes	
C87200-C87900	Silicon bronzes & brasses	Cu, Zn, Si
C90200-C91700	Tin bronzes	Cu, Sn
C92200-C92900	Leaded tin bronzes	Cu, Sn, Pb
C93200-C94500	High-leaded tin bronzes	Cu, Sn, Pb
C94700-C94900	Nickel-tin bronzes	Cu, Sn, Ni
C95200-C95800	Aluminium bronzes	Cu, Al, Fe, Ni
C96200-C96600	Copper Nickels	Cu, Ni, Fe
C97300-C97800	Nickel silvers	Cu, Ni, Zn
C98200-C98800	Leaded coppers	Cu, Pb
C99300-C99700	Special alloys	Cu, Ni, Fe, Al, Zn

To table for Wrought Alloys >>>

5.2. Copper

The great majority of copper alloys cannot be hardened by heat treatment. They are hardened by cold-work, such as hammering, as in primitive times. (There is no "lost secret of the ancients" for hardening copper.) With subsequent reheating, there are several "tempers" available (e.g., quarter-hard, half-hard) with different capabilities for flaring or rolling. Modern technology has given us a few precipitation-hardening alloys (copper plus chromium or zirconium) and a grade which is dispersion-strengthened copper (e.g., C15710).

5.3. Brass

Modern brasses contain anywhere from 5 to 45% zinc. As the zinc content is increased, the characteristic red brass color is first observed, up to 10 to 15% zinc (C23000). The yellow brass next appears commercially in the range 25 to 30% zinc (C26000). As the zinc concentration is further increased to approximately 38% (C46400, naval brass), the red color returns (due to the formation of a secondary beta phase in lieu of alpha brass³ until, at approximately 42% zinc, the color is again a close match to 90-10 red brass. Small amounts of lead, which is insoluble in copper, may be added to brasses or bronzes to improve machinability and lubricity (as in bearing alloys). Unfortunately, the lead particles can also function as corrosion initiation sites in some environments.

waters, ranging from potable water to seawater. To combat this type of attacking seawater, the British developed admiralty metal by adding 1% tin to a 70-30 yellow brass. In modern practice, the beneficial effect of tin is increased synergistically by additions of approximately 0.2% arsenic, antimony, or phosphorus. These additions provide the three (roughly equivalent) alloys; admiralty 13 (C44300), C (C44000), and D (C44500), respectively. Inhibiting additions of tin and arsenic are also made to other high-zinc alloys (e.g., aluminum brass, C68700; leaded muntzmetal, C36600) intended for service in corrosive waters or other aggressive environments.

Another major weakness of brass and of other high strength copper alloys is a susceptibility to environment cracking, especially SCC and LMC (e.g., by mercury), as described in Chapter 8.

5.4. Bronze

There are four general categories of bronzes which are of interest from the corrosion engineering standpoint, although there are a great number of variants used in materials engineering of metal products. Bronzes and brasses (the nomenclature has always been rather loose until the advent of the UNS) have been widely used for naval and military applications, as well as architectural and machinery uses. Beryllium bronze is employed for improved hardness and wear-resistance (e.g., as in nonsparking tools).

5.4.1. Phosphor Bronze

These tin bronzes have taken their popular name from the use of phosphorus as a deoxidizer. The tin, usually used in concentrations of up to approximately 10% (e.g., C52400), confers strength and increases corrosion resistance in some environments. Casting bronzes may be more complex, e.g., leaded phosphor bronze (ounce metal, C54400 [85%Cu-5%Sn-5%Zn-5%Pb]), because of the variety of properties desired, such as fluidity in casting, strength, galling resistance, machinability, and corrosion resistance.

5.4.2. Silicon Bronze

Silicon bronzes are copper plus 1 to 3% silicon (e.g., C64900, C65500), noted particularly for strength and cryogenic suitability. However, these alloys are hot-short, because of the presence of a low-melting constituent at the grain boundaries. At 700 to 800°C (1,290 to 1,475°F), as from welding or hot-work, microfissuring occurs under stress. After welding, brazing or hot-working, the microfissures may become apparent as macrocracks after only a few hours. On the other hand, they may take several years to become apparent. The intergranular cracking is difficult to distinguish from SCC under the optical microscope. (The alloys are susceptible to SCC in ammonia or even uncontaminated steam.) LMC, as by mercury or its salts, is also difficult to distinguish from hot-short cracking, although the scanning electron microscope and microprobe analysis techniques should enable one to do so.

6. Light Metals

For specific CPI applications ...

6.1. Aluminum and Its Alloys

6.1.1. General

Aluminum and its alloys are light-weight (density approximately 2.7 g/cm^3 , approximately one-third that of carbon steel), reasonably strong, and quite resistant to natural environments in spite of their anodic position in the galvanic series. (This resistance is due to the presence of a protective oxide film.) These materials are relatively easy to fabricate, available in most standard forms, and can be joined by most of the common methods of welding and brazing.

Commercially pure aluminum and its alloys have UNS numbers (see Chapter 3 .4.5), with identifications derived from the older Aluminum Association (AA) designations. The general format is A9xxxx for wrought materials, and A0xxxx for castings. As seen in Table 10.1, the second digit (A9xxxx) indicates the major alloying element. The third digit (A9xxx) indicates whether there are controls on impurities, while the last two digits (A9xxxx) are arbitrary holdovers from the older AA system. Alloys commonly used in the process industries include A93003, A95083, A95086, A95154, and A96061.

6.1.2. Properties

Annealed aluminum alloys (e.g., A91100) have mechanical properties of the order of 110 MPa (16 ksi) tensile strength, and 41MPa (6 ksi) yield strength. These alloys can be hardened by cold work (i.e., strain-hardened). Other wrought alloys can be heat-treated (i.e., age-hardened or precipitation hardened). In such cases, the alloy designations carry a suffix: "H" for strain-hardened, "T" for tempered (i.e., precipitation-hardened, followed by drawing to the desired hardness). The "T" designation is followed by a number indicative of the specific procedure.

Table 2.1 : UNS Numbers for Aluminum Alloys

Alloy No.	Example	Major Alloying Element
A9lxxx	A91100	None, 99.00% aluminum minimum

A92xxx	A92020	Copper
A93xxx	A93003	Manganese
A94xxx	A94002	Silicon
A95xxx	A95154	Magnesium
A96xxx	A96063	Magnesium and silicon
A97xxx	A97001	Zinc
A98xxx	A98013	Miscellaneous (e.g., chromium)

In the process industries, one does not, look for anything stronger than, for example, A96061 - T6. This indicates an alloy of approximately 310 MPa (45,000 psi) tensile, 276 MPa (40,000 psi) yield, and approximately 12% elongation. One of the strongest available heat-treated alloys is A97075 in the T-4 condition, which can attain 572 MPa (83,000 psi) yield strength, while maintaining 10% elongation.

For most purposes, joining with the inert gas-shielded welding processes, e.g., GTAW (TIG) or GMAW (TIG) is preferred, but shielded metal arc (SMA or stick electrode) is acceptable, and gas-welding is permissible. Of course, in hardened alloys, the strength of HAZ is drastically reduced by the annealing effect of the welding heat input.

Aluminum has excellent low-temperature properties with high impact strengths and is used widely in noncorrosive cryogenic services, such as gas-treating and air separation.

6.1.3. Corrosion

Usually, corrosion resistance of aluminum in uncontaminated atmospheres is good. However, it will become unsightly after a time because of the initial rate of attack, which stifles itself by the development of a protective film or architectural applications, an electrolytically-induced film may be pre-developed by a process called anodizing. This gives a more aesthetically pleasing and more stable surface.

The A92000 series of alloys (and the similar copper-bearing castings of the A02000 series) do not have good resistance. This is particularly evident in contaminated industrial or marine atmospheres. An insidious subsurface intergranular attack (exfoliation) develops, and corrosion proceeds along the grain-boundaries of the cathodic copper-rich phases. The attack may not be evident on the surface, which may show only a frosted appearance, while the thickness of the metal may actually increase as a result of the corrosion products within the alloy structure. Aluminum alloys intended for industrial applications should contain no more than 2.5% copper.

Except for the copper-bearing grades, aluminum has good resistance to many natural waters, as witnessed by the use of aluminum boats even in seawater. However, aluminum is subject to pitting under stagnant conditions in saline waters, particularly as a heat transfer surface (e.g., in heat exchangers).

In water and dilute aqueous solutions, pH from 4.5 to 9.5 should show rates of less than one mpy. The situation is complicated by chlorides or other halides, deposits, and by the characteristic nature of aluminum, which is amphoteric (that is subject to attack by either acidic [pH<4] or alkaline [pH>10] environments). Because aluminum is anodic to most other common metals except zinc and magnesium, it is subject to attack by the ions of heavy metals (e.g., iron, copper, lead, and mercury) due to cementation. Heavy metal ions easily can be present, of course, in industrial waters, as a result from corrosion of equipment upstream.

Many organic chemicals are fully compatible with aluminum. Aldehydes, ketones, esters, amines, and organic acids and anhydrides can be shipped and stored in aluminum, as dry refined products. It should be emphasized, however, that some organic chlorides (i.e., chloro-organic compounds such as chloroform or ethylene dichloride) and alcohols can react catastrophically with aluminum, with the attendant danger of fires or explosion due to hydrogen liberated in the corrosion process. In some solvents, water may be an effective inhibitor. This is not true universally, however, as in the case of hydrolyzable organic chlorides (which simply liberate hydrochloric acid upon warming with water).

Among the inorganic products, concentrated nitric acid (greater than 90%) and hydrogen peroxide are commercially handled in aluminum. The non-oxidizing acids, and alkalis or aqueous ammonia derivatives, are corrosive.

Even in relatively innocuous media, galvanic couples (except with zinc) must be avoided. Galvanized surfaces and zinc-pigmented coatings afford CP to aluminum. CP is also utilized in Alclad products, in which a surface layer of an anodic aluminum alloy corrodes sacrificially to prevent pitting of a more cathodic substrate.

In addition to the exfoliation previously described, some aluminum alloys (e.g., A97074) are subject to IGA of the weld HAZ in corrosive environments.

Environmental cracking is encountered only in the heat-treated, high-strength alloys. Such cracking is a problem primarily in aircraft and marine structures seeking a high strength-to-weight ratio. A typically susceptible material is A97075-T6. However, the same alloy in the T73 temper has good resistance to environmental cracking, which illustrates once again the importance of sound materials engineering.

In the CPI, the predominant aluminum alloys are those of the 3000, 5000, and 6000 series. High-strength alloys of the 7000 series are subject to SCC.

6.2. Magnesium

The two outstanding characteristics of magnesium are its very light weight (the density of approximately 1.8 being approximately two-thirds that of aluminum) and its highly anodic position in the galvanic series in water. It is anodic to all common engineering metals in aqueous environments.

Magnesium is widely used as sacrificial anodes in the CP of steel piping or structures underground. Aside from the aircraft industry, magnesium is rarely encountered by the engineer concerned with materials of construction.

6.3. Suggested Resource Information

7. Lead, Tin and Zinc

*For special purposes – “Amphoteric” metals,
with some peculiarities ...*

7.1. General

These three metals are grouped together for discussion because they share an amphoteric nature (i.e., they can be attacked by both acids and alkalis), because they are all employed as metallic coatings, and because it is convenient to separate them from other nonferrous metals, such as copper and nickel, more commonly employed in corrosive service.

7.2. Lead and Its Alloys

Lead is a weak, heavy metal (almost half again as heavy as steel) which has difficulty supporting even its own weight. However, it has enjoyed widespread industrial use, particularly because of its resistance to sulfuric acid. In nature, it is usually associated with copper and silver. Applications of lead have been greatly diminished in modern practice, because of toxicity problems associated with its joining ("lead-burning").

7.2.1. Types of Lead

There are a number of lead alloys developed specifically to increase endurance limit and hardness (or ability to work-harden) and to prevent excessive grain growth.

Chemical lead is lead with traces of copper and silver left in it. It is not economical to recover the silver, and the copper content is thought to improve general corrosion resistance.

Antimonial lead (also called hard lead) has been alloyed with from two to six percent antimony to improve the mechanical properties. This is effective in services up to approximately 93°C (200°F), above which both strength and corrosion resistance rapidly diminish. Tellurium lead has been strengthened by the addition of a fraction of a percent of tellurium. It will work-harden under strain thus it has better resistance to fatigue failure induced by vibration.

There are also proprietary alloys (e.g., Asarcon) to which copper and other elements have been deliberately added for improved corrosion and creep resistance. Nalco~ has been alloyed specifically for improved corrosion resistance in chromic acid plating baths.

7.2.2. Forms

Lead is available in pipe, tubing, and valves, as well as sheet or process vessels. Sheet lead is also used as a membrane in acid brick-lined vessels. Lead-clad steel plate is also available. because it will not easily support its own weight, lead is subject to creep and static fatigue. Creep is characterized by stretching under constant load. Static fatigue is characterized by a "crazing" effect and, sometimes, by IGA.

For these reasons, lead vessels are usually externally supported by wooden or steel structures, or fabricated from clad metal i.e., homogeneously bonded lead-clad steel). Since the steel supplies the mechanical strength, any grade of lead may be used as the cladding, at the discretion of the manufacturer.

7.2.3. Corrosion Resistance

Lead is an amphoteric metal, i.e. susceptible to attack by both acids and alkalis under certain conditions. That it has excellent resistance in many environments is due largely to the insolubility of some of its corrosion products, which tend to form protective films in the appropriate services.

Lead tends to resist sulfuric, sulfurous, chromic, and phosphoric acids, and cold hydrofluoric acid (see Chapters 19 to 32 on specific environments). It is attacked by hydrochloric acid and by nitric acid, as well as organic acids, if they are dilute or if they contain oxidizing agents.

The usefulness of lead in caustic is limited to concentrations of more than 10% up to approximately 90° (195°). It suffers little attack in cold, strong amines, but is attacked by dilute aqueous amine solutions. Lead will resist most natural waters, but is not suitable in soft aggressive waters. It must not be used to handle potable (i.e., drinking) water, because of the toxicity of lead salts.

Although lead is anodic initially to more highly alloyed materials, it may become cathodic in time due to the film of insoluble corrosion products formed on its surface. As an example, alloys 20-Cb3 (UNS N08020) and C-276 (N10276) valves may suffer accelerated attack in lead piping systems in sulfuric acid services unless electrically isolated from the piping.

7.3. Tin

Tin is of somewhat limited availability in the United States, since all of it must be imported. It is a major alloying element in "phosphor" and other types of bronzes, but its major usage as a material of construction is as tin-plate and solder.

The use of tin as a packaging medium (e.g., as tooth-paste tubes, foil, etc.) has largely given way before other materials, such as plastics. However, tin-plate (e.g., over steel) is produced both as a hot-dipped and as an electroplated coating. Attempts to replace "tin" cans for canned peaches and apricots have been unsuccessful from a marketing standpoint, because the organotin complex (which gives the products their characteristic taste) does not form in plastic or glass containers.

Tin is encountered to a limited extent in terneplate (a hot-dipped steel for roofing purposes). The most common solder is a 50-50 lead alloy.

7.4. Zinc

Zinc is a major alloying element in brass. For materials of construction, the major engineering usage is as the hot-dipped galvanized steel and as a sacrificial pigment in certain types of paints. Electroplated zinc coatings are also encountered. The electrochemical protection is directly proportional to the thickness of the zinc, so the method of application to steel is selected on the basis of feasibility and economics.

Zinc die-castings are used for some artifacts not intended for exposure to corrosion. Zinc anodes are widely used for CP in salt-water services, such as to protect rudder irons from corrosion and propellers from cavitation.

7.5. Suggested Resource Information

- ☐ ASM Handbook, Vol. 2, Properties and Selection-Nonferrous Alloys and Special Purpose Materials (Materials Park, OH: ASM International, 19913).
- ☐ The Metals Red Book, Vol. 2, Nonferrous Metals (Edmonton, Alberta, CAN: CASTI Publishing, 1993).

8. Reactive, Refractory and Noble (Precious) Metals

The ultimate resistance (sometimes) ...

8.1. Introduction

Reactive metals are so named because of their affinity for hydrogen and oxygen, particularly at elevated temperatures (e.g., during welding). This is a misnomer to the extent that these metals and their alloys are corrosion-resistant in many severe environments. A refractory metal has a very high melting point. The noble metals (as opposed to base metals) are those which are found free and unreacted in the natural environment. These terms are somewhat obsolete; the noble metals are now generally called precious metals, because of their monetary value.

8.2. Reactive and Refractory Metals

The reactive metals of practical interest are titanium, tantalum and, zirconium. Tantalum is also classified as a refractory metal, because of its high melting range and high-temperature strength. All three are refractory in the sense of being difficult to win from their corresponding ores.

8.2.1. Titanium

Titanium is the ninth most abundant element on earth, but so reactive with the ordinary constituents of air at elevated temperatures that only in the 1950s did it become commercially available as an engineering material. As we learned to extract, refine, alloy and fabricate it, titanium became increasingly important. With a melting range of approximately 1,670°C (3,040°F), a low density (sp gr 4.5; approximately 60% that of steel), high strength (414 MPa [60,000 psi] minimum tensile strength) and good corrosion resistance, it showed great promise. As discussed further below, it does have good corrosion resistance in strongly oxidizing environments, but not with reducing acids. Furthermore, the mechanical strength drops off rapidly with increasing temperature and its reactivity with hydrogen, oxygen, water vapor, and nitrogen effectively limits applications to less than approximately 535°C (995°F),

except perhaps in controlled inert atmospheres. All welding, for example, must be done with &MAW, GTAW, or similar inert-gas processes. Because of the absolute exclusion of atmospheric contaminants required, field fabrication is somewhat difficult.

The strength of titanium can be increased by alloying (some alloys reaching 1,300 MPa or 190,000 psi), although at some cost in corrosion resistance. Titanium has good impact strength at cryogenic temperatures (although it must not be used in liquid oxygen because of the potential for explosion). It can be readily shaped and formed and is available in conventional forms.

The more important commercial grades of titanium and its alloys are listed in Table 17.1. Of these, Grade 2 (R50400) is the most commonly used, although Grade 1 (R50250) has optimum ductility and Grade 3 (R50550) higher strength.

The feature that moves titanium from its anodic position in the EMF series to a noble position in the Galvanic Series is the development of an inert, passive surface film in oxidizing environments. It is widely used in such strongly oxidizing media as wet chlorine and strong nitric acid. Titanium shows excellent resistance to seawater and other saline environments.

Titanium is generally not useful in non-oxidizing or reducing acids except in very dilute solutions (e.g., a few hundredths of a percent) or unless their redox potential is shifted by oxidizing contaminants (e.g., ferric ions, cupric ions, nitrites, etc.). Titanium is treacherous in hot organic acids (e.g., formic or acetic), in which it may suddenly lose its passivity and corrode at greatly accelerated rates. The addition of a small amount of platinum (e.g., grades 7, 11, and 16) greatly extends the tolerance for higher concentrations of reducing acids. In grade 12, small alloying additions of Ni and Mo improve resistance to crevice corrosion in brines and provides higher strength than unalloyed grades. Even moderately low corrosion rates can result in hydriding, with attendant loss of ductility, even before significant metal loss occurs. Titanium absolutely will not tolerate even trace amounts of fluorides, which cause severe hydriding and embrittlement as well as aggravated corrosion.

Table 9.1 : Titanium Used in CPI – ASTM Grade UNS Composition Characteristics

1 (C.P.)(A)	R50250	Unalloyed Ti	Ductility, lower strength
2 (C.P.)(A)	R50400	Unalloyed Ti	Good balance of moderate strength and ductility, common workhorse alloy
3 (C.P.)(A)	R50550	Unalloyed Ti	Moderate strength
7 & 11	R52400 & R52250	Ti-0.15%Pd	Improved resistance to reducing acids and superior crevice corrosion resistance
16	-	Ti-0.05%Pd	Resistance similar to Grade 7, but at lower cost
12	R53400	Ti-0.3%Mo-0.8%Ni	Reasonable strength and improved crevice corrosion resistance

9	R56320	Ti-3%Al -2.5%V	Medium strength and superior pressure code design allowables
18	-	Ti-3%Al-2.5%V -0.05%Pd	Same as Grade 9, but with improved resistance to reducing acids and crevice corrosion
5	R56400	Ti-6%Al-4%V	High strength and toughness

R. W. Schutz, Materials Performance 31, 1(3 (1992), p. 58.

(A) Chemically pure

SCC has been observed in low molecular weight alcohols (e.g., methanol, ethanol), which tendency is inhibited by traces of water but aggravated by traces of halides or halogen acids. SCC in chlorinated solvents can be inhibited with small amounts of butylene and triethylamine. Titanium can also suffer cracking in strong nitric acid and in d7V sodium chloride above approximately 300°C (570°F). HAC can occur in organic acids, due to galvanic effects of surface iron contamination unless the product is adequately pickled or anodized. There is also a problem in strong oxidants under some conditions. Although titanium is excellent in wet chlorine, it can burn in dry chlorine (Chapter 26) unless a minimum water content of 2,000 ppm is maintained. Crevice corrosion may be a problem even in wet chlorine, because of depletion of oxidizing species within the crevice. It can also react catastrophically with red fuming nitric acid (RFNA) as discussed in Chapter 22. It can be detonated in liquid oxygen, in which its good low-temperature properties and low NDTT would otherwise make it attractive.

In short, titanium is a marvelously useful material of construction with a number of severe limitations. It is also relatively expensive, except in the form of thin-walled heat exchanger tubing which is produced in large quantities. Currently, it is competitive with nickel-based alloys.

8.2.2. Zirconium

Zirconium is between titanium and steel in density (sp gr. 6.5) and has a strength of approximately 345 MPa (50 ksi) in the annealed condition. The strength can be increased to approximately 550 MPa (80 ksi) by cold-work. The melting point is approximately 1,850°C (3,360°F).

Unless specifically removed, approximately 2% hafnium is present in zirconium (e.g., unalloyed zirconium R60701 and R60702). Although this does not impact corrosion resistance, it is objectionable in nuclear applications, for which an unalloyed reactor grade (R60001) is available. Other alloys, also reactor grade, are available (e.g., R60802, R60804, R60901). Zirconium is deliberately alloyed with aluminum, copper, molybdenum, niobium, tantalum, titanium, and tin to increase strength and corrosion resistance.

Zirconium and its alloys are easily fabricated, except for a hot- gas pick-up analogous to that to which titanium is susceptible. Thoroughly shielded inert gas welding is required. Even nitrogen pick-up of as little as 500 ppm, while not affecting mechanical properties, will diminish corrosion resistance in supercritical waters in nuclear reactors. The materials are also notch-sensitive, and threaded parts such as tray support rods in distillation columns are susceptible to breakage if the column should be "bumped" in service. Zirconium is quite acid-resistant, withstanding not only oxidizing acids like nitric acid but also up to 60% phosphoric and up to 70% sulfuric acid, depending upon contaminants. It will also resist hydrochloric acid in the liquid phase, although not the hot vapors. In immersion service, arc-melted zirconium will resist HCl of all concentrations up to the atmospheric boiling point. However, if the material is not of high enough purity, corrosion of the weld HAZ may be a problem. This situation is exacerbated by the presence of oxidizing contaminants (e.g., ferric or cupric ions, nitrates, hypochlorites, chlorine, etc.). Zirconium is attacked by hydrofluoric and hydrobromic acids, but highly resistant to hot organic acids (e.g., acetic acid). In reducing acids contaminated with oxidizing ions (particularly hydrochloric and sulfuric acid solutions), pyrophoric corrosion products can be formed, which are a potential ignition source if flammable vapors are about (e.g., hydrogen emitted from pickling baths using zirconium heating coils).

Zirconium is caustic-resistant, but its use is rarely justified in such service. Hot molten metals (e.g., mercury, lead, bismuth) attack zirconium and its alloys.

Zirconium is more expensive than titanium, even in heat-exchanger tubing, but is competitive with titanium and the nickel-based alloys in many instances. It finds application in intermediate sulfuric acid strength services and in nuclear energy systems.

8.2.3. Tantalum

Tantalum is a very heavy, refractory metal, with a density more than twice that of steel (sp. gr. 16.6). Its melting point is almost 3,000°C (5,430°F). The tensile strength is approximately 345 MPa (50,000 psi), which can be approximately doubled by cold-work. Like titanium and zirconium, it is easy to fabricate, contingent upon completely inert conditions during welding, but is even more susceptible to hydrogen pick-up. Even in a simple galvanic couple at room temperature (e.g., with carbon steel in an aqueous environment), it will be severely embrittled by absorption of over 700 times its own volume of nascent hydrogen.

The corrosion resistance of tantalum is very similar to that of glass, resisting most acids but being attacked by hydrofluoric acid and by caustic. Unlike glass, however, it is attacked by fuming sulfuric acid, chlorosulfonic acid, and by sulfur dioxide.

Because of its very high cost, tantalum is usually used only in very thin sections, as a lining or thin cladding, or as a uniquely pore-free electroplated coating on a copper or steel substrate such as for orifice plates). Tantalum-plated copper can be immersed in nitric acid, or tantalum-plated steel in hot-concentrated sulfuric acid, with no attack of the substrate (because of the absence of holidays in the plating).

Orifice plates, bayonet heaters, heat exchangers, valves and tantalum-plated steel tubes are of interest in the process industries. Tantalum patches are used to repair holidays in glass-lined steel vessels, but must be electrically isolated from other metallic components in the vessel (to prevent embrittlement by hydrogen absorption as the cathode in a galvanic couple).

8.3. Noble (Precious) Metals

The noble (or precious) metals are very expensive. Nevertheless, they do find some application in process equipment, under special conditions. If fully resistant, their salvage value may easily offset the initial cost. If consumed in use, they may nevertheless pay for themselves on a cost-to-life basis, if they are truly needed for the service.

8.3.1. Silver

Silver was used for certain specific services before the development of modern nickel-based alloys and plastics. In everyday use (e.g., jewelry, silverware), the most common observation concerning silver is that it tends to tarnish. This brownish-black film is caused by traces of hydrogen sulfide in the atmosphere, but the film is fairly protective.

Silver is rapidly attacked by cyanides, and by oxidizing acids(e.g., nitric acid, strong sulfuric acid). It can form explosive compounds, called azides, with ammonia and its derivatives (whence the hazard from old ammoniacal silver nitrate solutions in the laboratory), but has been used successfully in some urea plants .

Silver resists organic acids, and, prior to the development of the nickel-chromium-molybdenum alloys (e.g., N10276), was used rather widely in such applications. Silver heating coils were used, for example, in type 316~ (S31603) acetic acid storage tanks, where stainless coils give excessive iron contamination. Silver has also been used in handling and storage of phenols, acidic food- stuffs, and pharmaceuticals. It has been used for dilute hydrochloric acid, although ingress of air impairs its service life. Good resistance to hydrofluoric acid has led to its use in some applications related to the manufacture of fluorinated solvents (e.g., refrigerators and propellants).

Silver is usually resistant to high temperature caustics and alkalis, and has been used to handle molten alkaline salts.

8.3.2. Gold

Gold has been used for gaskets in certain severe services and, as the alloy of gold and platinum, for "spinnerettes" in the rayon industry. Gold is readily attacked by cyanides and by halogens. This is why, although it readily withstands nitric and hydrochloric acids separately, it is attacked by aqua regia (a 3:1 mixture of hydrochloric and nitric acids, which releases nascent chlorine). It does, however, resist sulfuric acid.

Gold will resist alkalis well, although the cost is seldom justified, but is attacked by alkaline sulfides in a manner analogous to silver.

8.3.3. Platinum

Although platinum is even more expensive than gold, it is used for electrical contacts in oxidizing atmospheres. It is very resistant to acids and alkalis except for aqua regia, halogens in general (i.e., chlorine, bromine, iodine) and halogen acids above 100°C (212°F).

All of the noble metals can be used as electroplated coatings but this is quite dangerous for corrosive services because they are strongly cathodic to any substrate of baser metals, leading to localized corrosion at holidays in the plating.

8.4. Suggested Resource Information

- ☐ ASM Hand book, Vol . 2, Properties and Selection: Nonferrous Alloys and Special-Purpose Materials (Materials Park, OH: ASM International, 1991). ASM Handbook, Vol. 13, Corrosion (Materials Park, OH: AS International, 1987).
- ☐ D. R. McIntyre, C. P. Dillon, Guidelines for Preventing Stress Corrosion Cracking in the Chemical Process Industries. MTI Publication No. 15 (Houston, TX: NACE International, 1985).
- ☐ D. R. McIntyre, C. P. Dillon, Pyrophoric Behavior and Combustion of Reactive Metal, MTI Publication No. 32 (Houston, TX: NACE International, 1988).
- ☐ The Metals Red Book, Vol. 2, Nonferrous Metals (Edmonton, Alberta, CA~: CASTI Publishing, 1993).
- ☐ B. J. Moniz, W. I. Pollock, eds., Process Industries Corrosion-The Theory and Practice (Houston, TX: NACE International, 1988), pp. 503 and 545.
- ☐ R. W. Schutz, "Understanding and Preventing Crevice Corrosion of Titanium Alloys," Part I, Materials Performance 31, 10 (October, 19~2), p. 57; Part II, Materials Performance 31, 11 (November, 1 992), p. 54.

The possible alternative(s) ...

There are a variety of *organic* and *inorganic* materials, in addition to metals and alloys, with which the working engineer should have at least a nodding acquaintance. It is important to recognize that, although the nonmetallics do not corrode in the sense of metals and alloys, they are not thereby cure-alls, because they have their own problems as to chemical resistance, as well as certain strength and temperature limitations. Paints and coatings are materials, but not of construction, and are considered separately in Paragraph 10.4 at the end of this Chapter.

It is a general misconception that the *history* of (synthetic) polymers is of a much more recent date than the development of metallic alloys. Since the development of *celluloid* in 1869, engineers have been interested in potential industrial applications of plastic materials. In 1906 the Belgian Leo Baekeland developed in Gent a polymer that became coined as “*bakeliet*”, the first synthetic resin in history.

A *plastic* is a material that contains as an essential ingredient an organic compound of high molecular weight, is a solid in the finished state, and, at some stage in its manufacture or processing, can be shaped or formed.

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9.2.1. Thermoplastics

The thermoplastics are the most widely used organic materials of construction. When not modified or reinforced, their mechanical properties are the lowest of the several materials of interest, and rapid diminution of strength is encountered with only moderate temperature increases. However, the physical and mechanical properties are entirely adequate for many applications.

9.2.1.a. Properties

(1) **Strength** — The tensile and flexural strengths of the thermoplastic materials are rather poor, dropping off rapidly with increasing temperature. However, the use of organic or inorganic reinforcing agents can upgrade the strength, as can "alloying" with other resinous materials.

(2) **Hardness** — The original hardness of plastics is relatively unimportant, because resistance to wear and abrasion is more related to resilience than hardness. However, changes in hardness are an important criterion in evaluating chemical resistance. Changes in hardness, plus or minus, after exposure indicate a significant chemical attack (as do changes in volume, indicative of absorption or dissolution).

(3) **Creep** — Distension under constant strain at ambient temperature is roughly comparable to that of carbon steel at approximately 500°C (930°F). Consideration must be given to support of thermoplastic structures, particularly if exposed to heat, even direct sunlight.

(4) **Modulus** — This property, as well as thermal expansion (see below), deserves the greatest consideration in design of thermoplastic structures. The modulus is low and, in flexure, there really is no straight-line relationship between stress and strain.

(5) **Thermal Expansion** — Although the data are readily available in the literature, all too often the designer fails to provide adequate allowance for thermal expansion (which may be fifteen times that of an austenitic stainless steel).

Reinforced materials like *fiberglass-reinforced plastics* (FRP) have much lower coefficients than do the thermoplastics. There must be adequate room for the structure to expand and contract, while still providing adequate mechanical support.

(6) **Impact** — Thermoplastic materials, as a group, are tough materials. However, most of the materials are notch-sensitive, and impact values of notched materials can be low (a factor to be considered before threading a product, for example).

(7) **Conductivity** — Unmodified resins are usually good insulators of both thermal and electrical conductivity. However, conductivity can be induced or enhanced by the addition of inorganic compounds, with significant variation in the final properties.

9.2.1.b. Environmental Resistance

Plastic materials do not corrode by electrochemical mechanisms, as do metals and alloys. The degradation of the material or its properties is related to the structural interaction between the material and the environment and/or to the permeability of the material.

Permeability is controlled by the solubility of the material in the environment and by the rate of diffusion of the environment into the plastic (primarily under temperature control) .

When diffusion into the plastic matrix occurs and the environment is chemically incompatible, *all mechanical properties* of the plastic are downgraded. A simple hardness test will often give an indication of the rate and extent of degradation.

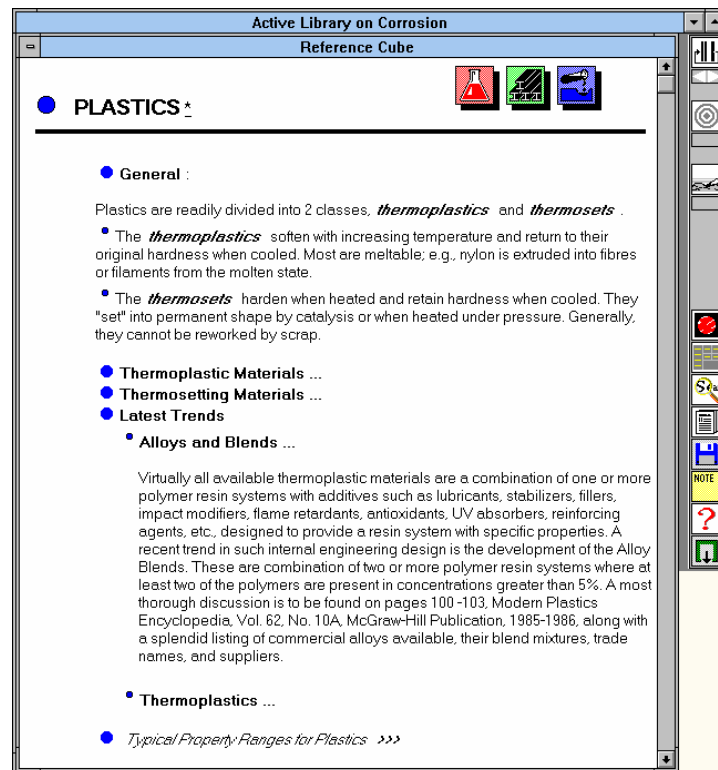
Specific comments about chemical resistance of types of plastics are given in the "Specific Materials" section below.

9.2.1.c. Fabrication

Most of the thermoplastic materials can be hot-fusion welded, or solvent welded, at properly designed joints. Threaded couplings can be used for many materials, with careful attention to notch sensitivity. Solvent-welding is usually preferred for joining all but the polyolefins (polymers of ethylene, propylene, and butylene) for which fusion-welding is normally employed.

9.2.1.d. Specifications

There are a large number of ASTM specifications covering materials, qualification tests, test procedures, and properties. Commodity standards and military (MIL) specifications are also relevant.



9.2.1.e. Specific Materials

(1) **Polyethylene** — Polyethylene (PE), the polymer of ethylene $[(C_2H_4)_n]$ is the most widely used plastic today, and is available in the form of gaskets, solid drums or containers, drum liners, piping, and small molded parts for process equipment. PE can be joined by thermal welding. PE is widely used up to approximately 60°C (140°F), especially for water service applications.

It is also available as *fiber-reinforced product* for improved strength. *Ultrahigh density* polyethylene (UDPE) has improved mechanical properties, greater thermal stability and improved solvent resistance compared with the older type of formulations.

It is attacked by strong oxidants and is susceptible to environmental stress cracking (ESC) by some inorganic (e.g., 48% hydrofluoric acid) and organic chemicals (notably detergents, wetting agents, alcohols, ketones, aldehydes, and organic acids). Hydrocarbons (both aliphatic and aromatic), chlorinated solvents, and strong oxidants are to be avoided. A black-pigmented version is required to resist UV degradation.

(2) **Polypropylene** — Polypropylene (PP) is the next higher member of the polyolefin family. Stronger and somewhat more resistant chemically than PE, it is used both as a plastic liner for steel pipe and as solid pipe or sheet material. Its strength and weldability make it a prime candidate for piping for corrosive waters, dilute acids and many waste waters (provided there are no incompatible organic species contained therein). However, it is susceptible to SCC in hot brine solutions and in 98% sulfuric acid, unless copolymerized with other materials.

(3) **PVC** — Polyvinyl chloride (PVC) piping is very popular for water service, particularly in the presence of chlorine or other oxidants. Piping may be joined by hot-air welding or solvent-welding. Sheet-lining of vessels is a common application.

PVC *Type I* is an unplasticized form with good chemical resistance. *Type II* has been modified by the addition of styrene-butadiene rubber, improving notch toughness and impact strength at some sacrifice in chemical resistance.

A variant, CPVC (*chlorinated PVC*), is used for hot-water services.

PVC and CPVC have excellent resistance to both acids and alkalis, but their solvent resistance is very limited. Straight-chain hydrocarbons (i.e., aliphatics like kerosene or oil) do not affect them.

(4) **PVDC** — Polyvinylidene chloride. *Saran*TM (PVDC) is a variant of PVC, having both chlorine atoms on the same end of the monomer (instead of opposite ends, as with vinyl chloride).

PVDC has improved strength, hardness, and chemical resistance, especially to organic solvents, mineral acids, and oxidants. Formerly, a major market was in Saran-lined steel pipe. Currently, it is more often found in valves, pumps, and piping.

(5) **ABS** — Acrylonitrile-butadiene-styrene (ABS) is one of the older standbys, particularly for piping systems. This material can have considerable variation in properties, depending on the ratio of acrylonitrile to the other components. Higher strength, better toughness, greater dimensional stability and other properties can be obtained, although sometimes at the expense of other characteristics.

The ABS plastic will withstand attack by only a few organic compounds, is attacked by oxidizing agents and strong acids, and will stress-crack in the presence of certain organic species. Problems with ultraviolet (UV) degradation have been largely overcome through the use of protective additives.

CAB is normally used (only) where its good weathering characteristics and *transparency* are desired.

(7) **Fluorocarbons** — These are the most versatile and important group of plastics for the process industries. Maximum chemical resistance and heat stability are provided by this class of materials as pipe liners, tank linings, impellers, mixers, spargers, tower packing, lined valves, etc.

Modifications of the original PTFE developed rapidly. The modified variants have somewhat lower heat stability limits and slightly reduced chemical resistance, but are much more amenable to fabrication by welding, hot-forming, cold-working, and adhesion. Substantially impermeable linings or coatings, which cannot be made with PTFE, can be produced from some of these modifications. "Spaghetti-type" heat exchangers are also available.

Each has specific properties and characteristics, and special source books and manufacturers' literature should be consulted. A proper understanding of the available products is necessary to assure selection of the optimum material for a specific application.

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(9) Acetals — The acetal resins are competitive with nylon in mechanical properties, and greatly superior in chemical resistance. Proprietary resins like *Delrin* and *Celcon* have three times the dimensional stability of nylon.

(10) Polycarbonates — The polycarbonate resins (e.g., LexanTM) have mechanical properties equivalent to the acetals. Their usefulness in industrial applications, however, is limited by their susceptibility to environmental cracking in even mild atmospheric exposure.

(11) Others — Specific useful properties can be found in such other, less frequently used plastics as *polysulfones*, *acrylics*, *styrenes*, and *polyphenylene oxide* (PPO) or *sulfide*. For example, a new thermoplastic, polybenzimidazole (PBI), has outstanding heat resistance, withstanding temperatures as high as 430°C [806°F] and in short duration, 760°C [1,400°F]. It is finding increasing application in a number of specific services (examples include: in seats and seals for valves in the CPI and for high-temperature seals, packings and insulators in oil-field applications).

9.2.2. Thermosetting Resins

There are a number of thermosetting resin materials available, including *isophthalates* and *terephthalates*, *vinyl esters*, *bisphenol*, *epoxy*, *phenolic*, and *furan*.

This group of plastics is hard and often brittle at ambient temperatures. At higher temperatures, some loss in properties may occur, but in general these are retained until the materials degrade (usually by carbonization or oxidation). For engineering applications, all the thermosetting resins are reinforced by some means.

9.2.2.a. Reinforcement

Although silica, asbestos, paper, linen, and other plastics and materials are added as reinforcing materials, *glass fiber or cloth* is by far the most popular. Glass contents varying from 25 to 80% are used in the form of woven cloth and random veil, but the greatest strength is achieved by glass filaments overlaid at the proper angle. Other benefits are improved modulus and a much lower coefficient of thermal expansion than the unreinforced resin.

9.2.2.b. Fillers

Various other siliceous materials, as well as carbon and metal powders or fibers, can be added to produce even greater modulus values, greater strength, differing thermal and/or electrical properties, and desired colors in the composite products.

9.2.2.c. Physical and Mechanical Properties

With the almost infinite number of materials combinations possible, it is obvious that specific properties of almost any type can be designed into the product (even the strength of a carbon-steel). Heat-shields for re-entry from space, and graphite-fiber-reinforced golf clubs, tennis racquets, and fishing rods are examples of such specific applications.

9.2.2.e. Specific Materials

(2) Phenolics — Phenolics are heat-curing resins which offer a combination of excellent properties. Many forms of apparatus are available (e.g., pipe, fitting, pumps, valves, column sections, and heat exchanger components). Phenolics are resistant to many solvents and acids, being adversely affected primarily by alkalis, oxidants and amines. Their temperature limit is approximately 110°C (230°F). Many types of process equipment use the phenolic resin for the inside, the exterior being "armored" with epoxy or polyester laminates.

(3) Polyester — The most common designation for this type of construction is *FRP* (fiberglass-reinforced plastic) or *GRP* (glass-reinforced plastic). RTP (reinforced thermoset plastic) is now the designation used in ASTM standards and the ASME B&PV Code (Boiler & Pressure Vessel Code).

The different resins have different chemical resistance to specific environments, but in general are better than epoxies or phenolics in oxidizing situations. A large amount of tankage, piping, duct-work, etc., is so constructed. Common applications include underground tanks for gasoline, storage tanks for mineral acids (e.g., hydrochloric, phosphoric), and piping for aggressive waters (e.g., seawater and other untreated water).

Utilization of FRP equipment in general has been limited to some extent by the lack of a proper design and construction code. In 1989, ASME issued RTP-1, "Reinforced Thermoset Plastic Corrosion Resistant Equipment", to correct this deficiency.

(4) *Furanes* — The furanes, which are derived from furfuryl alcohol, have outstanding resistance, being chemically attacked only by certain nitrogenous or chlorinated organic compounds. Their application was limited previously by problems of aging and cracking, but modern formulations and supplemental reinforcement have extended their usefulness in industry.

9.3. Rubber and Elastomers

The term *rubber* originally applied to the natural material. *Elastomer* is a term derived from the words "elastic" and "polymer," and is broadly used to embrace both natural and synthetic rubbers as well as plastics formulated to have rubber-like or elastomeric properties.

9.3.1. Specific Materials

9.3.1.a. Natural Rubber

Natural rubbers are made by processing the sap of the rubber tree, and compounding it with vulcanizing agents, antioxidants, fillers, pigments, etc. Red, black, and white rubbers are made with different pigments (e.g., iron oxide, carbon black, zinc oxide).

Natural rubbers have poor resistance to atmospheric oxygen, ozone, sunlight (ultraviolet [UV] rays), petroleum derivatives, and many organic chemicals. Resistance to non-oxidizing acids, such as hydrochloric, and alkalies is good.

Rubber has been used for pumps, valves, piping, hoses, and machined products (when hardened by vulcanization). However, many of the historical applications have been taken over by the newer plastic materials.

9.3.1.b. Synthetic Rubbers

(1) Buna S — This is a copolymer of *butadiene* and *styrene* used in tires, hose, and miscellaneous goods. It offers no particular advantage over natural or other synthetic rubbers in chemical service.

(2) Buna N — The copolymer of *butadiene* and *acrylonitrile*, also called HycarTM, is produced in ratios varying from 25:75 to 75:25. The manufacturer's designation should identify the percentage of acrylonitrile.

Compared with natural rubber, it has good oil resistance, and is used for hose, gaskets and packing (e.g., O-rings). Chemical resistance is fair to poor generally, especially towards solvents. It has fair resistance to ozone and UV, but is severely embrittled at low temperatures.

(3) Butyl — Butyl rubber is a polymer of *isobutylene*, with small additions of isoprene or butadiene. It is remarkably impermeable to gases and is used for tire inner tubes and hoses.

It resists aging and ozone, and is more resistant to organic chemicals (except aromatic compounds) than are most synthetic rubbers.

(4) Neoprene — Neoprene is a polymer of *chloroprene* and was developed for resistance to oil and solvents. It is resistant to aging, ozone, and moderately elevated temperatures, and has good abrasion and wear characteristics.

It is widely used for hoses, gaskets, motor belts, tires, tank linings, etc.

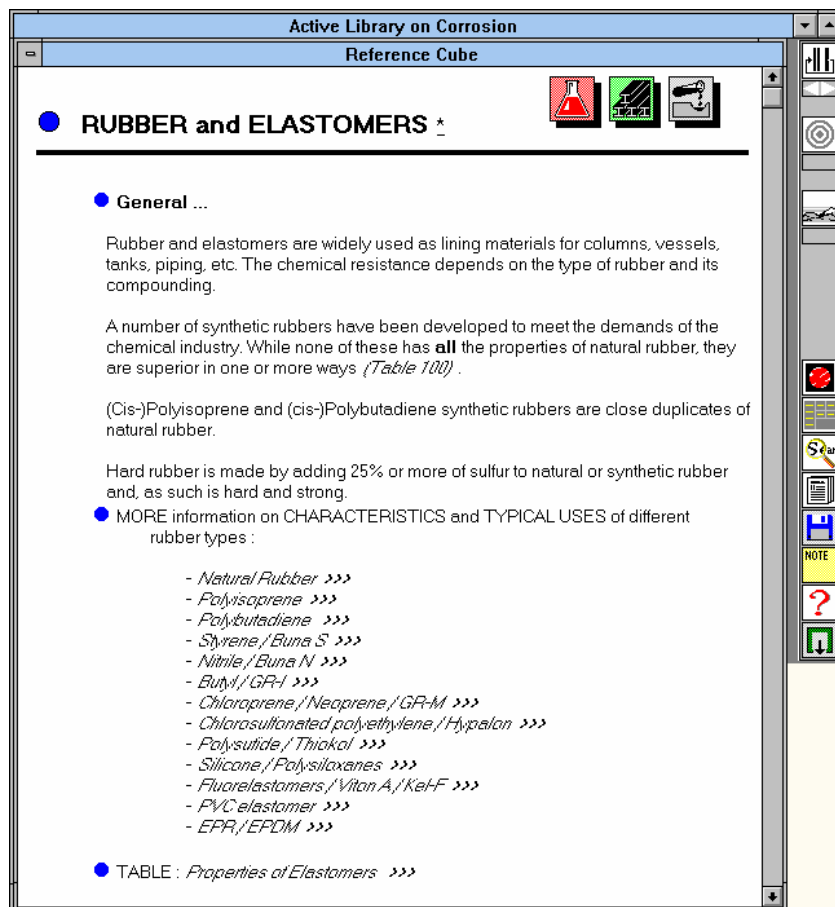
(5) EPDM — *Ethylene-propylene diene methylene* (EPDM or EPR) is a copolymer of ethylene and propylene.

It has become the standard lining material for steam hoses. EPDM is widely used in chemical services as well, having a broad spectrum of resistance.

(a) Silicone rubbers are based on silicon (rather than carbon) linkages. Although chemical resistance is relatively poor, silicone rubbers withstand ageing and ozone, as well as oil, and can tolerate temperature extremes from -75°C (-103°F) to 200°C (390°F).

(c) Fluorinated elastomers, such as *Kel-F*TM and *Viton*TM will withstand oxidants, and have temperature capabilities up to 300°C (570°F) for short periods of time. However, contrary to what one might expect by analogy with the fluorinated plastics, they mostly have poor resistance in solvents or organic media. They do resist acids and alkalis.

Super-fluorinated Viton also has enhanced chemical resistance.



9.4. Other Nonmetallic Materials

Besides the plastics and elastomers, there are a number of other nonmetallic materials of interest to the process industries (or to industry in general). These materials are used both as *materials of construction* in their own right and as *linings, barriers, or coatings* of one kind or another.

9.4.1. Carbon and Graphite

Carbon products have a homogeneous structure, which is usually produced below 1,230°C (2,250°F). *Graphite* is a crystalline form of carbon produced by processing at temperatures in excess of 1,980°C (3,600°F).

The main use of carbon and graphite per se is as brick for lining process vessels and as ring packing for fractionation columns. In fiber form (e.g., GrafoilTM), graphite is used to replace asbestos in gaskets, because of high heat resistance, excellent chemical resistance and outstanding sealing characteristics.

There is an appreciable difference in corrosion resistance. Within certain limits, carbon will withstand more powerful oxidizing agents, such as hot concentrated sulfuric acid or halogens (which will attack graphite rapidly). Both forms will withstand mineral and organic acids, alkalis, salts, organic solvents, etc.

Where thermal conductivity is required (e.g., for heat exchanger tubes), impervious graphite or KarbateTM is manufactured by forming the desired shape from graphite, evacuating the pores, and impregnating with a resinous material (e.g., a phenolic resin). The impregnation seals the porosity but limits both the corrosion resistance and the maximum service temperature. New developments include *impregnation with PTFE or carbon*. The latter treatment permits operation to 400°C (750°F) maximum.

In addition to heat exchangers, whose thermal conductivity is close to that of copper-tubed items, impervious graphite pumps and valves are available and find broad application in process services. They are, of course, susceptible to brittle failure by thermal or mechanical shock.

Active Library on Corrosion			
Corrosion Engineer's Reference Book			
PROPERTIES OF GRAPHITE AND SILICON CARBIDE		To Table of Contents	
	Graphite	Impervious Graphite	Impervious Silicon Carbide
Specific gravity	1.4-1.8	1.75	3.10
Tensile strength, psi (MPa)	400-1400 (3-10)	2600 (18)	20,650 (143)
Compressive strength psi (MPa)	2000-6000 (14-42)	10,500 (72)	150,000 (1000)
Flexural strength, psi (MPa)	750-3000 (5-21)	4700 (32)	-
Modulus of elasticity (x 10 ⁶), psi (MPa)	0.5-1.8 (0.3-12 x 10 ⁴)	2.3 (1.6 x 10 ⁴)	56 (39 x 10 ⁴)
Thermal expansion, in/in/°F x 10 ⁶ (mm/mm/°C)	0.7-2.1 (1.3-3.8)	2.5 (4.5)	1.80 (3.4)
Thermal conductivity, Btu/hr/ft ² /°F/ft (Watts/m, K)	15-97 (85-350)	85 (480)	60 (340)
Max. working temp (inert atm) °F (°C)	5000 (2800)	350 (180)	4200 (2300)
Max. working temp (oxidizing atm) °F (°C)	660 (350)	350 (180)	3000 (1650)

Source: Carborundum Co.

9.4.2. Glass

"Glass equipment" is of two types: *solid glass* and *glass-coated steel*.

In glass-lined (or externally glass-coated) equipment, one may purchase a *crystallized* glass (e.g., PyroceramTM) with outstanding resistance to thermal shock, which is a potential problem with conventional glass. Crystallized glass can be heated to at least 800°C (1,470°F) and quenched in ice-water without cracking. All glasses, however, are substantially equivalent in corrosion resistance and susceptibility to mechanical damage.

Soft glass was formerly used in laboratory apparatus, but has been replaced with the tougher and stronger *Pyrex*TM glass. Pyrex glass is available also as pipe, distillation columns, and heat exchangers. Glass-lined equipment is available in the form of tanks, vessels, piping, valves, agitators, and pumps. The normal service temperature limitation is 175°C (345°F).

Glass will resist mineral and organic acids, except *hydrofluoric* and phosphoric acid containing fluoride contaminants, up to the atmospheric boiling point. Above those temperatures, measurable dissolution will occur. *Strong alkalis* (e.g., sodium or potassium hydroxides as opposed to ammonium hydroxide) will attack glass, although some glass formulations will withstand a pH of 12.

Note that some "glass-lined" vessels such as beer tanks are only intended to prevent iron contaminations; they are not capable of withstanding truly corrosive liquids.

9.4.3. Ceramics

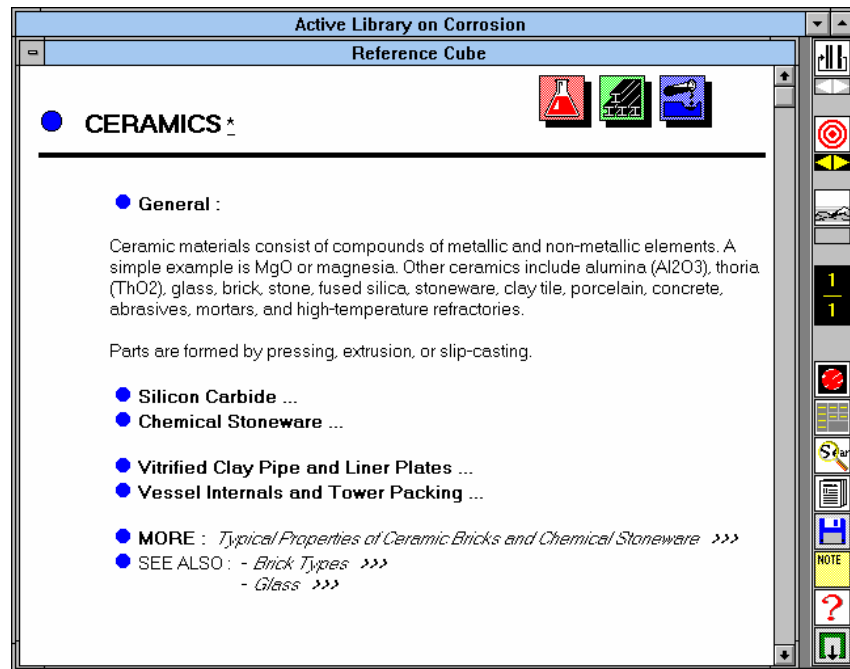
Ceramics include not only the *traditional silicate-based materials* but also *metallic oxides*, *borides*, *nitrides*, *carbides*, etc. These are formed into useful shapes, and given permanence and durability, by heating to high temperatures.

In the process industries, the major applications are as chemical stoneware, porcelain, and acid-brick. *Stoneware* and *porcelain* differ in appearance and porosity. They are attacked by hydrofluoric acid, fluoride-bearing phosphoric acid and alkalis, in a manner analogous to glass. However, a special proprietary grade, *Body 97*TM, will resist up to 20% caustic to approximately 100°C (212°F).

Ceramics are brittle materials, much stronger in compression than in tension, and must be protected against both thermal and mechanical shock. An important exception is a *high-alumina* (i.e., aluminum oxide) material, such as *Alite*TM, which can be used up to 1,000°C (1,830°F) and is more shock-resistant than other stoneware. In general, ceramics will tolerate more rapid cooling than heating, and start-up procedures can be very critical in this regard.

Acid-brick is used for lining vessels in many severely corrosive services. The brick is susceptible to penetration through its pores and at the joints. Its primary function is to reduce the temperature at which the environment encounters the substrate. With rare exceptions, it should not be used without a *membrane* (of rubber, plastic, or lead) to protect the metallic substrate, which is usually steel and low in resistance to the environment.

An important development is that of thermally conductive, highly corrosion-resistant materials in the form of heat-exchanger tubing. *Hexoloy*TM (alpha-silicon carbide) heat-exchanger has a thermal conductivity close to that of copper and resists many corrosives inimical even to tantalum.



9.4.4. Refractories

Most refractories employed in process industries are castables, which comprise an *aggregate* (e.g., brick, shale, alumina, etc.) in a *binder* such as calcium aluminate, silicate, etc.

The refractories are highly heat-resistant. They are classified as acidic, basic or neutral, the classification being indicative of their corrosion resistance. Acidic materials, like silica (i.e., silicon dioxide), are suitable when the environment is not alkaline (i.e., when it is neutral or acidic). Alkaline environments require alkaline refractories, such as alumina, zirconia, or magnesite.

One should always consider the possible presence of sodium salts in furnace applications because these can be oxidized to sodium oxide, with attendant attack on an acid refractory.

9.4.5. Concrete

Conventional concrete is a mixture of *portland cement* with an *inert aggregate*, such as sand or gravel. The cement itself is a mixture of calcium salts (e.g., silicates, aluminates, carbonates), which tends to resist most natural environments, such as air or water.

There are two major problems. One is the *corrosion of the steel reinforcing bars*, commonly known as *rebar*; the second is *corrosion of the concrete itself*.

Internal ***rusting of the rebar*** can occur within the concrete itself, due to ingress of moisture, salts, and oxygen through the pores of the material. Since rust occupies approximately seven

times the volume of the corroded steel, great internal pressures are developed, which tend to crack or spall the concrete. Rebar corrosion may be minimized by coatings (e.g., epoxy or galvanizing), sealing the concrete against ingress of corrosive species, or (with suitable design) by cathodic protection of the steel rebar within the structure.

There are three basic mechanisms for the **corrosion of concrete** formulated with portland cement:

(1) *Corrosion I* is the leaching of free lime (e.g., by soft waters or carbonic acid), or direct acid attack upon the calcium carbonate constituent.

(2) *Corrosion II* is a base-exchange reaction between the readily soluble components of the acid and an aggressive solution. The reaction products may either be leached out or remain in place in a non-binding form (e.g., magnesium ions will react to form insoluble salts, leaving a gelatinous mass in the voids).

(3) *Corrosion III* is the formation of new internal salts, whose crystallization and expansion destroy the concrete by internal stresses. Sulfate ions, even from neutral salts, react with tricalcium aluminate to form calcium sulfoaluminate hydrate (the so-called sulfate bacillus) with a large crystallized water content (i.e., 31 mols of water/mol of salt).

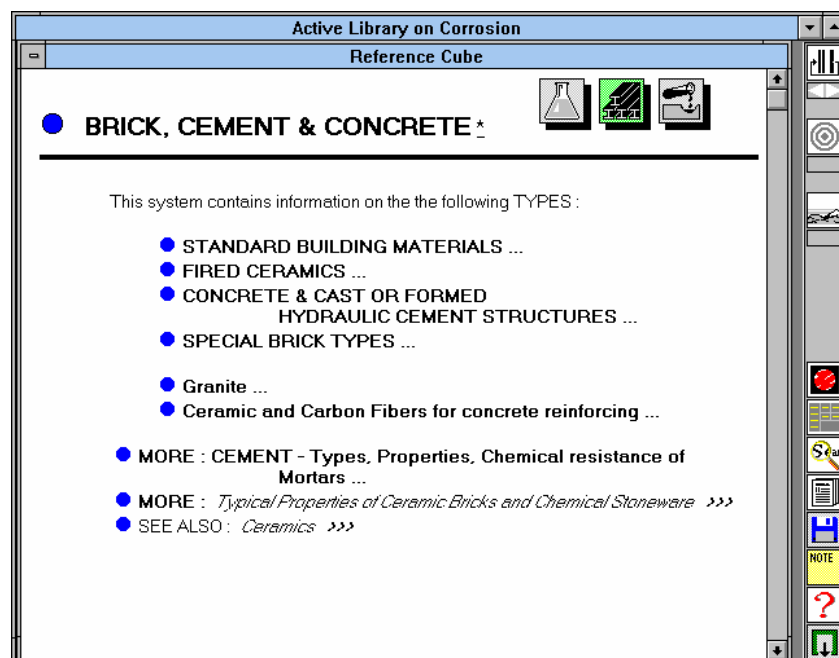
Concrete is also attacked by certain organic solvents that react with calcium (e.g., ethyl acetoacetate and other esters).

Sulfate attack is more of a problem with flowing waters than under stagnant conditions or seeping water. Ammonium, magnesium, sodium, and calcium sulfates are particularly destructive. The first level of sulfate resistance is achieved by limiting the permissible concentration of tricalcium aluminate, but this effects only a nominal improvement. The suggested sulfate concentration limits for ASTM C 150 portland cements under flowing conditions are 150 ppm, 500 ppm, and 1,500 ppm for Types I, II, and V, respectively.

The adverse affect of sulfates is ameliorated by increasing chloride concentration in the water. Although quantitative parameters have not been established, it is well-known that Type I cement is entirely adequate for seawater, despite the high sulfate content (approx. 4,000 ppm) of that environment.

For more severe conditions, the cement can be pretreated with sulfite liquors or gypsum solutions to form the hydrated salts in situ while the cement is still in the plastic state (e.g., supersulfated cement). However, trass or pozzolanic cements (which give amorphous silicic hydrates in the structure) are more reliable (e.g., ASTM C 595, Types IP and P). In extreme cases, special alumina-based cements are used.

A special warning is in order as regards use of concrete in wastewaters, where sulfates may be present, yet unanticipated. Also, hydrogen sulfide (from bacterial action or other sources) can accumulate in the vapor zone of concrete sewage pipe, oxidizing to sulfurous or sulfuric acid and causing direct acid attack.



9.4.6. Wood

Wooden tanks and piping are often an economical substitute for alloy construction, particularly in aqueous solutions containing acid salts.

The cellulose component in wood may be oxidized or hydrolyzed by acid conditions, while the lignin is subject to attack by alkalies.

Wooden construction is generally not suitable for alkaline solutions, although a pH of up to 11 may be tolerated. Strong acids like sulfuric, hydrochloric, and nitric will oxidize, hydrolyze, or dehydrate wood. Anhydrous hydrogen fluoride will char wood instantaneously. Oxidizing agents, such as nitric or chromic acid, permanganates, and hypochlorites, should not be used with wood. However, dilute acids and acid-salt solutions are handled well by wooden apparatus.

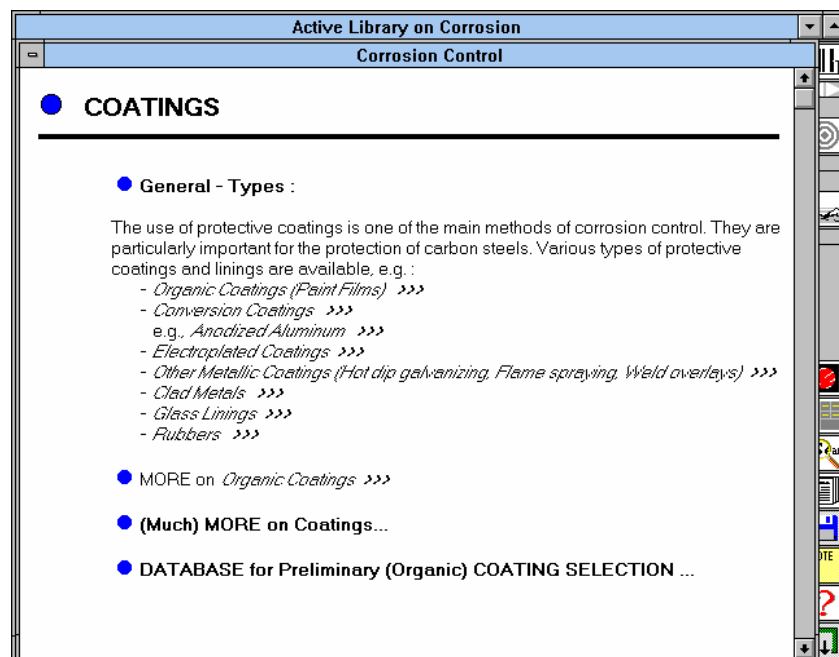
Several types of *cedar*, *cypress*, *fir*, *redwoods*, and *pine* have been used. Douglas fir is preferred for the more severe services, for example 95°C (205°F) in the pH range of 2 to 11, while redwood is used to 80°C (175°F) from pH 4 to 9. Heartwood is preferred for optimum resistance, while sapwood may be used where the process liquid itself actually preserves the wood (e.g., in brining or pickling foodstuffs).

Wood may be impregnated with *preservatives* to protect it from decay. It may also be married to plastics to make composite materials for special purposes. For example, small blocks of end-grained balsa wood can be held together with a fabric scrim or netting to serve as core for FRP to increase stiffness in large FRP tanks (e.g., horizontal tanks).

For corrosive and/or abrasive services particularly, professional assistance should be sought in selecting the particular wood and the applicable specifications.

9.5. Paints, Coatings and Linings

See EFC video ! ...



9.6. Suggested Resource Information

- ☐ NN, *ASM Engineered Materials Handbook, Vol . 4, Ceramics and Glasses* (Materials Park, OH: ASM International, 1991).
- ☐ NN, *Managing Corrosion with Plastics* (Houston, Tx: NACE International).
- ☐ J. H. Mallinson, *Corrosion-Resistant Plastic Composites in Chemical Plant Design* (New York, NY: Marcel Dekker, 1989).
- ☐ B. J. Moniz, W. I., Pollock, eds., *Process Industries Corrosion —The Theory and Practice* (Houston, TX NACE-International, 1986), pp. 573, 577, 589, 639, 649, 661, 681, 695, 703, and 711.

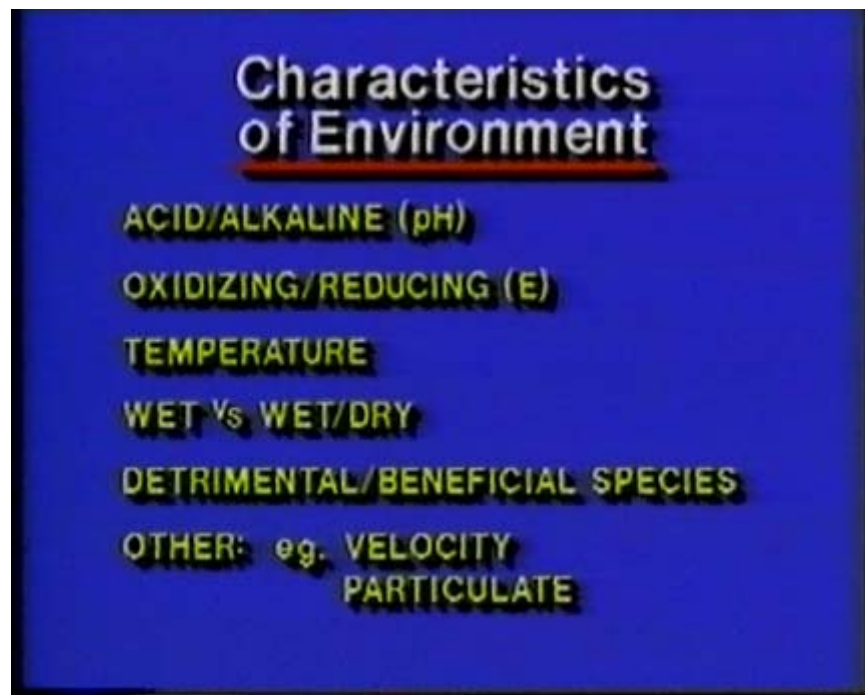
– General Corrosivity Factors & Specifics of some important Chemicals –

1. Overview

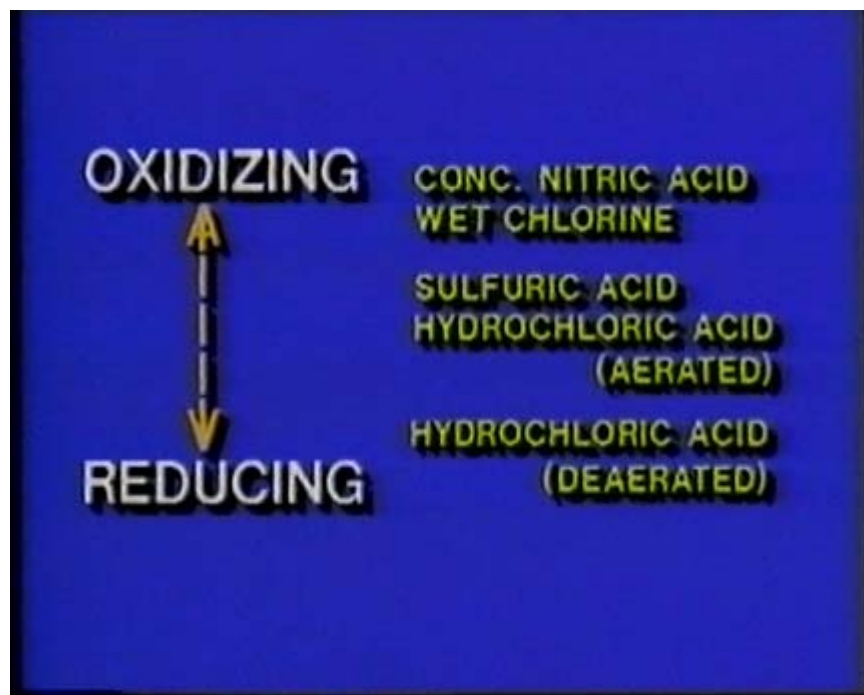
Environment Corrosivity Characteristics ...

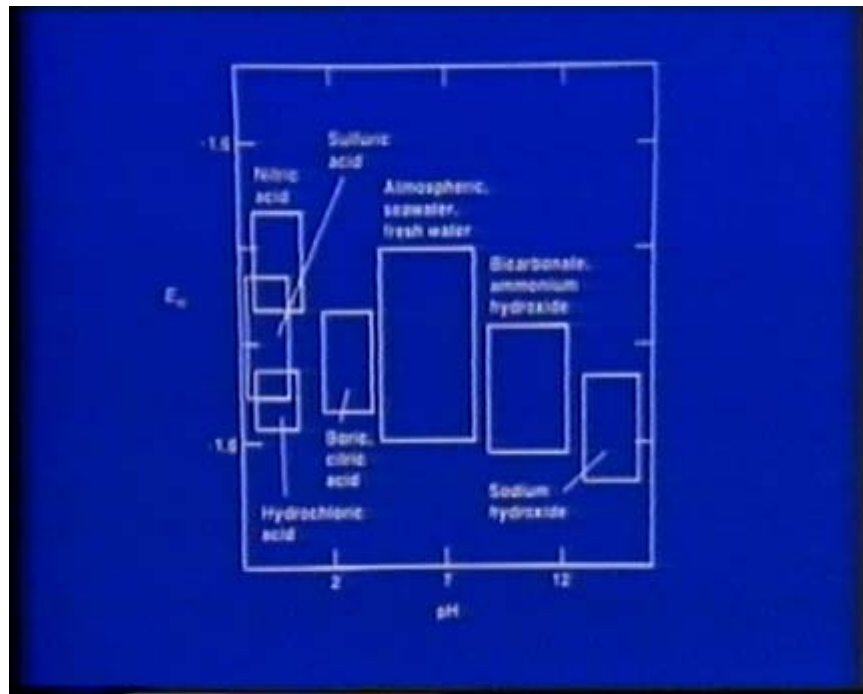
1.1. General

Cf. Video ...

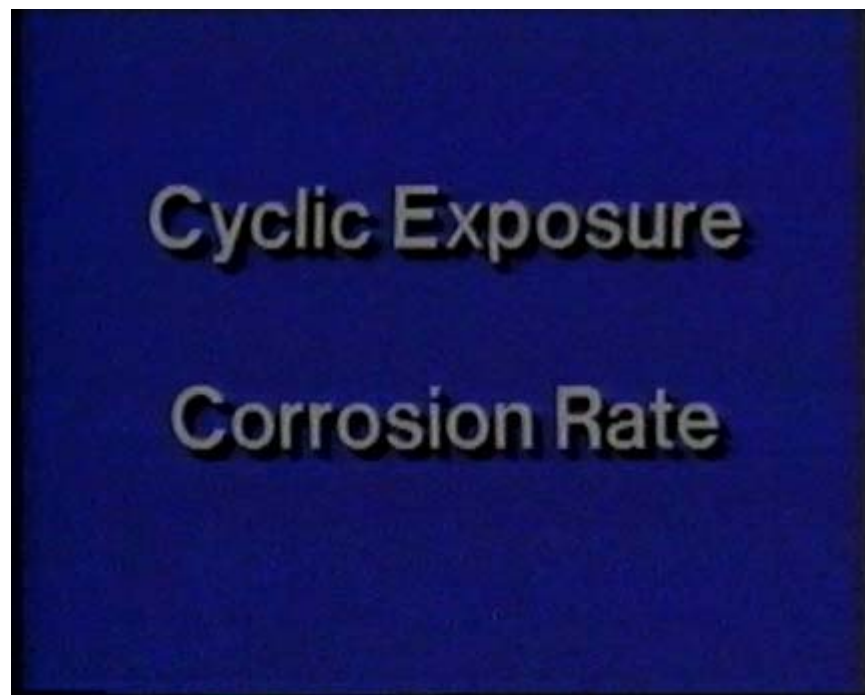
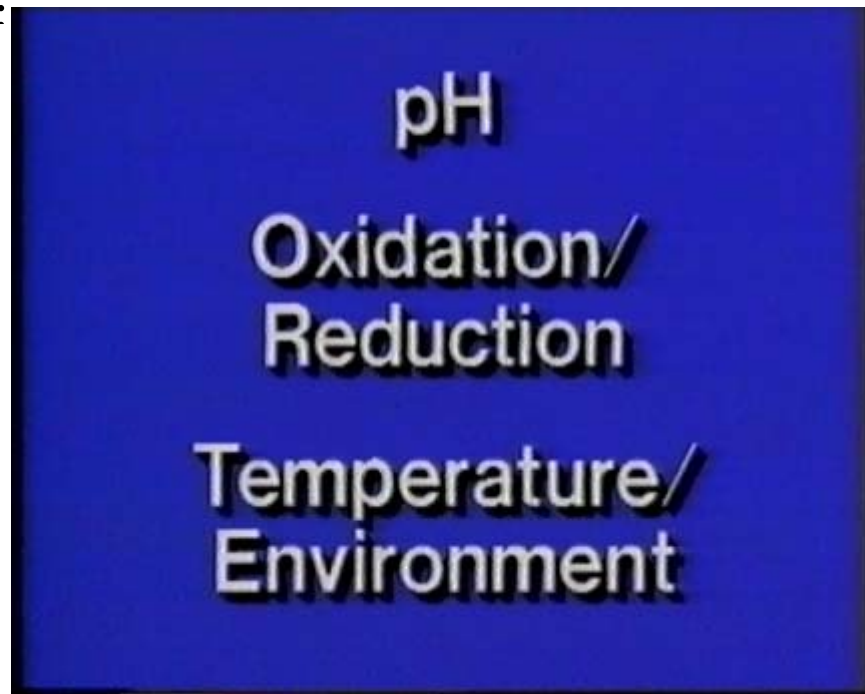


<u>ACID/ALKALINE</u>	
Solution	pH
HYDROCHLORIC ACID (1N)	0.1
SULFURIC ACID (1N)	0.3
BORIC ACID (0.1N)	5.2
SODIUM CARBONATE (0.1N)	11.6
AMMONIUM HYDROXIDE (1N)	11.6
SODIUM HYDROXIDE (1N)	14





<u>CHEMICAL SPECIES</u>	
<u>Detrimental</u>	<u>Beneficial</u>
★ Chloride	★ Inhibitors
★ Complexing	★ Passivating



2. Corrosion by Water and Steam

Corrosive water is omnipresent, in various forms ...

2.1. Introduction

In the following chapters concerning corrosion by specific environments, corrosion by water (and its contaminants) will be discussed first because the presence of water is a necessary condition for atmospheric corrosion and corrosion by soils and salts. Also, water is the most commonly encountered corrodent in both municipal and industrial applications and can be a major problem in any processes especially in its role as coolant.

Water is something that everybody uses without thinking very much about it; it is something that comes out of a tap or line to be used as needed. The professional water treatment specialist understands the true complexity of the subject, but *anyone* involved in corrosion/materials work should learn at least the fundamentals, if only to know when to get professional help.

Pure water is not really corrosive, except to anodic metals above at least 200°C (392°F). The corrosive action so often encountered at lower temperatures is due to gases and minerals dissolved in the water, plus the effects of bacteria and biomasses In some cases.

2.2. Water Chemistry

In order to evaluate properly the characteristics of a water proposed for some specific use, a complete analysis must be available. The Table below shows the basic minimum information which must be obtained and the units in which it is expressed to facilitate evaluation.

For a water sample to be truly representative for analysis, the sample bottle must be filled to the brim and tightly capped (to prevent loss of volatile species, such as carbon dioxide, or ingress of gaseous contaminants, such as air). The analytical data obtained can be used to diagnose the scaling characteristics and probable corrosivity of water.

Characteristics Measured in Basic Water Analysis

Variable Measured	Units
TDS (Total Dissolved Solids) ^(A)	ppm (parts per million)
Ca (Calcium Hardness) ^(A)	ppm as CaCO ₃
Mg (Magnesium Hardness)	ppm as CaCO ₃
TH (Total Hardness; Ca plus Mg)	ppm as CaCO ₃
PA (Phenolphthalein Alkalinity)	ppm as CaCO ₃
MOA (Methyl Orange Alkalinity) ^(A)	ppm as CaCO ₃
pH ^(A)	pH
Chlorides	ppm Cl ⁻
Sulfates	ppm SO ₄ ²⁻
Silica	ppm SiO ₂
Iron	ppm Fe
DO (Dissolved Oxygen)	ppm O ₂

^(A) Indicates use in scaling calculations; see previous page.

Calcium carbonate has *decreasing* solubility with rising temperature and/or increasing pH. Table 19.2 provides the data from which scaling characteristics can be estimated from the analytical data for pH, TDS, Ca, and MOA. Using these data, one can calculate *either* the pHs (pH of saturation of calcium carbonate) or the *temperature* at which scaling will occur at the *observed* pH.

The scale usually consists of calcareous deposits (mixtures of calcium carbonates and magnesium hydroxides). The calculations are based on Ryznar's modification of the *Langelier index*. In current terminology, the relationships are:

$$LSI = pH - pH_s \quad (1)$$

where LSI stands for Langelier saturation index, and

$$RSI = 2 pH_s - pH \quad (2)$$

where RSI stands for Ryznar stability index.

These relationships, together with the calculation of pH_s are given in the following Table. These calculations are only approximations but are often useful.

Scaling by Water⁽¹⁾

$$\text{pH}_s = (9.3 + A + B) - (C + D)$$

$$\text{LSI} = \text{pH} - \text{pH}_s$$

where O indicates balanced conditions;

+ indicates scale formation;

- indicates scale dissolution; and

$$\text{RSI} = 2 \text{pH}_s - \text{pH}$$

where values > 7.5 indicate scale dissolution

Total Solids	A	Ca as CaCO ₃	C	MO Alk	D
50-400	0.1	10-11	0.6	10-11	1.0
400-1000	0.2	12-13	0.7	12-13	1.1
		14-17	0.8	14-17	1.2
Temp. °F^(A)	B	18-22	0.9	18-22	1.3
		23-27	1.0	23-27	1.4
32-34	2.6	28-34	1.1	28-35	1.5
35-42	2.5	35-43	1.2	36-44	1.6
44-48	2.4	44-55	1.3	45-55	1.7
50-56	2.3	56-69	1.4	56-69	1.8
58-62	2.2	70-87	1.5	70-88	1.9
64-70	2.1	88-110	1.6	89-110	2.0
72-80	2.0	111-138	1.7	111-139	2.1
82-88	1.9	139-174	1.8	140-176	2.2
90-98	1.8	175-220	1.9	177-220	2.3
100-110	1.7	230-270	2.0	230-270	2.4
112-122	1.6	280-340	2.1	280-340	2.5
124-132	1.5	350-430	2.2	360-440	2.6
134-146	1.4	440-550	2.3	450-550	2.7
148-160	1.3	560-690	2.4	560-690	2.8
162-178	1.2	700-870	2.5	700-880	2.9
178-194	1.1	880-1,000	2.6	890-1,000	3.0
194-210	1.0	1,000-1,200	2.7	1,000-1,200	3.1

^(A) °C = 5/9 × (°F – 32).

Note: Use *actual* pH of water when calculating B, the temperature at which the water will scale.

⁽¹⁾ *Corrosion Basics—An Introduction* (Houston, TX: NACE, 1984).

A much more precise calculation can be made on a spreadsheet, using the formulas e.g. promulgated by the American Water Works Association (AWWA) in the March 1992 issue of 'Opflow'. The calculations take into account ionic strength, activity coefficients, etc. Once the

If the LSI is *positive*, the water is saturated with calcium carbonate at the observed temperature and pH and is therefore prone to scaling. A *negative* LSI shows a tendency to dissolve scale (or corrode cement or concrete or other calcareous material).

The RSI is simply a more meaningful refinement of the LSI. Values below 6.0 indicate increasing scaling tendencies. The LSI and RSI techniques are applicable to potable waters (see further below) and other fresh waters.

Two other indices of interest are the Stiff-Davis Index or SDI, which extends the usefulness of this type of calculation to oilfield brines and other high salinity waters, and the Aggressiveness Index or AI, which predicts corrosivity to cement from the pH, calcium hardness and methyl orange alkalinity (MOA), where $AI = pH + \log (Ca \times MOA)$, with values below 12 becoming increasingly aggressive to cement.

2.3. Corrosion of Steel by Water

Corrosion of steel (cast iron is slightly more resistant in most instances) increases with chloride content of the water to reach a maximum at approximately 6,000 ppm (Figure 2.1). Above that level, the chloride effect is offset by diminishing solubility of DO, as in seawater or brines.

where acidity is high without a corresponding drop in pH (as with carbonic and other weakly ionized acids), corrosion with hydrogen evolution may occur in the pH 5.0 to 5.5 range.

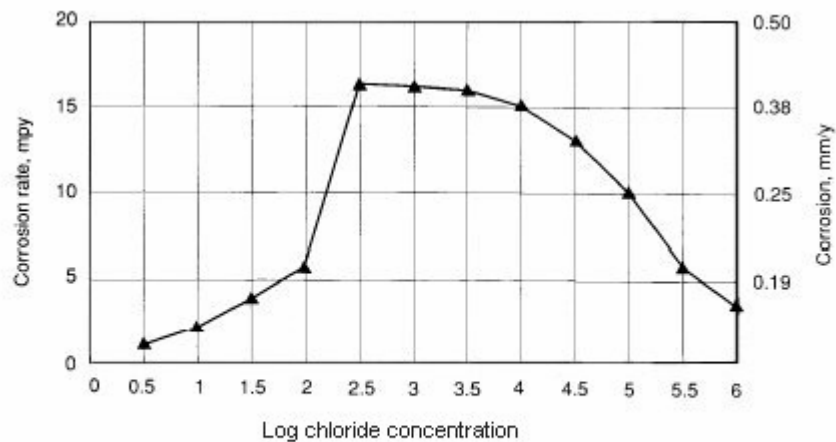


Figure 1 Corrosion of Steel vs Chlorides.

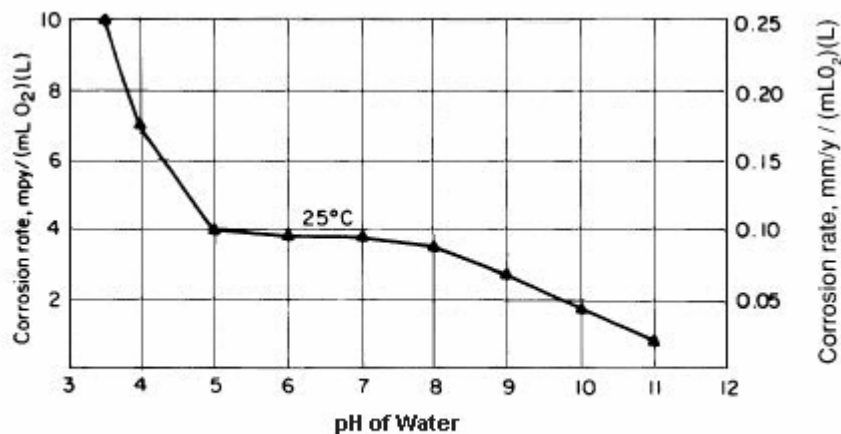


Figure 2 Steel: pH vs corrosion.

Historically, in an *open* container, corrosion reportedly reached a maximum at approximately 80°C (175°F) because of the decreasing solubility of DO (Figure 2.3). More recent investigations, using quartz rather than glass containers, indicates that the diminution of attack reported was enhanced by silicate inhibition resulting from some corrosion of the glass container. Note that, in a *closed* container, corrosion will increase with temperature more or less indefinitely because of retention of small amounts of DO under pressure. As we will discuss further below, this is the main basis for removal of DO from boiler feedwater.

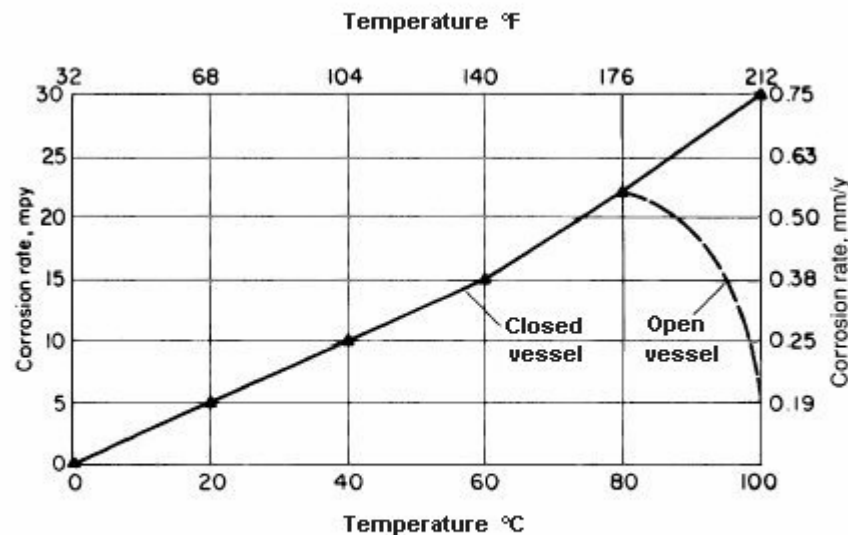


Figure 3 Steel: corrosion vs temperature.

2.4. Types of Water

Water may be classified in terms of origin, nature, and/or utilization. Many corrosion and materials problems arise from a basic misunderstanding of nomenclature and characteristics.

2.4.1. Origin

Waters may be classified as of surface or subsurface origin. *Surface waters* comprise the rivers, lakes, and seas which are the major source of water for industrial usage. *Subsurface waters* consist of waters from springs or wells and "produced water." Spring water comes to the surface from an aquifer, lifted by hydrostatic pressure. Well waters are brought forth by digging to a source. Artesian wells are those in which impermeable geological strata are perforated, allowing the water to surface by its own pressure. Other wells simply pump the water to the surface, usually using submerged pumps. Produced water is peculiar to oil and gas-well drilling operations, being co-produced with the hydrocarbons. It may be fossil water, entrapped for eons in the geological strata before being released by the drilling operation (as distinct from an aquifer which is replenished by drainage from surface sources or rainfall).

2.4.2. Natural Waters

Natural waters particularly are classified as *fresh*, *brackish*, or *salt* (e.g., seawater). Fresh water is also classified as hard or soft, although these are relative terms on a sliding scale and should be quantified according to the LSJ or RSI. Roughly, water considered soft if the

hardness is in the 0 to 75 ppm CaCO_3 range. Moderately hard water contains 75 to 150 ppm and hard water > 150 ppm calcium hardness.

(1) Fresh water typically contains less than 1,000 ppm of chloride ion.

(a) Soft water is low in calcium and magnesium salts, lathers easily with soap and is difficult to rinse.

(b) Hard water is relatively high in calcium and magnesium and tends to form insoluble curds when used with conventional sodium-based soaps. Originally, water hardness was actually determined by titration with standardized soap solutions, but these have been replaced with more modern analytical techniques (e.g., titration with ethylene diamine tetracetate; EDTA).

(2) Brackish waters typically contain more chlorides than fresh water, but less than seawater (e.g., 1,000 to 10,000 ppm). Such waters are found as surface waters due to salt deposits in the ground, as tidal waters (mixed from river and seawater), and as subsurface geological brines or saline wells.

(3) Seawater typically contains from 2.5 to 3.5% sodium chloride, depending on its geographical location. The salt content may increase due to surface evaporation, as in the Persian Gulf or the Dead Sea.

(4) Brines are still more concentrated salt solutions, either natural (as in oilfield or geothermal brines) or artificial (i.e., formulated for refrigeration purposes to take advantage of their low freezing point).

2.4.3. Use

From an industrial standpoint, waters are more often classified by their particular use. There are really three categories. The first (category I) involves nomenclature which clearly tells one something about the chemistry or nature of the water. In category II, there is an *implicit* (but not wholly reliable) statement about the nature of the water. In category III, the common name says really nothing about the nature or properties of the water despite the popular jargon.

2.4.3.a. Category I

Distilled water has been boiled and the vapors condensed specifically to separate it from its mineral salts. It is supposed to be pure and its major use is in the laboratory. Even so, the actual purity depends on the efficiency of the distillation system. Triple distilled water has the highest purity and is used in scientific work, where required, as *reagent water*.

Demineralized water (DM) has had both cations and anions removed by the action of specific ion exchange resins, substituting hydrogen ions for the cations and hydroxyl ions for the anions. The resulting water is free of almost all its mineral content except perhaps a little silica. It will contain a trace of organic species from the synthetic resin contact. In industrial use, demineralized water is considered to be equivalent to distilled water in quality (e.g., in nuclear reactor applications; as boiler feed water make-up for high pressure boilers). In fact, it can be contaminated with traces of material from the various operations involved, such as resin regeneration. The specific conductance of both distilled and demineralized water is a

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(5) **Desalinated water** is water produced from a seawater or other saline source by certain regimens of treatment. It is not necessarily a high-quality water.

(6) **Utility water** is a term sometimes used to describe a water of too high a salinity to be potable but otherwise sanitized to a degree which permits its use in eyebaths, safety showers, etc. However, in some instances, it may even be seawater.

2.4.3.c. Category III

(1) **Process water** is any kind of water applied to or recovered from a chemical or other process. It may thereby contain strange or unusual contaminants.

(2) **Chilled water** is a water specifically subcooled for temperature control of a reaction.

(3) **Tempered water** is held at some specific elevated temperature for the same purpose.

(4) **Produced water** (or *formation water*) is the water phase from an oil or gas well, usually containing variable amounts of chloride ions, carbon dioxide, hydrogen sulfide, etc.

(5) **Fire water** (or *fire-control water*) is any kind of water used for that purpose. It varies from potable water to seawater.

(6) **Cooling water** is used to remove sensible and latent heat from plant process streams. It may be from any source and of any quality.

(7) **Waste water** may be either municipal (which may combine sanitary waste with some industrial waste) or purely industrial. Industrial waste water may contain any and all types of organic and/or inorganic species. However, antipollution requirements are encouraging increasingly specific waste treatment facilities to protect the environment and encourage reuse of waste water for cooling or for BFWMU purposes. Sanitary waste water usually, but not always, originates as potable water, whereas municipal and industrial wastes are of indeterminate inorganic chemical composition.

2.5. Boilers, Steam and Condensate

A boiler is a device for generating steam by heating water to the boiling point at a particular pressure. The steam generated may be used for heating (e.g., as in reboilers) or to run engines or turbines (e.g., for generation of electricity). Fossil fuel boilers use coal or oil as fuel for combustion, while nuclear boilers utilize the heat from atomic reactors to boil the water.

Cooling Water Systems

2.5.1. Boiler Water

2.5.1.a. Boiler Water Treatment – General

In order to be non-scaling, the BFWMU must be softened or demineralized. In order to be noncorrosive to the steel and low alloy steel components from which boilers are usually constructed (nuclear plants also use steel in the secondary loops for steam), the water must be thoroughly deaerated.

Returned condensate, which is combined with BFWMU to constitute the BFW, may be treated (i.e., polished by filtration and ion exchange) to prevent accumulation of iron or other salts in the system.

2.5.1.b. Coagulation

2.5.1.c. *Phosphate*

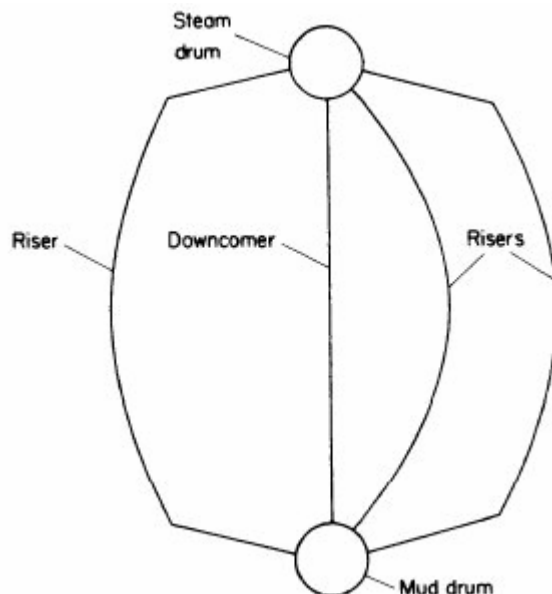
2.5.1.d. Coordinated Phosphate

2.5.1.e. *Chelant*

Regardless of the degree of external softening or demineralization, enough solids will eventually accumulate in the mud drum to pose operating problems unless it is subjected to *blowdown* (BD). This continuous or intermittent blowdown controls the residual solids. (Note:

The terms make-up and blowdown are also encountered in the discussion of recirculated water systems of other kinds.)

A simplified diagram of a two-drum boiler is shown in the Figure below.



2.5.2. Steam

Dry steam is noncorrosive to steel below approximately 370°C (700°F). Wet steam, or mixtures of steam and water as with the water tube of a boiler, is likewise noncorrosive in the absence of contaminants. However, it is not uncommon to experience entrainment of water salts or boiler-treatment chemicals. Sodium salts may react with oxide films or with the metal itself to liberate atomic hydrogen under certain conditions. More often, they simply cause *caustic gouging or caustic embrittlement*.

Silica (i.e., silicon dioxide) is quite volatile and may be carried over in high pressure steam (unless properly controlled) to form deposits on steam-driven turbines, for example, adversely affecting their balance.

2.5.3. Condensate

The steam condensate from a properly controlled boiler should likewise be noncorrosive. Unfortunately, it may be contaminated by carbon dioxide (e.g., from a high bicarbonate make-up water) or DO (e.g., by ingress to the condensate return; by improper deaeration of BFW). Corrosion in steam condensate systems is usually controlled, if required, through additions of either neutralizing or filming amines (e.g., morpholine, octadecylamine, etc.).

2.6. Cooling Water Systems

There are basically two kinds of cooling water systems, once-through and recirculated. The former is employed where there is an abundant source of surface water, but is falling into disfavor as the effects of thermal pollution are recognized. (Thermal pollution is the potentially adverse effect of relatively high-temperature discharged cooling water on aquatic life.)

2.6.1. Once-Through Systems

Where there is an adequate supply of inexpensive raw water, industries may elect simply to pump water through the plant heat exchangers and return it to the source. This is permissible if thermal pollution is not a problem and if there is adequate pollution control from the chemical standpoint.

Usually, the water source must be presumed to be corrosive since the surface waters are open to the atmosphere. In the past, some rivers had no DO (because of municipal or industrial pollution), but this condition does not now apply. It must be remembered that both fresh and saline waters are sufficiently corrosive to steel that more corrosion-resistant materials must be employed. The volume of water circulated through such a system effectively precludes chemical inhibition from a cost-effective standpoint.

In fresh water, galvanized steel is often adequate but brackish or salt water requires more resistant materials (e.g., copper alloys; super stainless steels, plastic-lined steel; concrete, etc.). The Table below suggests recommended materials of construction for a variety of equipment in both fresh and seawater once-through systems.

In once-through systems, chlorination is usually necessary to control biological growth (e.g., bacteria, slime, marine organisms).

2.6.2. Recirculated Systems

When water is in short supply or when its chemistry must be rigorously controlled, recirculated systems are employed. These may be considered in two categories; closed and open.

2.6.2.a. Closed Recirculated Systems

In a closed recirculated system, there is no make-up after the initial charge (except to replace accidental leakage) and no blow-down. Since there is no opportunity for evaporation either, the water chemistry can be established and easily and inexpensively maintained at the initial charge. These systems are exemplified by the automobile radiator and by engine jacket cooling systems.

These systems may be treated either by rendering them sterile and anaerobic or by use of either oxidizing or non-oxidizing inhibitors. The cost of treatment, including softening and pH control, if required or desirable, is minimal.

Materials of Construction for Once-Through Systems

Equipment	Fresh Water	Seawater
Screens	Coated steel Alloy 400	FRP or coated cast iron body, alloy 400 screens
Filters	FRP or coated steel; Cu or alloy 400 elements	Same
Pumps	Stainless (SS) ^(A) , Bronze, Ni- Resist [†] with SS impeller duplex or austenitic alloys	Ni-Resist [†] with alloy 400 impeller; high-performance
Chlorinators	PVC- or Saran [†] -lined steel	Same
Piping	Cement-lined cast iron or concrete underground; FRP, Cu or galvanized steel aboveground	Concrete underground; FRP, 90-10 Cu-Ni, duplex or 6 Mo alloys
Valves	Bronze or SS	Alloy 400, bronze or high- performance alloys
Exchangers	Seawater in Tubes Only	
Tubes	Cu, admiralty, SS alloys 625 and C-276	Ti, Cu-Ni, 6 Mo alloys,
Tubesheets	Bronze, SS	Ti, Ti-clad, bronze, 6 Mo
Baffles	Steel, ^(B) bronze, SS	Same metal as shell
Tie-rods	Steel, ^(B) bronze, SS	Same metal as shell
Shell	Steel, ^(B) Cu, SS, FRP	Metal ^(C) or FRP
Heads	FRP, bronze, lined steel	FRP or 90-10 CuNi

^(A) Stainless Steels.

^(B) Only with water in tubes and steel compatible with process side.

^(C) Any metal/alloy compatible with process.

These systems may be treated either by rendering them sterile and anaerobic or by use of either oxidizing or non-oxidizing inhibitors. The cost of treatment, including softening and pH control, if required or desirable, is minimal.

The heat which would otherwise accumulate in the closed loop is removed either in air-cooled heat exchangers or in water-to-water exchangers cooled by an external cooling water system.

Bactericidal treatment may be required, using a nonoxidizing biocide, such as hexamethylene biguanide, if sulfate-reducing bacteria (SRB) would otherwise be a potential problem.

2.6.2.b. Open Recirculated Systems

Open recirculated systems use ponds, fountains, or cooling towers to dissipate heat by evaporative cooling. All of these types involve constant air saturation as well as some concentration of water-borne solids in the circulating water. Such systems are inevitably corrosive to steel (unless suitably inhibited) and potentially scaling unless the hardness, pH, and alkalinity are also controlled. Fortunately, as discussed below, they are usually amenable to economical treatment, unlike the once-through system with its higher water usage, especially if cooling towers (rather than fountains or ponds) are employed.

In a cooling tower system, the process equipment is cooled by the recirculated water, and the warmed water is then cooled by being sprayed over the tower packing while air is blown or drawn through the cycle water (Figure below). The total amount of water actually used is limited to that lost by evaporation plus the blowdown (BD) established to limit the buildup of salts and solids in the system. The extent of the soluble salt concentration is expressed as *cycles of concentration*, which is the ratio of chlorides in the BD to those in the make-up (MU), or the ratio of MUI BD in volume per unit time (e.g., L/s or gpm). For example, if three volumes of water were to be boiled away in a pan until only one volume of water remained, the residual water would contain three times the soluble salts of the original charge, analogous to three cycles of concentration.

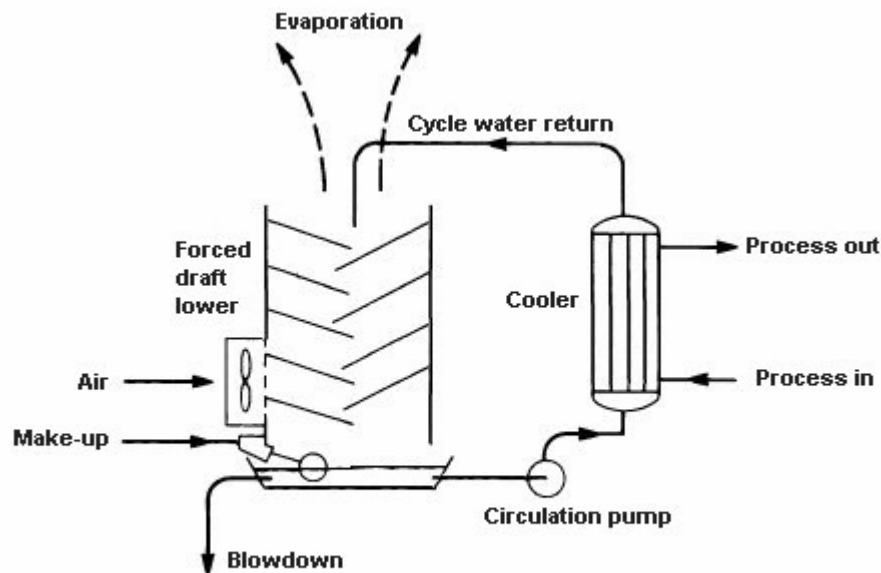


Diagram of cooling tower.

The amount of water evaporated in a cycle water system is determined by the circulation rate (CR) and the heat load on the system (which is indicated by the temperature difference (ΔT) in $^{\circ}\text{F}^{\circ}$) between the cool water from the basin or sump and the warm water returning to the tower from the plant). The evaporation rate (ER) is then:

$$\text{ER} = \text{CR} \times \Delta T / 1000 \quad (3)$$

while the cycles of concentration (C), makeup (MU) and blowdown (BD) are related as follows:

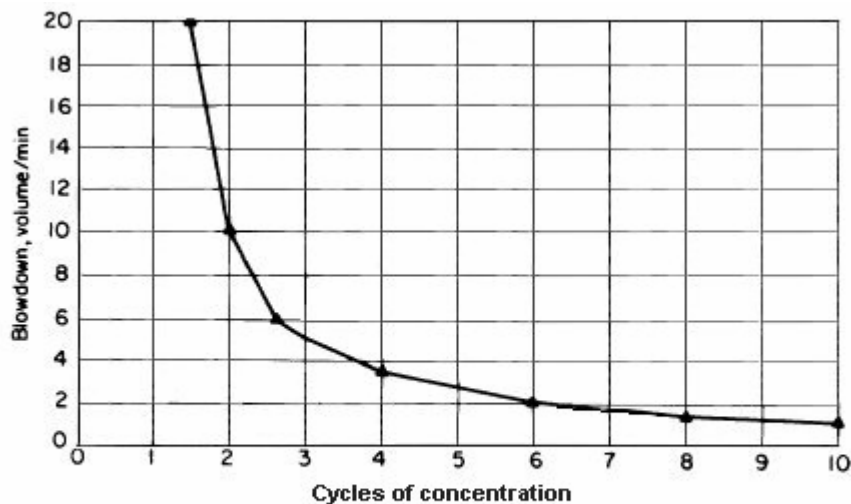
$$\text{MU} = \text{ER} + \text{BD} \quad (4)$$

$$C = \frac{\text{MU}}{\text{BD}} = \frac{\text{ER} + \text{BD}}{\text{BD}} \quad (5)$$

$$\text{BD} = \frac{\text{ER}}{C - 1} \quad (6)$$

Thus, for a cycle water system requiring 5,000 gallons per minute (19,000 L/min) circulation and a ΔT of 15°F (-3°C), the ER would be 75 gal/min (284 L/min). To maintain four cycles of concentration (which is a good working value), the $\text{BD} = 75/3 = 25$ gal/min (94 L/min) and the MU would be 100 gal/min (379 L/min). Note that this system only uses 100 gal/min while a once-through system would use the entire circulation rate of 5,000 gal/min (19,000 L/min). Actually, water-treatment chemicals need only be replaced in accordance with the *blowdown* rate. This feature is what makes open recirculated systems preferable when chemical treatment is required and closed systems are impractical.

In most such systems (water chemistry permitting), the optimum savings are effected at four to six cycles (Figure below). The additional savings from a higher number of cycles is usually offset by the increasing difficulty of coping with higher dissolved salt and hardness concentrations.



Water savings vs cycles of concentration.

Note that because of the warm temperatures and constant air scrubbing in the tower, the water is not only corrosive but a breeding ground for slime and algae introduced from air-borne spores. There is also a tendency to pick up particulate matter from the air.

Open recirculated systems must usually be corrosion-inhibited (if steel-tubed condensers are to be successfully employed), treated with biocides to control biological growths, and chemically treated to control scale and deposits. The cost of such treatment must be balanced against the obvious savings in water consumption. Such water treatment is an area in which even the competent corrosion engineer may need professional help from a specialized consultant or from a professional water-treating company.

Modern pollution control requirements are limiting some previously useful chemicals, such as chromate-based inhibitors, or requiring that they be removed from the blowdown. Fortunately, new treatments are being constantly studied and commercialized, although they may be of limited applicability in more aggressive high-chloride waters. The choice between corrosion inhibition vs resistant materials of construction is simply one of economics and pollution abatement considerations.

The Table below suggests suitable materials of construction for fresh-water type open recirculated systems.

Materials of Construction for Cooling Tower Systems

Equipment		Inhibited Water ^(A)
	Filters	FRP or cast iron
	Pumps	Steel or cast iron volutes, Bronze or SS ^(B) impellers
	Chlorinators	PVC-lined or Saran ⁴ -lined steel
	Piping	Carbon steel
	Valves	Cast iron or steel, SS trim
Exchangers	Water on shell	Water in Tubes
Tubes	Steel, Cu, admiralty, SS, or nickel alloys	Same
Tubesheets	Steel (if process compatible); Cu, SS or Ni (solid or clad)	Same
Baffles	Steel; other	Metal compatible with process
Tie-rods	Steel; other	Metal compatible with process
Shell	Carbon steel	Metal compatible with process
Heads	Metal compatible with process	FRP, lined or coated steel

^(A) Uninhibited aerated water is handled the same as once-through water (see Table 19.3).

(B) Stainless Steel.

2.7. Microbiologically Influenced Corrosion (MIC)

Some allusions have already been made to microbiologically influenced corrosion, commonly referred to as MIC. Strictly speaking, MIC is not a specific form of corrosion. Rather, it consists of both direct and indirect effects on specific materials by bacteria, fungi, algae, and yeasts. Microbes can selectively consume molecular hydrogen (promoting cathodic polarization), oxidize metal ions, or produce ammonia, methane, sulfur, or hydrogen sulfide. Biomasses of one kind or another can induce localized corrosion, such as underdeposit corrosion (UDC) by concentration cells, when adhering to a metal surface. Some forms of localized corrosion, such as pitting, dealloying, IGA, and environmental cracking (SCC or SSC), can be caused by specific chemical agents (e.g., ammonia, sulfides, ferric, or manganic chlorides) produced by metabolic processes in, or decay of, biomasses. Any films or deposits can occlude and concentrate chloride ions on the metal surface, in larger concentrations than exist in the bulk solution.

Aerobic bacteria, such as the "iron-eating" *Gallionella* and *Crenothrix* which metabolize iron and manganese salts and excrete metallic hydrated oxides, are often associated with unexpected chloride effects. Both type 300 series stainless steel and some high-performance alloys have suffered pitting and SCC due to this effect.

More commonly, problems arise from *anaerobic bacteria* such as the sulfate-reducing bacteria (SRB) strains found in many waters and water-bearing soils. Typically, these induce hydrogen sulfide-related problems or chloride-sulfate synergistic effects. SRBs are not entirely killed by ordinary chlorination and related bactericidal treatments. Small numbers survive in dormant conditions and can establish new colonies under locally anaerobic conditions.

It is important to not that SRBs can grow under films or deposits in otherwise aerated water.

2.8. Behavior of Materials

Some generalizations are given below which characterize the behavior of engineering materials in water service.

2.8.1. Carbon and Low Alloy Steels

With the exception of steam condensate (in which an ASTM A242 weathering steel may show some advantage), carbon and low alloy steels show approximately equivalent corrosion in water. Corrosion is primarily under the control of DO (or other oxidizing agents, such as chlorine or dissolved sulfur) over a broad pH range, as shown in Figure 2 above (cf. Section 2.3). Corrosion reaches a maximum at approximately 6,000 ppm chloride ion.

Generally speaking, steel should not be used in uninhibited water systems. However, a useful life is obtained if the water is naturally anaerobic (with no bacterial action) as from artesian wells, or in essentially closed systems (e.g., fire control water storage, hot water heating). In closed systems, the water becomes self-deaerated by superficial corrosion and noncorrosive until or unless fresh DO effects entry to the system, or unless SRBs provide dissolved sulfur as an alternative corrosive agent. A Corrosion Index for steel in aerated, uninhibited water is:

$$CI = \frac{(me\ Cl^- + me\ SO_4^{2-})}{me\ M\ Alk^{(A)}} \quad (7)$$

^(A) As $CaCO_3$.

Higher CI numbers indicates higher corrosivity, other factors being equal.

2.8.2. Cast Iron

Cast iron has an inherently better resistance than steel in most natural waters because the graphite flakes tend to aid in the adherence of a more protective rust film. The resistance is still frequently inadequate for long-term service, and modern usage usually calls for internal cementitious coatings or organic films. Soft aggressive waters cause graphitic corrosion of cast iron, as do acidic waters (e.g., coal-mine runoff).

2.8.3. Zinc

Zinc has good resistance in its own right to many natural waters. However, because of its anodic nature, it corrodes preferentially in contact with steel. Galvanized steel resists fresh water attack until the substrate is exposed, after which the zinc coating corrodes preferentially to protect the steel. The corrosion rate of zinc is linear with time, so protection is a function of the thickness of the zinc, whether galvanized or electroplated.

Galvanized steel lacks adequate resistance in high chloride waters or seawater, and is generally unsuitable in waters of <140 ppm hardness. Further, the potential of zinc becomes cathodic to steel in some fresh waters of specific chemistry (e.g., a high bicarbonate-to-chloride ratio; Cl-10 ppm or less), and accelerates corrosion of the substrate. This condition is aggravated by nitrates. Accelerated pitting of some hot water systems has been ascribed to this reversal of potential and an unproven water should be tested at approximately 80°C (175°F) to determine the possibility of this phenomenon.

2.8.4. Aluminum

Aluminum and many of its alloys have good resistance in many natural waters. However, resistance is affected by water chemistry and flow conditions. High chloride waters will pit aluminum under stagnant conditions. Aluminum is also subject to attack under deposits (UDC) by oxygen cell effects and under organic matter (*poultice corrosion*). It is corroded by heavy metal salts from other equipment upstream (cementation). It has, however, good resistance to steam condensate, in the absence of appreciable iron or caustic contamination.

2.8.5. Copper Alloys

Except for dezincification of brasses containing more than 15% zinc (unless specifically inhibited), copper and its alloys are the most reliable and cost-effective alloys for many water services. Copper, red brass, admiralty brasses, aluminum brass, aluminum bronze, and cupronickels, in that order, are used for waters of increasing salinity and/or velocity. In seawater, 90-10 Cu-Ni with iron should be specified for condenser tubing in most cases where a copper alloy is desired.

Soft waters can be *highly* corrosive to copper alloys in the presence of DO, and the "super" grades of stainless steels, high-performance alloys, or plastic construction is recommended. Also, copper can suffer pitting under some conditions. Sulfide films can cause pitting in seawater, while three kinds of pitting have been described in fresh waters. Type 1 pitting is apparently caused by residual carbonaceous films from the tube manufacturing process. Type 2 is associated with hot soft waters ($> 60^{\circ}\text{C}$), while Type 3 pitting may occur in cold water of high pH and low salt concentrations, for unknown reasons.

2.8.6. Stainless Steels

Stainless steels will resist pure water. It is the dissolved salt that causes problems. Any 12 chromium stainless steel will resist condensate or even BPWMU, if the water is totally deaerated. The type 300 series stainless steels are prone to pitting (and SCC at moderately elevated temperatures) even in potable water under stagnant conditions, usually due to UOC or MIC, although aerated *high-velocity* seawater can be handled in type 316 (if it is kept flowing). Nominal chloride limitations are approximately <500 ppm Cl^- for type 304 and <3000 ppm for type 316L. Type 300 series stainless steel grades can be used for water-cooled condensers if the tube-wall temperature does not exceed 50°C .

Optimum reliability in water service is provided by the "superferritic" grades and by the high-performance stainless steels or the 6% molybdenum alloys.

2.8.7. Nickel Alloys

Alloy 400 (UNS N04400) can be attacked in soft waters of critical CO_2 -to-DO ratios, and as heat -exchanger tubing can pit in fresh waters. However, it is widely used for long-term fresh water and many seawater applications. Alloy 625 (N06625) or C-276 (N10276) is used for seawater-cooled condensers where the process-side conditions are incompatible with copper or titanium alloys.

2.8.8. Titanium and Zirconium

Titanium is one of the most cost-effective materials for seawater applications, especially as condenser tubing. However, it has been known to pit in very hot seawater under severe conditions. Zirconium is equally good, although more expensive and used only where process-side conditions require. Zircalloys (e.g., R60802) find application in water-cooled nuclear reactors.

2.8.9. Plastics and Elastomers

Within their inherent temperature and pressure limitations, the plastic materials in general are excellent for water service. PVC, CPVC, PE, PP, and others are useful in all kinds of natural waters. FRP systems based on many resin systems (e.g., epoxy, phenolic, polyester, vinyl ester) are used where still greater strength is required. Plastic-lined steel is useful where still higher strength and temperature limits are required. Elastomers are useful to approximately 80°C (175°F), with EPDM withstanding even low pressure steam.

These comments refer to natural waters, inhibited or not. In waste waters, both plastics and elastomers can suffer degradation by continually absorbing trace amounts of incompatible organic species (e.g., sorbic acid vs polypropylene; aromatic hydrocarbons or chlorinated solvents vs rubber).

2.8.10. Concrete

Portland cement-type concrete structures are suitable for water immersion if a type appropriate to the sulfate concentration, chlorides and other chemical variants is selected. Even Type I cement is suitable in seawater, as previously described.

3. Corrosion by Soil

Dry soil is not corrosive, however ...

3.1. Introduction

Dry soil is not corrosive. It becomes so by virtue of the water content and related water-soluble salts which allow it to function as an electrolyte. In that event, we are dealing with an immersion condition similar to that encountered in corrosion by water. Just how corrosive a soil may be to a specific material (and we are primarily concerned with steel and cast iron) depends upon the specific constituents in the soil, its degree of aeration, and its bacterial content.

3.2. Types of Corrosion

Moisture transferred to the soil from the atmosphere contains specific contaminants (as discussed further in Chapter 21) and picks up specific water-soluble materials from the soil (e.g., salts of aluminum, calcium, magnesium, and sodium; sulfates, chlorides, carbonates, phosphates, silicates, etc.). For this reason, all of the types of corrosion to which construction materials are susceptible can be encountered.

Besides conventional phenomena and localized cells, however, buried structures of significant length (e.g., pipelines) are subject to *macrocell* action. Whole sections of line may become anodic to other long sections because of differences in soil chemistry, soil compaction, bacterial action, and thermal effects, as by gas compression heating effects or down-hole temperature gradients. As previously mentioned, stray DC currents will cause electrolysis.

In addition, fluctuations in the earth's magnetic field can induce *telluric currents*, and AC power lines can induce stray currents, both of which can cause corrosion of buried structures.

3.3. Factors in Soil Corrosion

There are three factors which influence the corrosivity of soil; resistivity, chemistry, and physical characteristics.

3.3.1. Resistivity

Resistivity is the property of a material, as opposed to resistance which is the resultant property of a physical entity. For example, copper has a certain resistivity but a piece of copper wire has resistance.

Soil resistivity is the net result of many chemical and physical aspects of the soil. The resistivity is determined by passing a known current, I , through a known volume of soil (volume = depth x width x length) and measuring the difference in voltage E due to current flow. By Ohms' Law,

$$\mathbf{R} = \frac{\mathbf{E}}{\mathbf{I}} \quad (1)$$

and resistivity (ρ) is

$$\rho = R \times \frac{w \times d}{l} \quad (2)$$

where w is width, d is diameter and l is length. If R is expressed in ohms (Ω), area ($w \times d$) in square centimeters, and length (l) in centimeters, resistivity must be expressed in ohm-centimeters ($\Omega\text{-cm}$). For example, seawater has a resistivity of 25 to 75 $\Omega\text{-cm}$; only a specific *volume* of seawater has so many ohms resistance.

This concept is useful in categorizing soils because of the interaction of chemical and physical effects cited. Generally, soil is considered highly corrosive if its resistivity is 2,000 Ω -cm or less. Between 2,000 and 10,000 Ω -cm, it is moderately corrosive, while at 10 to 20,000 Ω -cm it is normally considered only slightly corrosive. In everyday life, CP is recommended for buried steel pipelines if the soil is below 25,000 Ω -cm. Rare instances have been cited of corrosion in 100,000 Ω -cm soil.

3.3.2. Soil Chemistry

As mentioned above, different types of soil can contain a wide variety of chemical species. Some of these will not only influence the electrolytic nature of the soil but will also have specific ion effects (e.g., chlorides for pitting or SCC; sulfides for SSC).

Varying amounts of water may be available from water-table or atmospheric ingress. DO will vary with physical condition and with effects of decaying organic material and bacterial action, as by SRBs.

Some investigators indicate that the overall redox potential (i.e., the potential which is the net result of all the possible oxidation and reduction reactions in the soil) is very important. So, of course, is the pH of the soil.

3.3.3. Composition and Condition

Soil may consist of different components, perhaps even in different strata. Sand, clay, loam, and rock are four major categories.

Any of these, with the exception of nonporous rock, can have varying degrees of moisture and chemical contaminants. Wet, salty sand is a totally different environment than dry desert sand.

Ordinary earth will also have different degrees of compaction. Freshly excavated and filled trenches will have far more accessibility to moisture and oxygen than undisturbed soil.

3.3.4. Overall Corrosivity

Rather than judging a soil solely by its resistivity, several authorities have devised tables for overall rating of soil according to the several parameters described in the Table below. This table gives different arithmetical point figures for the several parameters, which can be totaled for an overall appraisal of the soil corrosivity. The parameters usually considered include pH, chloride content, redox potential, type of soil, and soil resistivity. Point allocations are higher with the more corrosive conditions, with high cumulative scores indicating greater corrosivity (e.g., 15+ indicating severe conditions, 0 to 5 mild corrosion only).

Assessment of Overall Soil Corrosivity to Steel

1. pH	Points	4. Soil Type	Points
0-2	5	Clay (Blue-Gray)	10
2-4	3	Clay/Stone	5
4-8.5	0	Clay	3
8.5+	3	Silt	2
		Clean sand	0
2. Cl⁻, ppm		5. Soil Resistivity	
1,000+	10	<1000	10
500-1,000	6	1,000-1,500	8
200-500	4	1,500-2,500	6
50-200	2	2,500-5,000	4
0-50	0	5,000-10,000	2
		10,000+	0
3. Redox, mV (vs Cu:CuSO₄)		6. Overall Rating	
Negative	5	Severe	15+
0-50	4	Appreciable	10-15
50-100	3.5	Moderate	5-10
100+	0	Mild	0-5

3.4.1. Steels

Basically, steel items should not be exposed to soil without corrosion control measures as described below. This is because steel can be rapidly attacked under even temporarily aggravated conditions and because corrosion control is a very small part of the installed cost. Also, a buried structure or a tank bottom is going to be generally inaccessible for an extended period of time, so protective measures must be incorporated initially if a satisfactory life is to be obtained. Steels are also susceptible to corrosion by external influences (e.g., stray currents, telluric currents, galvanic effects, bacterial action, etc.). As described further in Chapter 38, steels are best protected underground by a combination of coatings and CP.

3.4.2. Cast Iron

Historical records indicate that cast iron pipe in the soil may last as little as 5 or as much as 75 years, depending upon specific

Aluminum gives useful service underground provided it is protected from galvanic demands and specific ion effects (e.g., chlorides). Great care must be taken in use of CP, because of the possibility of generating high alkali concentrations which cause corrosion of this amphoteric material.

3.4.3. Stainless Steels

All of the stainless steels are subject to pitting by high chlorides and/or oxygen concentration cells. Stray current effects are inherent in the use of DC reverse polarity welding of type 300 series stainless steel lines in the ground. Austenitic stainless steel piping should be coated and cathodically protected for underground installations. One never knows when corrosive conditions will arise, and the localized attack characteristic of conventional stainless steels can lead to rapid penetration.

3.4.4. Lead

Lead sheathing has been successfully used in telephone cable sheathing underground for many years. It is generally resistant except for stray current effects, but can be corroded by specific chemical contaminants.

3.4.5. Copper Alloys

The behavior of copper alloys in soil follows along the lines discussed for water. Soft, acidic waters arise in soil from organic matter deteriorating in marshlands. Sulfate-reducing bacteria (SRB) can cause corrosion by sulfides. If ammonia is formed by rotting of nitrogenous

compounds, corrosion or SCC can ensue. Nevertheless, copper is usually satisfactory even in saline soils because of the static nature of the exposure, unless local cell action develops.

3.4.6. Concrete

The corrosion behavior of concrete in soil follows the principles described for water, especially as regards pH and sulfate effects. However, even sulfate-bearing soils are less aggressive than the corresponding waters under flowing conditions. Concrete cylinder pipe and cement-asbestos pipe have a long history of successful application in soil. It should be remembered, however, that the so-called cement bacillus (i.e., sulfate ion effects) was reported first in high-sulfate soils.

3.4.7. Plastics

Where conditions of temperature and pressure otherwise permit, plastic pipe and tanks (e.g., PE, PP, FRP) are ideal for service in soil. FRP underground tanks are largely replacing coated steel for gasoline storage. The major problem is of mechanical damage from rock fill and other foreign objects, due to ground subsidence or surface traffic imposing a loading force against the pipe or vessel wall.

3.5. Corrosion Control

All five of the standard corrosion control procedures apply, although some are more useful and prevalent than others.

3.5.1. Materials Selection

Most often, the engineer is faced with an established material, such as a steel pipeline, a stainless transfer line, a copper water or gas line.

Opportunities for materials selection are limited in soil-type applications.

3.5.2. Environmental Control

Usually, the soil conditions are relatively fixed. Occasionally, the corrosivity of the soil can be lessened by mixing extraneous materials in the back-fill, such as sand, lime, or water-repellents.

3.5.3. Barrier Coatings

Various types of barrier coatings, usually those with a high dielectric constant and good alkali resistance, are employed in soil service. These conjointly with CP (see below), are the major practical means of corrosion control. Their primary function is to decrease the current demand

of the buried structure, facilitating CP, but they also serve to exclude specific corrosive species.

3.5.4. Electrochemical Techniques

CP, specifically, is the major means of corrosion control for underground structures, using either sacrificial anodes or an impressed current system.

3.5.5. Design

There is good and bad design of underground installations, as in other engineering works. Major aspects of good design, from the corrosion standpoint, include electrical grounding practices, allowance for thermal expansion and contraction, soil control and compaction, and the design elements inherent in the CP systems.

4. Atmospheric Corrosion

Another environment where water plays an important role ...

4.1. Introduction

Atmospheric corrosion is the third area in which water plays a significant role, although the corrosion is also largely due to the 20% oxygen in air. The combined action of water and oxygen can be severe on the less resistant metals, and is exacerbated by certain contaminants. Atmospheric corrosion is unique in the sense that the corrosion products tend to remain on the metal surface, to a great extent. Therefore, a layer of such products become the rate limiting mechanism for many metals upon exposure to the atmosphere. Atmospheric corrosion is a very large part of the overall cost of corrosion, affecting consumer items such as automobiles and appliances as well as industrial plants.

4.2. Types of Corrosion

All types of corrosion phenomena may be encountered, depending upon the particular materials and specific atmospheric contaminants involved. Because of the large amount of steel potentially subject to atmospheric corrosion, general corrosion is the rule. However, localized forms such as pitting, IGA and SCC may be encountered with susceptible alloys.

The possibility of galvanic corrosion is somewhat minimized because the electrolyte available consists only of a thin film of condensed or adsorbed moisture, instead of the freely conductive volume available under immersion conditions. There is also a possibility that the accumulation of corrosion products between the mating surfaces of dissimilar metals may spread them apart and break the electrical contact. This cannot be relied on, however, and galvanic corrosion must always be considered in design for atmospheric exposures.

4.3. Controlling factors

Both chemical and physical factors affect behavior of materials in atmospheric exposure.

Table 21.1
Atmospheric Contaminants

Type	Volatile	Particles
Natural	Carbon dioxide	Sea salts (NaCl)
	Sulfur dioxide	Ashes
	Hydrogen Sulfide	Dust
	Ammonia	
	Oxides of nitrogen	
Synthetic	Carbon dioxide	Coal dust
	Sulfur dioxide	Fly ash
	Sulfuric acid	Smoke
	Chlorine	Fumes
	Hydrogen chloride	Road salt
	Oxides of nitrogen	Cement dust
	Ozone	

4.3.2. Physical Factors

The degree of shelter from particulate fall-out; orientation relative to sunshine, rainfall, and prevailing wind; even the time of year of initial exposure can affect initial and ultimate corrosion rates.

4.4. Types of Atmospheres

Although meteorologists classify air systems as to temperature and moisture (e.g., polar, temperate, tropical, desert, marine), corrosion specialists have traditionally classified exposure conditions as *rural*, *marine*, *industrial*, and *indoor*.

A rural atmosphere traditionally was that of the inland farm. Marine atmospheres are associated with coastal areas of up to several miles inland, at least. Industrial atmospheres originally meant the coal-polluted atmospheres of commercial cities. An indoor exposure suggested the temperature, humidity, and freedom from contamination of an office or warehouse. Even in the original context, it is evident that there is no clear line of demarcation between these categories.

Thanks to increasing concern over the environment, the atmosphere is generally less polluted today. Nevertheless, there can be industrial pollution of rural atmospheres, which may also have routinely high humidities. Mixtures of marine and industrial effects are common in many areas, each type of contaminant aggravating the other. Whether marine atmospheres effectively cease 100 meters from the shore or ten kilometers inland depends upon the

Indoor atmospheres may be as pristine as a controlled atmosphere room for precision watch-making or as severe as those around a pickling bath in a steel mill. Really, any atmospheric condition should be defined in terms of temperature, humidity, and contaminants *or* its corrosivity quantified in relation to the materials of interest (e.g., steel, zinc, aluminum, copper alloys). One should always consider special circumstances such as cooling tower drift or spray, or spills or releases of water or chemicals

4.5.1. Materials Selection

4.5.2. Environmental Control

4.5.3. Barrier Coatings

4.5.4. Electrochemical Techniques

4.5.5. Design

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rust discoloration on adjoining concrete structures. Copper alloys cause a similar discoloration problem (green), but to a much lesser degree.

4.6. Specific Materials

Following is a brief resume of the important properties of specific metals and alloys in atmospheric exposure.

4.6.1. Magnesium

Despite its very anodic nature, magnesium will resist mild atmospheric exposure. It is used for ladders and other light-weight structural assemblies (e.g., in lighter-than-air craft).

4.6.2. Aluminum

Aluminum may often be freely exposed to the atmosphere, as with vessels, tank trucks, aircraft, etc. Performance will vary with the alloy and heat treatment (IGA and SCC may be problems in industrial or marine atmospheres) and with specific contaminants. Even in apparently similar marine atmospheres, there may be as much as a tenfold difference in pitting proclivity between different alloy and location combinations. Aluminum is amphoteric, being attacked by both acidic and alkaline contaminants. However, it is useful in hydrogen sulfide- and sulfur dioxide-type atmospheres. Chlorides are conducive to pitting and SCC, and aluminum is very subject to under-deposit or poultice attack. Anodizing, by chemical or electrochemical means, will reinforce the surface oxide film and improve performance in atmospheric exposure. Aluminum is also successfully used as a hot-dipped coating and metallic pigment for paints and coatings, as well as a metallized surface for some marine applications.

4.6.3. Iron and Steel

Except in the most innocuous atmospheres, iron and steel must be protected from corrosion by one of several means. Temporary rust preventatives, painting, galvanizing, and other protective coatings may be employed, depending upon the severity of the atmosphere and the required performance or life.

There is a group of low alloy steels of relatively high strength, known as *weathering steels* (ASTM standards A 2421 and A 5882), which form self-protective rust films when boldly exposed to many industrial, as well as uncontaminated, atmospheres. An example is 'Corten'. Such steels are used for structural purposes and rolling stock, unpainted, where advantage can be taken both of their higher strength and improved corrosion resistance, as compared with carbon steel. They will not resist chloride-contaminated industrial or industrial-marine atmospheres. Crevices, as in riveted lapped joints, must be sealed with some sort of mastic against ingress of atmospheric moisture.

4.6.9. Higher Alloys

The high-nickel alloys (e.g., alloys 625 [UNS N06625], C-276 [N 10276], C-22 [N06022], and 59 [N06059]) and titanium and its alloys should remain bright, retaining even a mirror finish in atmospheric exposure.

4.7. Special Problems

There are three special problems, arising from or akin to atmospheric corrosion, which should be mentioned.

4.7.1. Corrosion Under Thermal Insulation (CUI)

Thermal insulation when exposed to water can hold a reservoir of available moisture on the metal surface which, together with the permeability of air, causes severe attack up to several *tenths* of an inch per year (200 to 300 mpy [4 to 6 mm/y]) particularly on warm steel surfaces. On cold insulated surfaces, severe corrosion may occur where structural members abut the insulated pipe or vessel, permitting rime ice to form. With other specific contaminants, insulation can cause SCC of high strength copper alloys and external SCC (ESCC) of type 300 series stainless steels. Aluminum is rapidly attacked in the presence of chlorides or alkaline contaminants. Vessels and large piping may be coated with an appropriate organic system (such as a catalyzed epoxy-phenolic and modified silicone), prior to insulating, to help prevent such corrosion in the event of ingress of water. For stainless steels, the coatings should be zinc- and chloride-free, as previously discussed.

4.7.2. Cryogenic Plants

Cryogenics relates to very low temperature operations, in which two types of problems are encountered. First of all, any structural members which are fastened to the vessels and extend out through the insulation are chilled by the service temperatures. Moisture tends to condense and freeze on the chilled surfaces. The immediately adjacent areas, as well as the frozen areas which thaw during shut-down, are subject to high rates of attack. High quality coating systems are required to withstand corrosion in near-freezing zones.

In some vessels, the top may be at sub-zero temperatures but the bottom at 40 to 80°C (105 to 175°F). In such cases, atmospheric moisture is drawn in through the insulation to freeze on the colder parts. Some of it melts (all of it during shutdown) and runs down behind the insulation to cause severe corrosion of steel. Steel and alloy-steel vessels in low temperature service should be coated with a good quality, heavy-duty paint system before the insulation is applied.

4.7.3. Threaded Fasteners

Because of the stresses and crevices inherent in a nut-and-bolt assembly, corrosion of steel is greatly aggravated in aggressive atmospheres. Cadmium-plated steel is useful only for indoor and noncorrosive service. Galvanized steel bolts perform well in mild to moderate

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5. Oxidizing Acids

Some of the most corrosive environments, or just not ...

5.1. General

Because the corrosion of metals to their ions necessarily entails oxidation (i.e., the loss of electrons), there is some confusion over what constitutes corrosion under "oxidizing" conditions. Acids, after water, are the most common corrosives and it is customary to classify them as *oxidizing* or *reducing acids*.

With a reducing acid, while the anodic oxidation of the metal is occurring, the cathodic reaction is primarily the reduction of hydrogen ions to atomic, then molecular, hydrogen. This is exemplified by the evolution of hydrogen by zinc in dilute hydrochloric acid.

In an oxidizing acid, the cathodic reaction is the reduction of the acidic anion rather than hydrogen evolution. For example, brown oxides of nitrogen are liberated by the reaction of dilute to moderate concentrates of nitric acid on steel.

It is important to note, however, that the characteristics of a metal/acid reaction are also influenced by the nature of the metal component. For example, boiling 55% sulfuric acid is a reducing acid to steel or type 300 series stainless steel, liberating hydrogen, while it is oxidizing to the cast silicon-nickel alloy, the sulfate ion being reduced to sulfur dioxide and hydrogen sulfide (and elemental sulfur being formed as a consequence of their interaction). This is in accord with the generality that any "oxidizing agent" can be a reducing agent in the presence of a stronger oxidant.

In some combinations (e.g., type 300 series stainless steel vs dilute sulfuric acid), oxidizing cations like ferric or cupric ions move the redox potential in an oxidizing direction by providing an alternative cathodic reaction (i.e., reduction of cupric or ferric ions) to hydrogen evolution. We then have oxidizing conditions although not, strictly speaking, an oxidizing acid.

Solutions of oxidizing acid salts (e.g., ammonium nitrate) act like dilute solutions of the parent acid.

In general, oxidizing acids tend to corrode metals which do not form a passive oxide film (e.g., copper, lead) rather than those which do, such as chromium-bearing alloys, titanium, and aluminum. Reducing acids are sometimes *more* aggressive to the normally passive metals than to active metals, because of the reaction of nascent hydrogen with the oxide film or direct

Nitric acid is not only a strong mineral acid but a powerful oxidizing agent, even in dilute

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The following discussion relates to the corrosivity of pure nitric acid to the common materials

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the rate being substantially nil in strong acid at high temperatures. The corrosion resistance is due to formation of an adherent siliceous film.

5.2.1.d. Stainless Steels

Stainless steels of the ferritic type (e.g., type 430 17%chromium stainless steel, [S43000]) were among the first used in nitric acid service. Welding problems, and the brittleness of the cast forms, ultimately led to their replacement with the austenitic grades.

The molybdenum-free austenitic stainless steels of the type 300 series variety are outstanding for their resistance to nitric acid in the annealed condition. However, the potential for IGA is high, and the low carbon type 304L or stabilized grades (e.g., type 347) are required for welded equipment which is not amenable to solution annealing. A nitric acid grade (NAG), which has <0.02 C and very low phosphorus by virtue of AOD production, is currently used.

IGA can also occur, regardless of composition or heat treatment, if hexavalent chromium (CrVI) ions accumulate in the acid to some concentration level. Wrought type 316L should not be used in nitric acid because of corrosion of sigma phase, although annealed castings (CF- 3M) are acceptable if properly heat-treated.

Higher alloy grades, such as type 310L have been used at elevated temperatures; a NAG variant is available. New developments in silicon-rich stainless steels (18%Cr-18%Ni-5%Si) are replacing the 25%Cr-20%Ni alloys above 70% nitric acid at >80°C (175°F).

Stainless steel tanks have been severely attacked in the *vapor* phase of strong nitric acid, 93 to 99%, apparently due to an autocatalytic effect of the nitric oxides.

5.2.1.e. Titanium

Titanium is highly resistant to nitric acid below 25% and in the 65 to 90% range at the atmospheric boiling point. In 25 to 50% boiling acid, rates are 0.25 mm/yr (10 mpy) or more. Titanium also resists fuming acid but there is danger of violent pyrophoric reactions if the water content is less than approximately 1.3% or the nitrogen dioxide content is greater than 6%. SCC can also occur in red fuming nitric acid. Only a professional corrosion engineer should select materials for this type of service.

5.2.1.f. Other Metals

Copper and nickel alloys (except for the chromium-bearing varieties, such as alloys 600 (UNS N06600), 625 (N06625), and C-276 (N 10276), are rapidly attacked by even dilute nitric acid. The chromium-bearing nickel alloys are not usually economically attractive compared with stainless steels.

Lead is nonresistant in nitric acid.

Of the reactive metals, zirconium is better than titanium in 65 to 90% acid. However, it is subject to SCC at concentrations greater than 70% and fails rapidly in boiling 94% nitric acid. Tantalum has excellent resistance up to the atmospheric boiling point.

Of the noble metals, gold and platinum are resistant but silver is rapidly attacked. A 3:1 mixture of hydrochloric and nitric acid, *aqua regia*, is the classical solution for dissolving gold, due to oxidation of the HCl to nascent chlorine.

PTFE, plain or glass-filled, is routinely employed in nitric acid service. Carbon is a useful material, provided it is free of oxidizable binders. Other organic materials are limited by the temperature and concentration of the acid, which control its oxidizing capacity. Some suggested limitations are given in Table 22.1.

Following is a listing of materials of construction which are thought to constitute good engineering practice for a variety of items, subject to specific limitations previously discussed:

One cannot set the limits for oxidizing characteristics of sulfuric acid independently of the materials to which it is exposed. However, it *starts* to have a definite oxidizing nature at approximately 5 Normal (25%), being reduced by nickel or alloy 400 at the boiling point and at room temperature by finely divided ("Raney") nickel. By 60%, at approximately 80°C (175°F), it will carbonize PVDC over a prolonged exposure period. At 95% and 25°C (77°F), it carbonizes FRP instantaneously. Concentrated sulfuric acid can be considered 70 to 100% acid. Oleum is 100% acid plus dissolved sulfur trioxide, and is generally designated as, for example, 20% oleum, which is equivalent to 104.5% acid if all the SO₃ is converted to H₂SO₄.

5.3.1. Materials of Construction

The behavior of common materials in concentrated sulfuric acid and oleum is discussed briefly below.

5.3.1.a. Aluminum

Aluminum and other light metals are, for practical purposes, nonresistant to concentrated acid below 96%. It has been used successfully above 96%, even at elevated temperature, provided there is no opportunity for inadvertent dilution.

5.3.1.b. Cast Iron and Steel

Cast iron and steel are just beginning to be useful at 70% concentration. Steel is more resistant in the 70 to 80% range than in 80 to 90% acid. Concentrations above 90% are routinely handled in iron and steel *provided* velocities are below approximately 0.7 m/s (2 ft/s) for steel and below 1.5 m/s (5 ft/s) for ductile cast iron, whose ferric sulfate film is more tenacious. (Conventional gray cast iron is no longer used in modern applications, for safety reasons.) Steel shows a decided corrosion peak at approximately 101 % sulfuric (5% oleum) but can be used in 20 to 30% oleum.

Ordinary gray cast iron is totally unacceptable in oleum because of internal corrosion by the free sulfur trioxide along the graphite flakes. The gaseous products plus iron sulfates and silica (from oxidation of silicon) have caused explosions of conventional cast iron vessels. For this reason, ductile cast iron or a specialty material, Procon, *must* be used in oleum.

In storage of concentrated acid, localized dilution by ingress of atmospheric moisture can cause attack in the vapor space under high-humidity conditions, unless a *desiccating* vent is provided.

Silicon iron (14.5% [UNS F47003]) is resistant up to the boiling point in concentrated sulfuric acid, and would replace ordinary iron or steel at temperatures above approximately 50°C (122°F). It is, however, a very brittle material and must be protected *from* thermal or mechanical shock. The high-silicon iron must not be exposed to oleum.

Austenitic nickel cast irons, such as UNS F41 000 and F41 004, are successfully used to resist corrosion, erosion, and abrasion in oleum at ambient temperature.

5.3.1.c. Lead

Lead has been a longtime favorite in the sulfuric acid industry, only recently falling somewhat into disfavor because of toxicity during joining ("lead-burning"). Depending on a sulfate film for resistance, like steel, lead is very susceptible to velocity effects above approximately 1 m/s (3.3 ft/s). Also, solubility of lead sulfate increases sharply at and above 95% concentration and also at lower concentrations (e.g., 80%) at approximately 120°C (250°F). It is not resistant to oleum.

Austenitic Type 300 Series Stainless Steels

Austenitic type 300 series stainless steels are resistant to cold concentrated sulfuric acid. Type 304L is routinely used for piping in sizes below 75 mm (3 in.), where cast iron is not

available. With increased velocity and turbulence, higher alloys are employed (e.g., CF-3M for valves, CN-7M [N08007]) for pumps). The molybdenum-free grades (i.e., types 304 and 304L) should be used in concentrations greater than 93 % acid and in oleum. In oleum of less than 14% concentration, corrosion may be aggravated by velocity effects at temperatures as low as 60°C (140°F). Higher alloys like type 309 (S30900) are successfully used at elevated temperatures and the new 5% silicon grades resist sulfuric acid better than conventional grades.

5.3.1.d. Copper and Nickel

Copper alloys are not used in concentrated acid, because of its oxidizing nature.

The lower nickel alloys are nonresistant to oxidizing acids and the chromium-bearing nickel alloys are not economical in conventional applications. However, alloy B-2 (UNS NI0665) is resistant to the atmospheric boiling point unless traces of nitric acid or ferric ion contamination are present. It is not resistant to oleum, however. Nickel-chromium-molybdenum alloys (e.g., alloy C-276 [UNS N 10276]) will withstand oleum, but they are not usually economically competitive with lower-cost materials.

5.3.1.e. Reactive Metals

Tantalum will withstand 95% acid to 175°C (350°F) and lower concentrations to the atmospheric boiling point. It is attacked by sulfur trioxide, making it unsuitable for oleum service, and suffers hydrogen attack in galvanic couples. Titanium and zirconium are not resistant in concentrated acid, as defined.

5.3.1.f. Noble Metals

Gold (UNS P00010) and platinum (P04898) have been widely used in sulfuric acid concentrators, but silver is not resistant.

5.3.1.g. Nonmetallic Materials

Pure carbon is resistant to boiling 100% acid and resists 115% acid to approximately 70°C (160°F). Impervious graphite (e.g., Karbate) will perform up to approximately 150°C (300°F) *unless* it has cemented joints, which impose a limit of 60°C (140°F).

Glass, porcelain, stoneware, and acid-brick are useful in many applications involving hot concentrated acid.

Fluorinated plastics (e.g., PFA, PTFE, FEP, PVDF, Kynar) in acid are restricted only by their inherent temperature limitations but permeability poses problems in oleum service.

Other plastics (e.g., PE, PP, PVDC, PVC) will withstand 75% acid to 50°C (120°F) and 90% acid at 30°C (85°F); above these limits, carbonization will occur. FRP, with a suitable resin, will withstand 75% acid and 25°C (77°F) maximum. They will not withstand oleum.

Elastomers, other than the fluorinated variety, are limited to a maximum of 75% acid and not more than 80°C (175°F) even at 70%. However, Kalrez 1045, a fully fluorinated elastomer filled with titania, can be used for oleum service.

5.3.2. Handling and Storage

Following is a list of materials of construction for various items of equipment, which list is considered good engineering practice for the handling and storage of concentrated acid at ambient temperatures:

Equipment	Typical Engineering Materials
Tanks	Carbon steel (with drying vent); coat with baked phenolic or anodically protect (AP) if iron contamination is objectionable
Piping	Ductile cast iron (304L for small diameter); <i>Note</i> : electric or hot-water tracing only
Valves	CF-3M (or CN-7M for "throttling")
Pumps	CN-7M
Gaskets	Stainless steel/spiral-wound PTFE
Dilution	PTFE-lined or Kynar-lined; alloy C-276 tee check valves.

Similar recommendations for oleum are as follows:

Equipment	Typical Engineering Materials
Tanks	Carbon steel
Piping	304; velocity max 1.3 m/s (4 ft/s)
Valves	CF-8M
Pumps	CF3M or Pro-Iron with Lewmet impellers and 20Cb-3 (alloy 20) shafts
Gaskets	Kalrez 1045; spiral-wound 304/PTFE

elastomers to what is nominally hydrochloric acid. The discussion below refers specifically to pure hydrochloric acid, except where otherwise noted.

6.2.2. Specific Materials

The behavior of specific categories of materials in hydrochloric acid is as follows:

6.2.2.a. Light Alloys

Aluminum and magnesium alloys are severely attacked by hydrochloric acid.

6.2.2.b. Iron and Steel

These metals are inherently nonresistant to hydrochloric acid. However, steel piping and vessels can be chemically cleaned with *inhibited* acid for a few hours at a time up to 65°C (150°F) under controlled conditions (e.g., controlled velocity; no cast iron or stainless components in the system). Inhibitors are ineffective with cast iron, because of the galvanic influence of the contained graphite.

6.2.2.c. Stainless Steels

Stainless steels of all kinds are incompatible with hydrochloric acid. Further, residual chlorides can contribute to pitting or SCC in subsequent service (e.g., after acid cleaning).

6.2.2.d. Copper Alloys

Copper and its alloys are attacked by hydrochloric acid in the presence of DO or oxidizing ions. Since the cupric ion is itself an oxidant, few practical applications will be found. Dealloying is also a potential problem (e.g., dezincification, dealuminumification, destannification) for brasses and bronzes.

6.2.2.e. Lead

Lead shows reasonable resistance in laboratory tests up to approximately 30% acid at 25°C (77°F) and to 20% at 100°C (212°F) but field experience has not been good. Corrosion products are quite soluble and easily washed away by flow.

6.2.2.f. Nickel

Nickel and its alloys are superior to copper but not really useful until the 30% molybdenum alloy B-2 (UNS Ni0665) is employed (although alloy 600 [N06600] may replace type 300 series stainless steels where only trace amounts of acid are encountered). Alloy B-2 (Ni0665) will resist boiling hydrochloric acid, but *not* if traces of oxidizing agents (e.g., Fe III) are present. The chromium-bearing grades (e.g., alloy C-276 [N 1 0276], C-4 [N06455]) will resist dilute acid plus ferric chloride, but only to intermediate temperatures.

6.2.2.g. Reactive Metals

Titanium is non-resistant, but zirconium can withstand concentrated acid to 107°C (225°F) provided there are no more than 50 ppm oxidizing species (e.g., Fe III, Cu II) present. With

6.2.2.h. Noble Metals

6.2.2.i. Nonmetallic Materials

Rubber-lined equipment is traditional for handling acid up to 80°C (175°F). However, organic solvent contaminants (e.g., chlorinated hydrocarbons or aromatic solvents such as benzene or toluene) can be preferentially absorbed and concentrated to cause failure either of the rubber or of its adhesive.

6.2.3. Handling and Storage

Equipment	Typical Engineering Materials
Tanks	FRP, rubber-lined steel
Piping	FRP, polypropylene-lined steel
Valves	Alloy B-2 (N-12M casting), PTFE-lined or FEP-lined
Pumps	Alloy B-2 or N-12M, impervious graphite, PTFE-lined
Gaskets	Rubber, felted PTFE, FEP envelope, flexible graphite

6.3. Phosphoric Acid

6.3.1. General

Phosphoric acid is a syrupy liquid whose process of manufacture profoundly affects its corrosion characteristics. Acid made by the "wet" process of digestion of phosphate rock with sulfuric acid is heavily contaminated with impurities such as fluorides, chlorides, sulfates, and metal ions. Used mostly in the fertilizer industry, its corrosion characteristics are highly variable. Acid made directly from combustion of phosphorus is much more predictable, although it too can at times be a problem as to predictability.

6.3.2. Specific Materials

Behavior of specific categories of materials in phosphoric acid is as follows:

6.3.2.a. Light Metals

Aluminum and magnesium are of no practical interest in phosphoric acid services, although aluminum can resist up to 20% acid to 65°C (150°F).

6.3.2.b. Iron and Steel

Steel forms a protective film in acid above 70%, but is not used for this service because of iron contamination. However, a 1% solution is sometimes used as a "wash-coat" to prepare a steel surface for painting, and cold syrupy phosphoric acid (e.g., 85%) will phosphatize a steel or iron surface against rusting (if subsequently oiled) in indoor atmospheres for a period of time.

Cast iron is similar to steel in phosphoric acid service. The austenitic nickel cast irons, such as UNS F43000, are resistant to slightly above room temperature. The 14% silicon iron (F47003) will resist all concentrations to the atmospheric boiling point, but this resistance is contingent upon no *fluoride* contamination.

6.3.2.c. Stainless Steels

Of the stainless steels, the 12% and 17% chromium grades have poor resistance to phosphoric acid. Despite optimistic laboratory data, field experience with type 304 or 304L has also been poor. Type 316L is usually reliable for tanks, piping, valves, and pumps handling *uncontaminated* acid up to 85% to approximately 80°C (175°F) maximum, although erosion-corrosion may occur at velocities in excess of 1 m/s (3.3 ft/s). Type 317L (S31703) or a high-performance grade (e.g., 20Cb-3* [N08020]) may be substituted for an extra margin of resistance. The *molybdenum-bearing* high alloy grades (e.g., alloys 825 [N08825] and 20Cb-3) will resist up to 85% acid at the atmospheric boiling point (in the absence of aggressive contaminants).

6.3.2.d. Lead

Lead is a traditional material for handling phosphoric acid (particularly prior to the development of modern high nickel alloys) and will withstand 80% pure (or 85 % impure)

6.3.2.e. Copper

6.3.2.f. Nickel

6.3.2.g. Reactive Metals

6.3.2.h. Noble Metals

6.3.2.i. Nonmetallics

FRP tanks and piping are widely used for atmospheric storage. Carbon and graphite are usually resistant to at least 350°C (700°F), but tube-and-shell heat exchangers may be limited by cemented joints.

6.3.3. Handling and Storage

Following is a listing of suggested materials of construction thought to constitute good engineering practice for a variety of items for uncontaminated acid, with minimum risk:

Equipment	Typical Engineering Materials
Tanks	FRP or 304L
Piping	FRP or 316L
Valves	CF-3M
Pumps	CF-3M
Gaskets	Elastomeric or graphic fiber

6.4. Sulfuric Acid

6.4.1. General

Dilute and intermediate concentrations (i.e., less than 70%) of sulfuric acid are entirely different from the oxidizing concentrated acid discussed in the previous chapter. The most important thing to recognize is that its corrosive nature is affected both by dilution (and temperature) and by contaminants. The latter profoundly affect the redox potential of the solution, and we will discuss in this section both oxidizing and reducing contaminants, while maintaining that dilute sulfuric acid is usually in itself a reducing acid, particularly in relation to ferrous alloys.

It should first be understood that there is a relationship between specific materials and various concentrations of sulfuric acid as to whether hydrogen gas is evolved (as from a reducing acid) or whether the sulfate ion is reduced. (The behavior of specific metals and alloys is discussed under "Specific Materials" on the next page.) For example, some authorities indicate that sulfuric acid starts to become an oxidizing acid at and above 5N concentration (approximately 25%). This may be based on measured "redox potential" 1 or on some thermodynamic calculation. Certainly, a broad range of concentrations evolve hydrogen during the corrosion of ferrous alloys. It is evident, however, that finely divided nickel (e.g., "Raney" nickel) will react with 25% acid at room temperature, liberating hydrogen sulfide by reduction of the sulfate ion. At the boiling point, 25% acid undergoes anion reduction in the presence of alloy 400 (N04400). Boiling 53 to 57% acid is similarly reduced during corrosion of the now obsolete high-silicon cast nickel alloy, Hastelloy D.

Over the entire range of dilution from approximately pH 2 (approximately 0.05%) to 90% concentration, specific oxidizing species (e.g., cations like Cu II or Fe III; anions like

6.4.2. Specific Materials

6.4.2.a. Light Metals

6.4.2.b. Iron and Steel

6.4.2.c. Stainless Steels

Corrosion of Steel in Dilute Sulfuric Acid

In these very dilute solutions, both dissolved oxygen (a weak passivation) and molybdenum content are significant. No doubt, chloride contamination would adversely influence these

rates, which therefore relate to distilled water or demineralized water (DM) only. Also, severe corrosion has been observed in the rolled joints of tube-shell heat exchangers, where the dilute acid concentrated locally to some intolerable level due to process-side heat.

In laboratory investigations, 50 to 65% acid at 80 to 90°C ([175 to 200°F] which would otherwise dissolve type 304 or 316) has been rendered totally noncorrosive by the addition of as little as 500 ppm Cu II. This would be potentially dangerous in the field, where the inhibitor might not access crevices or joints.

Of the superaustenitic grades, the alloy 20Cb-3* (N08020) was specifically developed for dilute and intermediate concentrations of sulfuric acid. The literature contains isocorrosion charts which define the ordinary limitations of concentration and temperature. It must be remembered that these parameters are profoundly affected by specific oxidizing, reducing, or halide contaminants. The newer grades with lower alloy contents (254 SMO* [S31254] and AL-6XN+ [N08367]) will have less resistance than alloy 20Cb-3* but more than type 316L.

6.4.2.d. Lead

Lead and its alloys have good resistance to a relatively wide range of sulfuric acid concentrations below the atmospheric boiling point (see isocorrosion charts in the suggested reading materials). However, not only is erosion a problem but the protective sulfate film may be removed by some organic contaminants (e.g., alkyl sulfates, organic acids). On the other hand, an intact sulfate film can render the lead cathodic to high alloy valves (e.g., CW -2M [alloy C-4 D, the reverse of the initial situation, with attendant galvanic corrosion of the valve unless it is electrically isolated).

6.4.2.e. Copper

The zinc-free copper alloys (e.g., coppers and bronzes) are profoundly influenced by oxidizing and reducing species. They will, in fact, resist dilute sulfuric acid but are corroded by as weak an oxidant as DO. Worse still, the stable corrosion products are the Cu II ions, which are themselves oxidizing species (as opposed to cuprous ions), so the attack is autocatalytic, accelerating with the accumulation of dissolved corrosion products. Copper alloys should only be used in non-oxidizing or reducing conditions.

6.4.2.f. Nickel

Of the nickel alloys, the non-chromium grades like alloy 200 (N02200), alloy 400 (N04400), and B-2 (N10665) resist nonaerated acids free of oxidants. Alloy 400 is similar to copper because of its high copper content (approximately 30%), but is used as auxiliary hardware in acid pickling operations where the hydrogen evolved from steel products keeps the iron and copper salts in a reduced state. Alloy 600 (N06600) is of little interest in dilute sulfuric, but the molybdenum-bearing grades like alloys 825 (N08825), 625 (N06625), and C-276 (N 10276) are useful (manufacturers' literature will have isocorrosion charts).

6.4.2.g. Reactive Metals

Of the reactive metals, titanium is not useful in dilute sulfuric acid unless oxidizing contaminants (e.g., Cu II, Fe III, nitrates) are present to maintain passivity. Zirconium resists up to 70% sulfuric acid at the boiling point, above which concentration rapid "breakaway" corrosion occurs. In some plant operations, it was found that the entire curve derived from

Tantalum will resist dilute sulfuric acids to the atmospheric boiling point. Only fluoride contamination poses a serious threat, as it does also with zirconium.

Of the noble metals, platinum and gold are quite resistant but see very few industrial applications. The corrosion rate for gold is adversely affected by oxidants. Silver is resistant in very dilute acid, but the rate increases significantly as the concentration or temperature is increased.

These are routinely used in dilute sulfuric services, with the following caveats.

- ### 6.4.3. Handling and Storage

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Equipment	Typical Engineering Materials
Tanks	Brick-lined, glass-lined, plastic-lined, rubber-lined, FRP
Piping	Plastic-lined, glass-lined, rubber-lined, Pyrex, FRP, alloy 625, alloy 20Cb-3 alloy 625, alloy C-276, zirconium
Valves	Plastic, rubber, or glass-lined; tantalum-plated, high-silicon cast iron, alloys as for piping above
Pumps	Same as valve materials; impervious graphite
Gaskets	Graphite fiber, felted PTFE, rubber and elastomers

6.5. Formic Acid

6.5.1. General

Formic acid is a strong acid, approaching the dilute mineral acids in its activity (i.e., its tendency to release hydrogen ions). It can be particularly aggressive when hot and anaerobic. In the anhydrous state, it is a powerful dehydrating agent. The acid has a tendency to decompose, liberating carbon monoxide and water.

6.5.2. Specific Materials

Following is a brief discussion of specific materials. For more comprehensive details, see the recommended reading materials listed at the end of this chapter:

6.5.2.a. Light Alloys

Although aluminum has been used to ship 95 to 99% formic acid, it is strongly attacked below approximately 30% at temperatures only slightly above ambient.

Iron and Steel. Iron and steel are rapidly corroded by formic acid. The 14% silicon grade (UNS F4 7003) resists water solutions but not anhydrous acid above room temperature.

6.5.3. Storage and Handling

Basically, formic acid is stored and handled in austenitic stainless steel. Heating coils in tanks should be of a high-performance grade, such as alloy 20Cb-3* (N08020) and pumps the cast equivalent, CN-7M (N08007).

6.6. Acetic Acid

6.6.1. General

Acetic acid is probably the most commercially important of the organic acids. The specifics of the manufacturing process have a lot to do with the corrosivity in the crude state (although refined or CP [chemically pure] acid is quite predictable). When produced by oxidation processes, peracids or peroxides are formed, which, although unstable, can profoundly affect the behavior of many metals and alloys.

6.6.2. Specific Materials

Behavior of specific categories of materials in acetic acid is as follows:

6.6.2.a. Light Metals

Aluminum is widely used for shipment and storage of refined concentrated acids, free of chlorides or heavy metal ions. (Dilute solutions can be severely corrosive because of increased ionization.) Even in cold concentrated products, a fine haze of aluminum salts may develop, which may be incompatible with product specifications.

6.6.2.b. Iron and Steel

Iron and steel are subject to attack at several hundredths of an inch per year in all concentrations of organic acids and cannot be used for shipment and storage. However, the high silicon iron (UNS F47003) will resist all concentrations at least to the atmospheric boiling point.

6.6.2.c. Stainless Steels

Stainless steels of conventional martensitic and ferritic groups are of no practical importance in this application, but the superferritics (e.g., alloys 29-4C [S44735] and 26-1 [S44626]) can be employed.

Austenitic grades, on the other hand, are very important. Type 304 is used for handling and storage of refined acids up to approximately 70°C (160°F), although "hot-wall" effects can be dangerous and type 316L has become the industry standard. Above that temperature range (or for steam-traced piping), type 316L must be used. Intergranular corrosion is a chronic phenomenon in all hot organic acids. To ensure continued passivity of even austenitic grades, at least trace amounts of oxygen or oxidants must be present. Selective corrosion of welds

The high-performance alloys (e.g., alloys 825 [N08825] and 20Cb-3 [N080201]) handle some very tough borderline conditions. They are sometimes used for welding type 316L vessels or weld-overlaying flange-faces and other areas subject to crevice corrosion. (4) *Lead*. Lead is not commercially useful in organic acids, although it has sometimes been successfully employed in very dilute acetic acid streams. Oxidizing agents severely aggravate attack.

The resistance of copper and its zinc-free alloys depends entirely upon the presence or absence of oxidizing agents. Copper and high-strength, zinc-free copper alloys are used in all concentrations of organic acids up to the atmospheric boiling point, but only under anaerobic and otherwise non-oxidizing conditions. Even slight attack will severely discolor the refined acid.

Alloy 200 is rarely employed in this type of service, although alloy 400 (N04400) is occasionally used in lieu of copper. Alloy 600 (N06600) is not usually of any interest in such applications. Alloy B-2 (N I 0665) is used only for special process conditions. However, alloys 625 (N06625) and C-276 (N I 0276) are used for the toughest services (e.g., acetic acid vaporizers, seawater cooled exchangers).

Titanium is the most commonly employed of the reactive metals. It has performed well under oxidizing conditions, but can corrode catastrophically otherwise. Zirconium is an acceptable but more expensive material, while tantalum is resistant but rarely required.

Silver was a traditional material for handling hot organic acids and for heating coils in stainless tanks, but it has been replaced to a great extent by modern nickel-based alloys.

Plastics are suspect because of the solvent effects of organic acids, but fluorinated grades are fully resistant and polyethylene drums are ideal for ambient temperature storage of c.p. acetic acid. The bisphenol polyesters have been successful in some applications. Rubber is a traditional material in dilute acetic acid storage. Above 5% concentration, only a few synthetic elastomers (e.g., butyl, EPDM) are resistant, and only butyl rubber will resist glacial acetic up to 80°C (175°F).

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6.6.3. Handling and Storage

The ambient storage of acetic acid presupposes aerobic conditions, because of the high solubility of dissolved oxygen. Following is a listing of materials of construction for a variety of equipment, which selection is thought to constitute good engineering practice with minimum risk:

Equipment	Typical Engineering Materials
Tanks	Aluminum or 304L
Piping	304L
Valves	CF-3M or CF-8M
Pumps	CF-3M
Gaskets	Spiral-wound PTFE/stainless steel

Acidic gas which form a weak reducing acid ...

7.1. Introduction

Carbon dioxide is an acidic gas which forms a weak reducing acid (carbonic acid) upon dissolution in water. It is a naturally occurring constituent in air (several hundred parts per million), from which it dissolves in condensed moisture or water, with a buffered pH of approximately 5.7, corresponding to approximately

12 to 15 ppm of CO₂ in the solution. At higher partial pressures of carbon dioxide, as when it is in a natural gas or process steam, a pH as low as 3.5 may be encountered. Dry carbon dioxide is noncorrosive.

The weak water solution (carbonic acid) is sometimes thought of as only mildly corrosive. This is because many of the studies have been conducted with natural waters, in which bicarbonates and other ions may buffer the acidity and otherwise influence corrosion.

In distilled water and in process streams containing water, carbonic acid can be severely corrosive to iron and steel. In fact, in carbonic acid, hydrogen evolution begins at approximately pH 5 and *total acidity* is a better indication of corrosivity than is pH.

Low pH solutions will lose carbon dioxide by volatilization at ordinary temperatures and pressures (like a carbonated beverage going flat). Great care must be taken in sampling water solutions for analysis (i.e., containers full to the brim and tightly sealed), to be sure that the samples are truly representative of the original dissolved gases.

7.2. Specific Materials

7.2.1. Light Metals

Magnesium is corroded by mildly acidic carbonic acid solutions, but aluminum and its alloys are resistant (in the absence of heavy metal ions like iron, copper, or lead, and in the absence of chlorides).

7.2.2. Zinc

Zinc, as galvanizing for example, is rapidly corroded by carbonic acid, both because of the acidity and because the corrosion products are quite soluble.

7.2.3. Ferrous Metals

Carbon dioxide alone (e.g., in the absence of dissolved oxygen [DO]) is often reported to be only slightly corrosive (e.g., in natural waters). However, if the carbon dioxide as carbonic acid is constantly replenished (e.g., either by flow or by a high partial pressure of carbon dioxide in the vapor space), corrosion of iron or steel will occur at rates of several tenths of an inch per year. Rates of the order of 200 m/y (5 mm/y) are observed at 25°C under 145 psi (1 MPa) CO₂ and at 50°C (122°F) under approximately 30 psi (207 kPa) partial pressure. In the presence of oxygen, there is a synergistic effect, the total corrosion being greater than would be caused by the same amount of DO and carbon dioxide acting separately. Also, cast iron suffers graphitic corrosion in such weak acid environments.

The ASTM A 242 steels of improved resistance to atmospheric corrosion (see Chapter 21) are somewhat better than carbon steel in steam condensate contaminated with carbon dioxide.

7.2.4. Stainless Steels

All grades of stainless steels are satisfactorily resistant to carbonic acid. Corrosion, when it does occur, is the result of contaminants, such as chlorides, or the conjoint or independent action of other species such as hydrogen sulfide, ammonia, or low-boiling alkyl amines.

7.2.5. Lead

Lead and its alloys are usually only slightly attacked by carbonic acid solutions, except under velocity conditions. However, corrosion is severe in the presence of oxygen, or particularly, peroxides or other strong oxidants.

7.2.6. Copper Alloys

Except for the problem of dezincification of yellow brass, corrosion of copper by carbonic acid is controlled solely by DO or other oxidants. In practice, copper alloys are rarely employed, because of the ever-present danger of oxygen ingress and the economic superiority and reliability of other materials, such as stainless steels.

7.2.7. Nickel Alloys

With the exception of alloy 400 (UNS N04400), which is attacked at certain critical ratios of oxygen to carbon dioxide in water, all nickel alloys resist attack by carbonic acid. However, they are not usually an economical choice unless there are other corrosive species, such as chloride, present simultaneously.

7.2.9. Nonmetallic Materials

All plastics and elastomers of industrial interest are resistant to carbonic acid corrosion within their normal temperature/pressure limitations.

Cement and concrete are subject to severe attack by carbonic acid, due to the solubilization of calcium compounds. However, glass, ceramics, carbon, and graphite are inert.

8. Corrosion in Alkaline Environments

From mildly alkaline, corrosion mitigating, environments to aggressive caustics ...

8.1. General

Pre-eminent among the alkaline environments are sodium hydroxide and ammonia (the latter is covered, together with its organic derivatives, the amines, in the next chapter). Sodium hydroxide is commonly called caustic soda. The term *caustic* refers to materials capable of eating away (or burning, especially as to flesh); it is loosely used for the group of strong alkalis like sodium hydroxide, potassium hydroxide (caustic potash), and calcium hydroxide (caustic lime). Sodium carbonate is a relatively strong alkali, but its major problem is a tendency to hydrolyze to sodium hydroxide at elevated temperatures.

8.2. Sodium Hydroxide

8.2.1. General: Properties

Sodium hydroxide (NaOH) is a white hygroscopic solid with a melting point of 318°C (604°F) and a solubility in water at room temperature which yields a 78% concentration.

With amphoteric metals (i.e., those attacked by both acids and alkalis, such as aluminum or zinc), the alkali reacts directly with the metal, liberating hydrogen, just as in acid attack. With other metals and alloys, reaction is characterized by the formation of relatively insoluble hydroxides on the surface, limiting the attack. For this reason, caustic or alkaline materials are not as universally corrosive as acids.

Corrosion, when it occurs, is due to special effects, such as the formation of complex compounds, double salts, basic salts, or double hydroxides. An example is the reaction of iron with caustic to form sodium ferroate. As the caustic solutions become hotter and more concentrated, there is a greater tendency for them to react directly with metal. In effect, iron and steel exhibit amphoteric characteristics in strong, hot sodium hydroxide.

8.2.2. Specific Materials

The following sections deal with resistance of the various groups of material to alkaline environments.

8.2.2.a. Light Metals

Aluminum and magnesium are non-resistant to caustic.

8.2.2.b. Iron and Steel

The corrosion resistance of iron and steel is usually acceptable up to approximately 70% caustic at 80°C (175°F), except for the problem of see (i.e., "caustic embrittlement"), if iron contamination is not objectionable. However, the corrosion rate increases rapidly with temperature, reaching more than 12.5 mm/y (500 mpy) at 100°C (212°F). This can cause high rates with steam-traced carbon steel piping, for example, when static rather than flowing conditions prevail.

Caustic embrittlement is a misnomer; the metal matrix retains its inherent ductility, although a brittle fracture typical of environmental cracking ensues. The parameters of temperature and concentration above which see is expected to occur are illustrated in Figure 27.1.

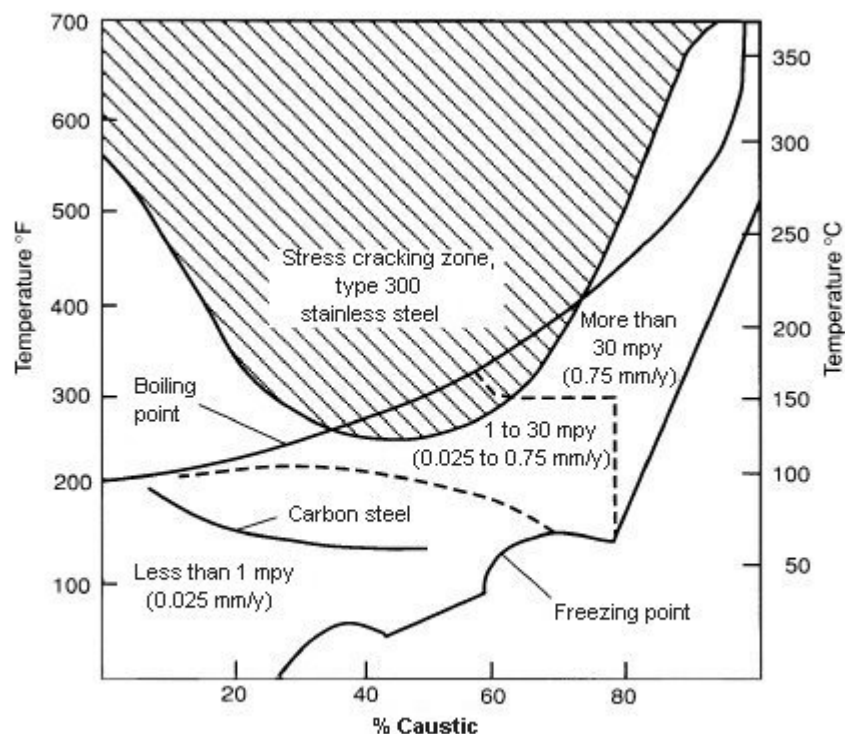


Figure 27.1 Caustic cracking curves for steel and 18-8 stainless steel.

The time to failure can be greatly extended by thermal stress-relief, which is mandatory for either *welded* or *cold-formed* steel equipment, (e.g., flared pipe), within the see limits. Applied stresses are also to be minimized. It is generally believed that stresses must be at or above the yield point for caustic cracking to occur. Because of the relatively high freezing point of concentrated sodium hydroxide (which necessitates heating lines and vessels), see is a problem even under ordinary storage conditions.

Additions of nickel to iron and steel greatly increase corrosion resistance. The high nickel cast irons (e.g., the several grades of Ni-Resist) are popular for caustic services.

8.2.2.c. Stainless Steels

The conventional straight chromium grade martensitic and ferritic stainless steels are unreliable in caustic above ambient temperatures. They may become active and exhibit less resistance than ordinary steel. The superferritics (e.g., alloy 26-1 [UNS S44626]) have distinctly different properties and have been used successfully in caustic evaporators.

Note: This application may be profoundly influenced by the concentration of residual oxidizing species, such as chlorates, in the caustic. At temperatures greater than approximately 300°C (570°F), see is a real problem.

The type 300 series is more resistant than ordinary 12% and 17% chromium grades, but can also lose passivity and suffer severe corrosion. The probable practical limits for types 304L and 316L are 50% caustic at 70°C (160°F) and 40% at 80°C (175°F).

At and above 300°C (570°F), the austenitic stainless steels including the superstainless grades, are easily stress-cracked by caustic, or even by sodium carbonate, because of hydrolysis effects. Sodium hydroxide of 10% concentration has caused SCC in autoclave tests. Plant failures are encountered in environments ranging from caustic-contaminated steam to molten sodium contaminated concentrations of water in parts per million. The temperature at which see of type 300 series stainless steel by caustic becomes a problem is not known with certainty, and probably varies with oxygen/oxidant content. A curve based on laboratory data in chemically pure sodium hydroxide is included in Figure 27.1 above, (the curve for steel is based on plant experience).

8.2.2.d. Copper Alloys

There is relatively little information about copper alloys in the literature, because copper contamination is objectionable in the rayon industry (color) and the soap industry (rancidity), both of which are major users of caustic. Nevertheless, in the absence of strong oxidants (e.g., chlorates, hypochlorites), copper alloys are very resistant. The cupronickels have been used in many applications in which copper contamination was not a problem. Low-zinc bronze valves and pumps are very economical for handling caustic (oxidant - free), while copper pipe has sometimes been used when it was impractical to stress-relieve steel pipe in the field.

8.2.2.e. Nickel Alloys

Commercially pure nickel (i.e., alloy 200 [UNS N02200]) will handle any and all caustic solutions and even molten 100% sodium hydroxide. Eventually, it may suffer see at temperatures of the order of 325°C (620°F) over a prolonged period of several years. It is widely used, in the form of nickel-clad steel vessels, to handle strong hot caustic. Above

Alloy 600 (N06600) is often preferred for piping, because it is more easily welded in the field. It is also preferred for heating coils, because of its greater strength at steam temperatures, although this may introduce trace amounts of hexavalent chromium ions (which may be detrimental to produce quality). see will eventually occur at temperatures greater than 300°C (757°F), but it takes months or years to develop (compared to within hours for type 300 series stainless steels).

Furthermore, its iron and copper content make it objectionable for the more meticulous applications. The higher nickel alloys (e.g., alloys B-2 [UNS N 10665] and C-276 [NI0276]) are rarely needed or considered for this type of service, but should be highly resistant.

Titanium has good resistance up to approximately 40% caustic at 80°C (175°F). Resistance is improved by anodizing the metal to reinforce the surface oxide film, and also by the presence of oxidizing species in the caustic. Galvanic couples may cause hydriding, and chloride contamination may lead to penetration of the protective oxide film at elevated temperature.

Tantalum is severely attacked by caustic.

Silver has excellent resistance to even very hot, concentrated caustic. It was the traditional material of construction prior to the development of the nickel alloys. Gold and platinum are fully resistant, but have no common industrial application.

Carbon and graphite are inherently resistant up to the atmospheric boiling point in all concentrations of caustic. However, commercial impervious graphite will suffer attack on the organic impregnant, and the use of cemented joints further limits its applicability. Phenolic resins are non-resistant, and even with epoxy resins applications are limited to 10% caustic (maximum) and approximately 125°C (255°F).

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PE, PP) are suitable for caustic solutions, within their normal limitations of temperature and pressure.

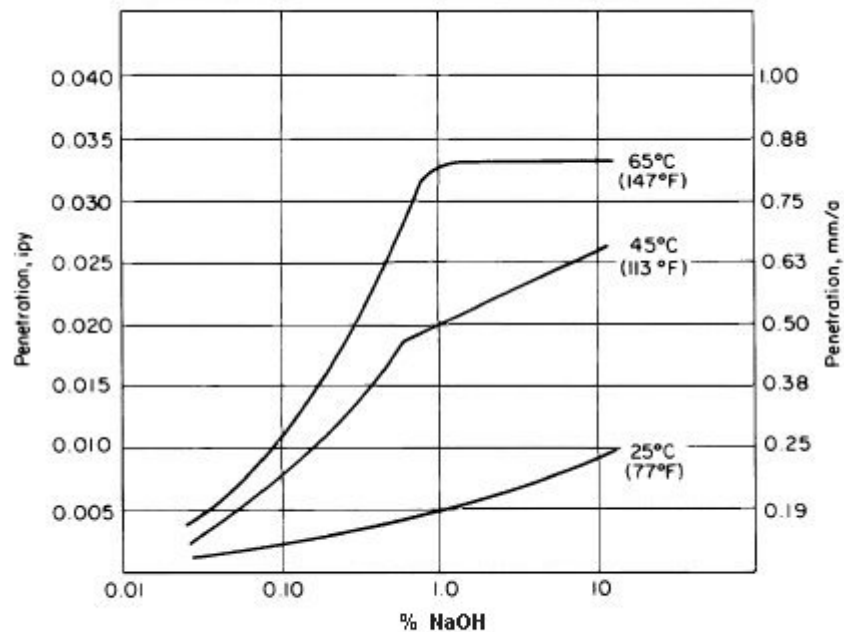


Figure 27.2 Caustic vs borosilicate glass.

FRP piping based on epoxy resins has been used for up to 50% caustic, within its temperature limitations. An incremental advantage is gained by incorporating a Dynel veil below the surface of the gel coat, to protect the fibers of the glass reinforcement from direct contact with alkali.

8.2.3. Handling and Storage

Following is a listing of materials of construction for various items of equipment, which listing is thought to constitute good engineering practice with minimum risk:

Equipment	Typical Engineering Materials
Tanks	Carbon steel, stress-relieved
Piping	Carbon steel, stress-relieved, cast iron; FRP (epoxy), plastic-lined steel, alloy 600
Valves	Ductile iron; low-zinc bronze; steel

.....

8.3. Potassium Hydroxide

8.3. Potassium Hydroxide

8.4. Calcium Hydroxide

8.4. Calcium Hydroxide

8.5. Alkaline Salts

8.5. Alkaline Salts

9. Ammonia and its Compounds

Important industrial gas, forming alkaline solutions and a number of derivatives ...

9.1. Introduction

Ammonia is a pungent gas which dissolves in water to form the alkaline ammonium hydroxide. Ammonium salts are encountered particularly in the fertilizer industry. Organic derivatives are called *amines*, the bulk of which are encountered as alkyl amines, alkylene amines such as ethylene diamine, or alkanolamines such as monoethanolamine (MEA).

9.2. Ammonia and Ammonium Hydroxide

9.2.1. General

Anhydrous ammonia is specific for SCC of carbon steel unless inhibited with approximately 2,000 ppm water. It is routinely handled in bulk storage in steel, however. The presence of moisture or the formation of an aqueous solution changes the corrosion characteristics considerably.

9.2.2. Specific Materials

The behavior of specific groups of materials to ammonia and ammonium hydroxide are as follows.

9.2.2.a. Light Metals

Aluminum and its alloys are mildly corroded (less than approximately 0.1 mm/y) in ammonium hydroxide up to approximately 50°C (120°F).

species is probably ammonium carbamate or a derivative, and can attack steel (and even stainless steel at higher temperatures and pressures) at rates of the order of 3 mm/y (120 mpy) or more. This is the probable cause of a number of corrosion failures in vessels stripping ammonia from a process environment, when the potential problems due to carbon dioxide ingress were not recognized in advance.

9.3. Amines

9.3.1. General

Certain characteristic problems arise from the handling of amines, either as the product itself or in acid-gas scrubbing systems used to remove carbon dioxide and/or hydrogen sulfide from other gases. The problems arise from the dual nature of amines, which are both strong organic solvents and (in water solution) alkalis.

9.3.2. Specific Materials

The corrosion resistance of specific groups of materials to amines is as follows.

9.3.2.a. Light Metals

Aluminum is commonly used for the shipment and storage of refined amines. However, it must not be used as a *heating coil* in hydroxylated amines (e.g., monoethanolamine) because of severe exothermic corrosion after an induction period of some indeterminate time.

9.3.2.b. Iron and Steel

Amines of all kinds readily form iron complexes with steel and may not be stored in steel when iron contamination is objectionable. Steel tanks are employed for MEA and other such products to be used in acid-gas scrubbing systems. Amines can be severely corrosive to steel under process conditions at elevated temperatures, particularly above 80°C (175°F). Amines are not specific for SCC. When encountered, cracking is usually due to contaminants, notably hydrogen sulfide, which causes SSC of critically hard-steel components (see Chapter 25), although cyanides in acid gas streams have also caused cracking.

9.3.2.c. Stainless Steel

Amines are successfully stored in type 304 tankage, but the molybdenum-bearing grades (e.g., type 316) are required above 100°C (212°F) in their manufacturing process. Intergranular corrosion, requiring type 316L, is not usually encountered unless there are specific contaminants present. Valves and pumps should be CF-8M or equivalent, rather than CA-6NM (J91540) or other lower alloys.

9.3.2.d. Lead

Lead is subject to corrosion by aqueous amines. Existing lead-lined tanks have been used for storage of MEA at ambient temperatures, when lead contamination was not objectionable.

9.3.2.e. Copper and its Alloys

As with ammonia, copper alloys can resist amines under anaerobic conditions. However, the ever-present danger of color formation, corrosion, and SCC (e.g., due to ingress of air and moisture) renders them generally unacceptable except for certain well-defined and controlled conditions.

9.3.2.f. Nickel and its Alloys

With a few exceptions, and because of cost considerations, nickel alloys are only rarely selected for amine-type services. Alloy C-276 (UNS N10276) centrifuges have been used, but only to combat specific process problems such as in urea plants or in amine manufacture.

9.3.2.g. Nonmetals

Carbon and graphite are inherently resistant, but the solvent action will attack phenolic impregnants. Epoxy-cemented impervious graphite heat exchangers are successfully used in acid-gas scrubbing systems such as for MEA solution interchangers.

10. Salts

Neutral, acidic, alkaline, oxidizing, reducing, halides ...

10.1. Overview

Salts are the products of reaction between an acid and a base (e.g., sodium chloride from caustic and hydrochloric acid). In this case, the salt is a neutral salt, having neither acidic nor base characteristics because it is the product of a strong acid and a strong base. Water solutions of neutral salts simply increase the electrical conductivity of the solution, although the effect of specific ions such as chlorides causing pitting or stress must also be considered. In some cases, an oxidizing anion will also have specific effects, as with sodium nitrite, for example.

Acid salts are formed by the interaction of a strong acid and a weak base, and act very much like a weak solution of the parent acid. For example, ammonium sulfate solutions act like dilute sulfuric acid except for reactions specific to the ammonium ion, as with copper. Also, oxidizing cations will affect the redox potential and the corrosion characteristics of the solution, as with cupric sulfate or ferric chloride, for example.

Basic salts are the product of a strong base (e.g., sodium hydroxide) and a weak acid (e.g., acetic acid). They act like a weak alkali. Any oxidizing capacity will derive from the acidic anion (e.g., as in sodium chromate, sodium nitrite, or sodium hypochlorite), as there are no strong oxidizing alkalis.

Oxidizing salts, whether acidic or basic, pose special problems and are discussed separately below.

10.2. Neutral Salts

These are usually sodium or potassium salts formed from the corresponding alkali. The sodium or potassium ions per se usually cause problems only in high temperature corrosion (Chapter 31). The anions do have specific effects, as with chlorides causing pitting or SCC, and sulfates being reduced by bacterial action to sulfides and dissolved sulfur.

Increasing concentrations of salt lower the solubility of dissolved oxygen. Note that a solution with 6,000 ppm of chloride ion in water has maximum corrosivity to steel, because of lower dissolved oxygen (DO) at higher concentrations.

The increased conductivity associated with any salt solution may aggravate galvanic corrosion by allowing greater cathode-to-anode ratios to come into play.

Neutral sulfates are aggressively corrosive to portland cement mixtures, as previously discussed

10.3. Acid Salts

Although these act like weak solutions of the parent acid, corrosivity diminishes with polybasic acids containing more than one hydrogen, as the hydrogen ions are successively replaced with less acidic cations. For example, monosodium phosphate is more corrosive than disodium phosphate. Trisodium phosphate is a mildly alkaline salt, as discussed further below.

Nonoxidizing acid chlorides (e.g., magnesium chloride) are not only corrosive to steel and other anodic materials by virtue of their acidic nature, but are highly specific for the SCC of type 300 series stainless steels, particularly.

Ammonium salts, in the presence of oxygen or oxidants, aggravate the corrosion of copper and nickel alloys (other than the chromium-bearing variety) by complexing and solubilizing the surface films which would otherwise limit corrosion.

10.4. Alkaline Salts

The alkaline salts are those resulting from the reaction of a strong base (e.g., sodium, potassium, lithium, etc.) with a weak acid. They act like a weak alkali. In most cases, the sodium salts are our primary concern.

Sodium carbonates and bicarbonates, particularly, may be thermally decomposed to yield free caustic, with its attendant problems. Otherwise, the sodium salts are a problem primarily with materials not resistant to alkalis. Trisodium phosphate, for example, is a mildly alkaline compound whose water solution is noncorrosive to copper and steel but has a mild etching effect on aluminum.

If the anion has oxidizing capacity, the corrosion characteristics can be drastically different.

10.5. Oxidizing Salts

Neutral or alkaline oxidizing salts, if they contain no halides as constituents or contaminants, are not very corrosive. Sodium chromate and sodium nitrite solutions can be handled in iron and steel, and are in fact, effective corrosion inhibitors for ferrous alloys in water (see Chapter 35). On the other hand, if sufficiently alkaline, solutions of oxidizing salts may attack amphoteric metals (e.g., lead).

The hypochlorites are corrosive to copper, nickel, and lead but are easily handled by some plastics (e.g., PVC). They will not corrode steel to a significant extent unless they also contain free chlorine, as with certain proprietary formulations such as HTH (high-test hypochlorite). However, sodium hypochlorite is unstable in steel and can cause pitting. Alloy C-276 (N10276) is resistant but causes slow decomposition. Titanium is the preferred material for storage. EPDM is usefully resistant, while PVC may be used for temporary storage and feed piping in chlorination systems.

With the acidic salts, oxidizing cations such as ferric (Fe^{III}) or cupric (Cu^{II}) convey oxidizing characteristics to solutions which would otherwise act simply like dilute acids. Ferric sulfate or cupric phosphate are more aggressive than the corresponding calcium or magnesium salts, because their cations (being capable of reduction) act as cathodic depolarizers.

Oxidizing halides, like ferric chloride or cupric chloride, are very corrosive and cause pitting and/or SCC in susceptible alloys, as well as general corrosion, IGA, and sometimes selective weld attack. At moderately elevated temperatures, even alloy C-276 (N21076) is of limited usefulness. For the more aggressive conditions, only tantalum, glass, fluorinated plastics, or carbonaceous materials will contain them.

It is interesting to note that ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), in the presence of an excess of acid to suppress internal hydrolysis, has a vapor pressure about equal to that of mercury. It can therefore travel about a process as a vapor (where its presence may not be anticipated), leaving severe corrosion, pitting, or SCC in its wake, depending upon the material of construction. Steel may show localized corrosion of welds; copper and nickel alloys suffer general corrosion; and stainless steels suffer pitting, crevice corrosion, and/or SCC.

Hot gas environments ...

11.1. Introduction

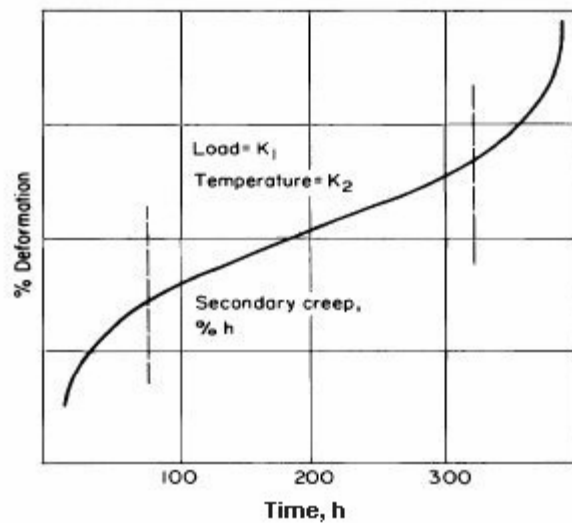
The earliest demand for good high temperature materials arose in the power-generating industry, whose temperature requirements for boilers have risen steadily.

At the present time, demands are also made by the petrochemical and nuclear industries, as for gas cracking in the 1,100°C (2,000°F) range, and by aerospace requirements.

11.2. Metal Behavior

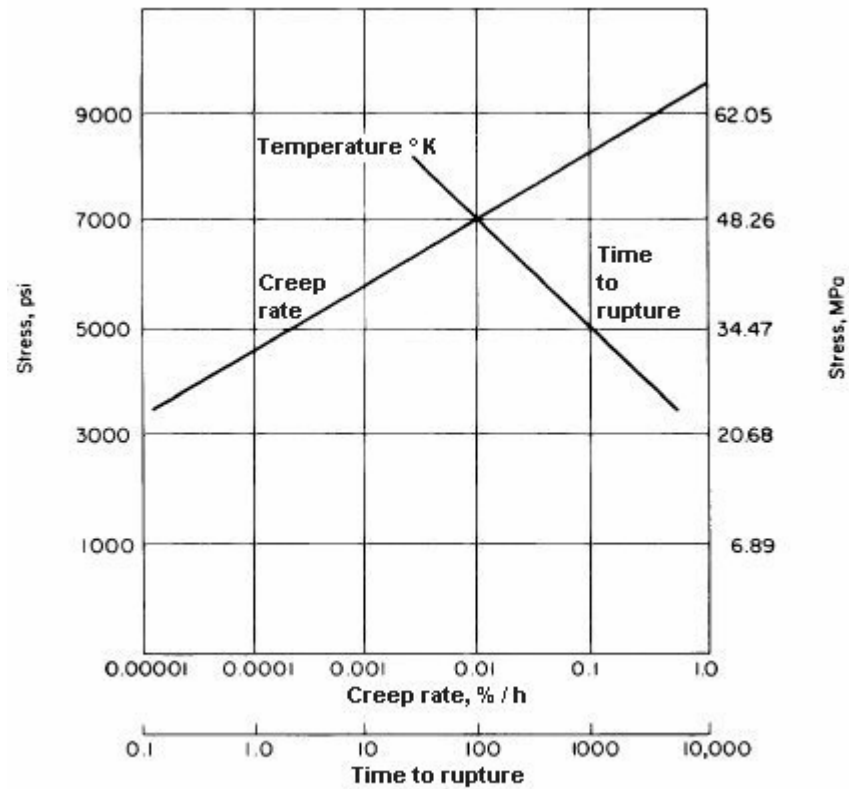
There is a fundamental change in a metal's behavior when the temperature exceeds approximately 35% of its absolute melting range (or 40 to 60% for some nickel-based and cobalt-based alloys). Below that value, application of mechanical loads below the yield strength results in no permanent deformation when the load is removed. After the load is released, the metal item resumes its original dimensions, for all practical purposes. (It should be noted, however, that metallurgical changes can and do occur at relatively low temperatures; e.g., tempering, recrystallization, age-hardening, embrittlement, etc.)

Above some critical temperature, *creep* becomes a factor. Creep is time-dependent strain under constant load. The longer the load at some temperature is endured, the greater the permanent deformation (until rupture occurs). Creep is expressed as percent deformation per thousand hours. A typical creep curve is illustrated in the Figure below.



Time-deformation (creep) curve.

Design stresses for bolting and for unfired pressure vessels are 100% of the creep strength for 0.01 % per 1,000 hours at temperature. ASME power boilers may also be designed at 60% of the 100,000-hour rupture strength (Figure below).



Creep Rate and Stress-Rupture Time.

11.3. Internal Stability

Temperature alone, without regard for the environment, can effect metallurgical changes in an alloy. In addition to the changes already mentioned, one may encounter *temper* or *blue embrittlement* in the 455 to 600°C (850 to 1,100°F) range and/or graphitization of steel. Sensitization can occur in austenitic stainless steels and formation of intermetallic compounds, such as sigma or chi phase, in specific alloy systems. Such internal changes may affect mechanical properties or corrosion resistance, or both.

11.4. Surface Stability

Depending on the nature and activity of the hot environment, an alloy may be subject to carburization, decarburization, or nitriding (sometimes severe, sometimes of a superficial nature).

11.5. High-Temperature Corrosion

11.5.1. Introduction

All forms of attack at elevated temperatures in which the metal is converted to a corrosion product (solid, liquid, or vapor, depending on the metal/environment combination) are considered to be *oxidation*, in a manner analogous to aqueous corrosion. There is even electron transfer involved, and an "electrolyte" (i.e., the semiconductive layer of corrosion products). There is a definite migration of ions and electrons between the three phases (i.e., the metal, corrosion product layer, and environment). Unlike metals, electron transfer increases with temperature in a semi-conductor.

There is an ordering of metals at high temperature, analogous to the electromotive series. Gold will remain bright and unoxidized up to its melting point, while less noble metals oxidize more easily. The important thing to note is the *reversibility* of the reaction of metals with oxygen to form the oxide, depending on the specific metal, the temperature, and the nature of the environment.

For example, mercuric oxide rapidly releases oxygen at atmospheric pressure at approximately 500°C (930°F). On the other hand, for nickel oxide to release oxygen at 1,200°C (2,200°F) requires that the partial pressure of oxygen be reduced to below 10^{-7} atm (0.01 Pa). Otherwise, the nickel oxide will remain stable.

Just as the electromotive series does not apply when one departs from pure metals at standard conditions, diagrams relating

the parameters for metal/metal oxide equilibria in different types of atmospheres (e.g., the Richardson diagram) do not apply to complex alloys. Also, the thermodynamics of a situation (which tell what *can* happen) do not reveal the kinetics of what *will* happen.

The rate at which a metal will oxidize depends upon how protective the oxide layer is. If it is wholly non-protective, the rate (i.e., usually weight gain) will be *linear* with time. If it is protective (and remains in place), the rate will be *parabolic* or *logarithmic*, diminishing with time. The structure of the oxide film also determines how easily metal ions can diffuse out (and gaseous species in).

In practice, cycling temperatures may spall off the surface oxidation products, leading to a *para-linear* rate (which just means that oxidation proceeds in a step-wise fashion). Changes in the nature of the environment, of course, can also remove or modify the surface products, as can mechanical effects.

11.5.2. Oxidation/Reduction

In hot air, oxygen, steam, carbon dioxide, etc., the environment will tend to oxidize a metal. With hydrogen, hydrogen-rich gases, or carbon monoxide, the environment is reducing, and tends to convert oxides back to the metallic state.

In *mixtures*, the ratio of carbon monoxide to carbon dioxide determines the carburization or decarburization conditions. The generalization extends to other combinations of oxidizing and reducing species, such as hydrogen and water vapor, nitric oxides and ammonia, and

sulfurous oxides with hydrogen sulfide. An atmosphere may be reducing to one component such as nickel but oxidizing to another such as chromium or silicon, which further complicates the picture. The most reliable data are those determined experimentally.

Catastrophic oxidation may also occur, as when silicon oxide dissolves in nickel, or when molybdenum is vaporized as the oxide (e.g., from type 316 under insulation or deposits).

11.5.3. Sulfidation

Sulfidation is directly analogous to oxidation, but is aggravated by the lower melting points of many metallic sulfides and by the formation of low-melting eutectics (as in welding of sulfur-contaminated nickel alloys). Also, sulfide scales are less protective than oxide films.

11.5.4. Halogens and Hydrohalides

Because of the volatility of many metal halides, chlorine and hydrogen chloride are very aggressive at elevated temperatures. Fortunately, nickel alloys tend to be resistant. However, gold and silver are readily attacked by hot chlorine. While in hydrogen chloride, silver is attacked at approximately 230°C (450°F), gold is good to approximately 870°C (1,600°F).

11.5.5. Molten Salts

Many molten salts, alkaline or halide, attack metals at high temperature because they flux the surface films, continuously exposing fresh metal to attack. This is analogous to activation of passive metals, or solubilizing of films by complex metal ion formation, in aqueous corrosion.

11.5.6. Fuel Ash Corrosion

This is a special form of hot salt corrosion, in which the combination of sodium sulfate and chloride with vanadium compounds (as from certain types of crude oil fuels, for example) provides a very low-melting eutectic compound. This aggravates the fluxing, causing it to occur at lower temperatures than one would otherwise expect.

11.5.7. Molten Metals

Certain molten metals (e.g., mercury, lead, bismuth, etc.) are used as coolants in special (experimental) nuclear reactor systems. A sodium-potassium alloy (NaK) is also used. Such metals may dissolve a metal in the hotter sections by solubilization and then deposit it in the cooler sections (where solubility is lower), causing physical blockage.

Contamination of molten metals by their own oxides (e.g., NaO in Na or NaK) can also cause specific corrosion phenomena.

11.6. Effects of Alloying Elements

Alloying additions, such as chromium, aluminum and silicon, tend to form protective films which effectively limit the transport of reactive metals to the environment and of the environment inward to the metal. For practical purposes, these alloying elements enhance the formation of stable, low-volatility films, free of pores and adherent to the substrate. Nickel reinforces the effectiveness of chromium and also increases resistance to carburization, gas sulfidation, and (up to approximately 80% nickel) attack by hot ammonia.

Chromium is the major alloying element in iron-, nickel- and cobalt-based alloys developed for high temperature resistance. Aluminum additions, while effective against oxidation, yield alloys which cannot be readily fabricated. Silicon is used as a minor, supplementary addition to increase the efficacy of chromium. Some rare earth metals also tend to improve the stability of the high temperature scale.

11.7. Heat-Resistant Alloys

11.7.1. General

This terminology usually refers to oxidation-resistant metals and alloys. However, it is necessary first to describe the temperature and oxidation limits for the carbon and low-alloy steels, which are in fact, used to at least moderately elevated temperatures.

11.7.2. Carbon Steel

Steel is not truly useful at temperatures above approximately 450°C (850°F), except in comparison with some non-ferrous alloys. Above this temperature, problems are encountered with high oxidation rates, temper embrittlement, loss of mechanical strength, and graphitization. Graphitization involves the decomposition of iron carbides, liberating free graphite, and is particularly deleterious in the heat-affected zone of welds.

11.7.3. Molybdenum Steel

The addition of approximately 0.5% molybdenum extends the usefulness of steel to approximately 565°C (1,050°F) maximum. On exceeding this limit, however, the familiar problems with oxidation, loss of strength, and graphitization recur. Today, this type of steel, although long a favorite for steam piping, has been practically abandoned in favor of more highly alloyed albeit still low-alloy steels.

11.7.4. Alloy Steels

1.25%Cr-0.5%Mo and 2.25%Cr-0.5%Mo steels are used in refinery applications, particularly, because of their good high-temperature resistance to hydrogen and traces of hydrogen sulfide. They are also used in some high-temperature steam applications.

11.7.5. Stainless Steels

(3) Higher-alloyed stainless steels, such as types 309 (UNS S30900), 310 (S31000), 25%Cr-12%Ni, 25%Cr-20%Ni, and 21 %Cr-33%Ni, extend the usefulness of the austenitic grades in terms of improved resistance to oxidation and carburization, although adequate strength is not obtained until the high-carbon cast variants are employed.

- (1) Alloy 802 (N08802), Cr-Fe-Ni plus W, Cb and Ti;
- (2) Alloy 601 (N06601), Ni-Cr-Fe; and
- (3) Stellite 6 (R30006), Co-27%Cr-4%W.

There is some evidence that internal porosity in centrifugally cast tubing aggravates the tendency for carburization of the internal surface of cracking sets. Much HK tubing purchased today is bored and honed to improve its resistance. A number of castings of proprietary composition are being marked, based on allegedly superior resistance to carburization.

D. Practical Materials Selection Procedure

*A number of Guidelines and
One possible ‘best practice’ Methodology ...*

Temperature Range is a way to start ...

- Oxidizing versus Reducing character,
- velocity,
- effects of slurries or abrasives,
- vibration or water hammer,
- stagnant, sedimentary conditions.

1.1.1.c. Consideration of Practical Constraints

No decision is made in a vacuum. There may be important constraints that will help narrow down the final materials choice.

1.1.1.d. Corrosion Testing of the most likely materials

Test whenever this is feasible. Even a simple test of a few hundred hours might uncover critical problems.

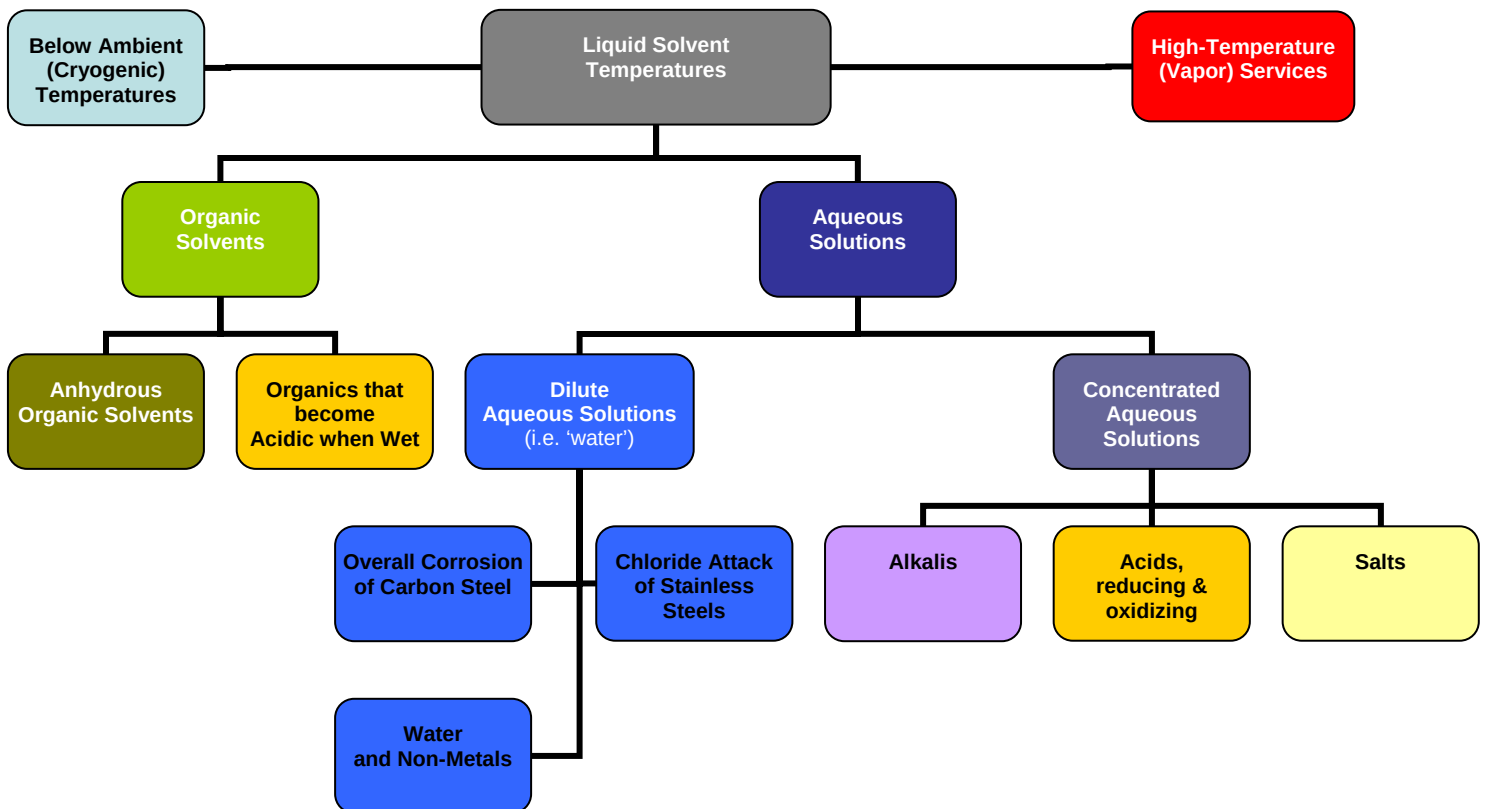
1.1.1.e. Report the results

Never misrepresent a material of construction! In your report recommending a material:

- o ***Define the problem you solved*** – List all the relevant service conditions, then ranges and variations, as described
- o ***List your recommended materials*** – List several materials if possible. Show your preferences: first choice, second choice, and so on. Tell why you rated the choices this way. Your reasons should include the practical constraints listed earlier. Include test results.
- o ***List the limitations on each material*** – The author was once asked about the feasibility of using a kettle-lined with semi-hard natural rubber in a new process to be run at temperatures up to 200°C (392°F). This would have quickly destroyed the rubber. List the limitations of each material to provide a record to guide people in future process additions.
- o **List any maintenance or repair problems**
- o **Estimate the anticipated service life if you can** — In one application, a more expensive modified phenolic mortar was selected over a furan mortar for two brick-lined kettles. The phenolic mortar could be put into permanent compression during curing. Maintenance records showed service lives of 13 to 19 yr for the phenolic mortar, but failures as soon as 5 yr for the furan mortar. This comparison justified the more expensive mortar.

1.1.2. A Practical Materials Selection Reasoning Procedure

The operating temperature range is of critical importance in selecting materials. The Figure below shows a breakdown of temperature ranges, each of which will now be shortly discussed in some more detail. For more practical guidelines and useful figures, the reader is referred to the Appendices at the end of the book.



1.2. Liquid Solvent Temperatures

Metals in conducting solutions corrode electrochemically. There is uniform or general corrosion, plus localized corrosion such as galvanic (bimetallic) interaction, pitting, crevice corrosion, stress-corrosion cracking, intergranular corrosion, selective leaching and velocity effects.

Organic materials degrade by solvent attack, excessive temperature, attack by oxidants, fire, mechanical assault, and fluid permeation, together with pressure/temperature cycling. Masonry or glass may degrade chemically by acid, fluoride, or caustic attack. Concrete may degrade by acid attack and many forms of chemical attack.

Regardless of temperature, any material can fail due to extended cyclic loading (fatigue), impact or excessive loading, or abrasion.

1.3. Low (cryogenic) Temperatures

At low temperatures, a material's notch toughness or impact strength is critical. The cracking apart of the Liberty ships in the cold Atlantic in World War II is the classic example. The carbon steel hulls had a body-centered-cubic metallic crystal structure that is particularly susceptible to such failure. Natural rubber, synthetic elastomers, and other plastics may also embrittle.

At low temperatures, the usual electrochemical corrosion may not be a problem, since any water or solvent phase present may be solid. Occasionally, however, chemical species may benignly accumulate at low temperatures, only to become corrosive whenever the system reaches ambient temperatures – for example, at shutdown.

In nominally “dry” chlorine service, ppm-level traces of water may accumulate in low-temperature equipment in the form of chlorine hydrate crystals. At ambient temperatures, this water may be released to induce severe wet-chlorine corrosion of otherwise suitable alloys such as carbon steel.

1.4. High Temperatures

Metals or alloys can degrade by several mechanisms at high temperatures (cf. *supra*).

Liquid solvent corrosion – This may be minimal if no liquid aqueous solution is present. For example, dry HCl gas can be handled in carbon steel. However, even in hot equipment, there may be colder zones or times (such as shutdowns or breakdowns) that will allow water to condense. Severe corrosion may result.

Reaction with the gaseous environment – Oxidation, nitride formation, sulfidation, chlorination and carburization are examples.

Warning – These chemical reactions involve compound formation. Thus, the surfaces of any test coupons become very important. Metal coupons may have to be sectioned and examined microscopically to look for oxides, nitrides, sulfides, carbides, and so on. Sulfides may penetrate the alloy's grain boundaries. This compound formation means that the corrosion test coupons may actually gain weight during exposure.

Creep rupture – Steady deformation under load may cause excessive dimensional changes or even failure. Lead may creep at room temperatures.

Alloy phase changes – Alloy properties may deteriorate at high temperatures as desirable metastable phases transform into stable but harmful phases. For example, carbon steel properties degrade with prolonged exposure at high temperatures, starting somewhere in the range of 343 to 482°C (650 to 900°F); this occurs because the strengthening iron carbide (Fe_3C) phase (“cementite”) transforms to graphite at elevated temperatures.

Sigma-phase precipitation at elevated temperatures may embrittle some stainless steels or nickel-base alloys. Carbide precipitation may rob an alloy matrix phase of critical elements necessary for corrosion resistance.

Organic materials – Natural rubber may harden, embrittle, and eventually “mud-crack” from prolonged overheating. Plastics may soften, lose their strength, or flow excessively. Protective coatings will crack and peel.

2. Liquid-solvent Temperatures

The majority of the CPI operating conditions ...

2.1. Introduction

In selecting materials of construction to operate at liquid-solvent temperatures, one must decide whether to use metal or polymers. The key considerations are the presence of each oxidizing acids and organic solvents, and strength and temperature limitations.

In general, polymers are more resistant to chloride ions and hydrochloric acids than metals are. Metals are more resistant to oxidizing acids such as concentrated sulfuric acid or nitric. Metals are better than polymers in resisting organic solvents. Compared with metals, polymers are much weaker and softer, with much lower temperature limitations.

2.2. Corrosion Reactions & Metals (general)

For metals, consider electrochemical corrosion. The solvent may be aqueous or organic. Corrosion occurs by galvanic interaction between anodic and cathodic areas.

- By convention, the anodic reaction causes the corroding metal to go into solution via an oxidation reaction that releases electrons.

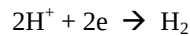
For metal M:



This occurs because most metals are in a more stable form as oxides or other compounds than as pure metals. Except for a few precious metals like gold or silver, they occur as compounds in their natural ores.

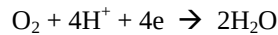
At the cathode, an electrochemically-equivalent reduction reaction occurs. Various types of reduction reactions are possible:

Hydrogen evolution in acid solutions:

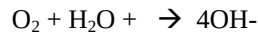


This reaction can be quite rapid since it involves small, relatively simple atomic species.

Oxygen reduction in acid solutions:

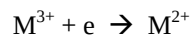


Oxygen reduction in neutral or alkaline solutions:

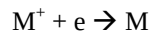


This slower, more complicated reaction is often the rate controlling step.

Metal-ion reduction:



Metal plating:



Hydrogen evolution and oxygen reduction are the most common cathodic reactions.

- Differences in electrochemical solution potentials between anodic and cathodic areas provide the driving force for corrosion. These include:

Differences between metals, alloys or alloy compositions – In a conducting solution such as seawater, zinc will be anodic relative to carbon steel. The steel will be the site of the supporting but noncorroding cathodic reaction. This is how zinc galvanizing protects steel.

In a multi-element alloy casting, the difference in composition between the as-cast grain interiors and the surrounding intergranular areas may accelerate corrosion, due to localized galvanic action.

Differences in the metallurgical condition from one area to another on the exposed metal– A heavily deformed area that has been cold-worked or work-hardened will be anodic and therefore more severely corroded than unworked areas.

Difference in the oxygen concentration of the aqueous solution from area to area – When water corrodes carbon steel, the high-oxygen regions of the solution in contact with the steel are cathodic, which will accelerate the corrosion of nearby oxygen-lean regions (the anodes). For this reason, areas just below the air-water interface of carbon steel vessels may show the most corrosion.

Differences in the dissolved-metal ion concentration from area to area – Regions in a solution that are high in the corroding metal's ion concentration will be cathodic, which will drive other regions to corrode by the anodic reaction.

2.3. Organic solvents

2.3.1. Polymers

Organic solvents may degrade polymers, causing excessive swelling, loss of strength or even disintegration. Temperature accelerates attack, which can occur within days or even hours. The Table below depicts the resistance of various polymers and resins to a range of organic solvents.

Cycling temperature or pressure can destroy any polymer, even polytetrafluoroethylene (PTFE) or fluorinated ethylene-propylene (FEP). Under such conditions, any fluid that has permeated the polymer may expand rapidly as a gas and locally burst the polymer, forming blisters.

Recommendations – Consult resin or polymer manufacturers' brochures for chemical compatibility data; run an exposure test whenever possible, especially for mixtures of chemicals.

		Thermosetting resins						Thermoplastics				Elastomers			
Solvent	Example	Epoxy (250-300° F)	Furan (250° F)	Phenolic (250° F)	Polyester FRP (220° F) (Bisphenol-A fumarate)	Vinyl ester FRP (200° F) (Low-temperature variety)	FEP/TFE (400/500° F)	Nylon 6/6 (200-250° F)	Polyethylene (150° F)	Polypropylene (225° F)	Polyvinyl chloride (140° F)	Polyvinylidene fluoride (275° F)	Butyl rubber (200° F)	Natural rubber (150°° F)	Neoprene (200° F)
Alcohols	Methanol	G	E	G	G	G	E	P	E	E	E	E	E	G	G
Aldehydes	Formaldehyde	G	E	G	G	G	E	E	G	E	G	G	G	G	E
Aliphatics	Heptane	G	E	E	G	E	E	G	P	G	G	E	P	P	G
Aliphatic amines	Diethylamine	G	E	P	P	P	E	P	G	G	—	G	—	—	—
Aromatics (and derivatives)	Benzene	E	G	G	P	P	E	G	P	G	P	G	P	P	P
	Aniline	P	G	G	P	P	E	P	G	E	P	G	G	P	P
	Phenol	G	G	G	F	P	E	P	G	G	P	G	P	P	P
	Xylene	G	E	E	G	G	E	G	P	F	P	G	P	P	P
Chlorinated aliphatics	Trichloroethylene	G	G	E	G	P	E	G	P	P	P	E	P	P	P
	Ethylene chloride	G	G	G	P	P	E	—	P	F	P	E	P	P	P
Ketones	Acetone	G	G	P	G	G	E	G	P	G	P	P	G	P	P
Miscellaneous:															
	Pyridine	P	P	P	P	P	E	F	F	E	P	F	P	P	P
	Tetrahydrofuran	—	P	—	P	—	E	F	P	F	P	F	P	P	P
	Furfural	G	E	P	G	P	E	—	P	P	P	F	—	—	—
Key															
E		= Recommended to maximum temperature of product form													
G		= Recommendation limited to somewhat lower temperature, or restricted in product form													
F		= Very limited recommendation; for ambient temperature only													
P		= Not recommended. Severe attack													
		(Listed temperatures are approximate maximum values for each polymer)													

2.3.2. Metals and anhydrous organic solvents

In the electrochemical theory of corrosion, both the anodic and cathodic reactions involve ions. The most common solvent in the CPI is water, which becomes conductive due to the ions in solution. However, other solvents may also support corrosion if they allow sufficient ionization of the appropriate species.

Methanol is one such solvent. One case involved “knifeline” corrosion along an Alloy B weld that was in HCl/methanol service. This was an anhydrous system. HCl at 0.01M strength ionizes up to 85% in methanol. In some studies of zirconium, anhydrous mixtures of HCl/methanol caused heavy corrosion that increased as the HCl concentration increased.

Adding water decreased the corrosion by starting to generate a protective surface film. At 10% H₂O, this film was complete and, therefore, fully protective. Below 5% H₂O, the film was incomplete and the zirconium was more susceptible to chloride pitting and (at boiling) to stress-corrosion cracking.

Similar examples of water-induced protective films have been observed for titanium in methanol/HCl, ethanol/HCl, methanol/NaCl, and methanol/ferric-chloride. The amounts of water necessary to induce the protective (“passive”) films varied from 0.6-10%.

Chromium can also be passivated by water additions to the methanol/HCl system. Nickel behaves similarly in dimethyl-formamide/H₂SO₄ solutions.

Tantalum can be pitted in anhydrous mixtures of methanol with chlorine, bromine or iodine.

Recommendation – Look for possible corrosion problems in an anhydrous organic/inorganic system if the organic solvent allows corrosives such as HCl, NaCl or H₂SO₄ to ionize.

2.3.3. Organics that become acidic when wet

Many organic chemicals (see Table below) are noncorrosive to metals when sufficiently dry, but become corrosive when wet. Carbon tetrachloride is an example. With no water layer present, carbon tetrachloride is noncorrosive to steel, with a corrosion rate of less than 0.1 mpy at both room temperature and the boiling point. However, with a water layer present, the corrosion rate increases to 8 mpy at room temperature and 160 mpy at the boiling point. Carbon steel would, therefore, be unsuitable for hot, wet carbon tetrachloride. The increased corrosion is due to hydrochloric acid generated by hydrolysis. Hydrolysis occurs more readily at elevated temperatures.

Do not specify Types 304/316 stainless steel for wet carbon chlorinated hydrocarbons that hydrolyze to produce hydrochloric acid. The hydrochloric acid will cause pitting and perhaps stress-corrosion cracking. Alloy 400 (65 Ni-32 Cu) is suitable, corroding at only 2 mpy in wet carbon tetrachloride at the boiling point. Alloy 400 is suitable for the resulting dilute hydrochloric acid so long as the conditions are not oxidizing, such as from excessive aeration.

Dimethyl sulfate (DMS) provides another example. Dry dimethyl sulfate is normally stored and handled in carbon steel. However, it is hydrolyzed by water, producing methanol and

sulfuric acid. Since DMS is also a strong solvent, designing for wet DMS would require either FFP/TFE or an alloy such as Alloy 20.

Recommendation – When an organic chemical includes a chemical group that is the anion for a common acid, inquire about the possibility of hydrolysis causing acidic conditions. This is especially true for chlorinated hydrocarbons with unsaturated bonds at temperatures near the boiling point.

Some organics that become acidic when wet		Table VII
Acetyl chloride	Dichlorodifluoromethane	
Acetylene tetrachloride	Diethyl ether	
Allyl chloride	Dimethyl sulfate	
Ammonium citrate	Dinitrochlorobenzene	
Ammonium oxalate	Ethyl chloride	
Amyl chloride	Ethylene dichloride	
Amyl propionate	Ethyl mercaptan	
Benzaldehyde	Hexachlorobutadiene	
Benzotrachloride	Hexachloroethane	
Benzene hexachloride	Hexaethyl tetraphosphate	
Benzene sulfonic acid	Lead acetate	
Benzyl chloride	Methylene chloride	
Butyl chloride	Nitrophenols	
Carbon tetrachloride	Potassium oxalate	
Chloroform	<i>n</i> -Propyl nitrate	
Chlorophenol	Trimethyl phosphite	
Chlorosulfonic acid	Vinyl chloride	
Citric acid		

2.4. Aqueous solutions

Never assume that dilute chemical solutions are inherently innocuous. Remember that 96% sulfuric acid can be handled in either carbon steel (at low velocities) or Type 316L stainless steel. But 30% sulfuric acid will attack either of these alloys vigorously. Similarly, a spray-applied neoprene-latex coating can be used over carbon steel to decrease iron pickup by 50% sodium hydroxide in storage tanks. This same coating is unsuitable for 20% sodium hydroxide, which is a more penetrating solution. And just plain water will permeate protective coatings, especially monolithic floor coatings when water puddles are present..

Analyze each corrosive situation separately and completely, whether it involves “water” or a concentrated acid.

2.4.1. Dilute solutions ('water')

The critical corrosive effects of dilute aqueous solutions –or “water”– include the overall corrosion of carbon steel, and chloride effects on stainless’ steels (including stress-corrosion cracking, pitting, and crevice corrosion).

2.4.1.a. Corrosion of carbon steel in water

The corrosion of carbon steel depends upon: solution pH, dissolved oxygen in the water, temperature, dissolved salts, solution velocity. Details have already been discussed in Section C, Chapter 2. Below, some important practical considerations are summarized.

Effects of dissolved oxygen and pH – In the absence of dissolved oxygen, the corrosion rate of carbon steel in room-temperature water becomes negligible. As the oxygen content is increased up to air saturation, the corrosion rate rises almost linearly (equation above) combinations of CO₂ and O₂ can make water very corrosive. Steel has been badly corroded when exposed to limestone scrubbing solutions containing CO₂ and O₂ at pH values no more acidic than 5. For steel condensate-return lines, CO₂/O₂ solutions at 60°C (140°F) have given corrosion rates of 30 to 50 mpy at pH values between 5 and 7.

An interesting rule-of-thumb:

For water of about neutral pH, the corrosion rate is given approximately by:

$$\text{Corrosion rate, mpy} = 2 \times \text{Oxygen content, mL/L}$$

At 6 mL oxygen/L, this means a corrosion rate of about 12 mpy. When HCl is added, the corrosion rate rises rapidly at a pH of about 4.

Temperature effects--In an open steel vessel, where oxygen is free to escape, the corrosion rate of steel in water of about neutral pH increases with temperature up to about 80°C (176°F). Above this, a marked decrease occurs, due to a drop in the oxygen solubility in water above 80°C. In a closed system, oxygen cannot escape, and the corrosion rate increases with temperature until all of the oxygen is consumed.

Effects of dissolved salts – A survey of almost 200 aqueous salt systems (all inorganic) showed that about 51% of the salts are highly corrosive to steel (corrosion rate greater than 50 mpy). See Table below.

Acidic or neutral salts tend to increase corrosion rates. Alkaline salts tend to lower corrosion rates.

Corrosion rates also depend upon whether the added salts yield soluble or insoluble reaction products. Where both the anodic and cathodic reaction products are soluble, salts (e.g., NaCl or Na₂SO₄) will increase the rate of attack. Where the cathodic reaction product is insoluble as when ZnSO₄ additions produce Zn(OH)₂--the corrosion rate is slightly reduced, because cathodic areas are shielded from oxygen. A similar reduction in corrosion rate occurs when a salt yields an insoluble anodic-reaction product.

Some inorganic salts that are highly corrosive to carbon steel

Table VIII

(Corrosion rate >50 mpy)

Aluminum sulfate	Magnesium fluosilicate
Ammonium bifluoride	Mercuric chloride
Ammonium bisulfite	Nickel chloride
Ammonium bromide	Nickel sulfate
Ammonium persulfate	Potassium bisulfate
Antimony trichloride	Potassium bisulfite
Beryllium chloride	Potassium sulfite
Cadmium chloride	Silver nitrate
Calcium hypochlorite	Sodium aluminum sulfate
Copper nitrate	Sodium bisulfate
Copper sulfate	Sodium hypochlorite
Cupric chloride	Sodium perchlorate
Cuprous chloride	Sodium thiocyanate
Ferric chloride	Stannic ammonium chloride
Ferric nitrate	Stannic chloride
Ferrous ammonium sulfate	Stannous chloride
Ferrous chloride	Uranyl nitrate
Ferrous sulfate	Zinc chloride
Lead nitrate	Zinc fluorosilicate
Lithium chloride	

Calcium salts are especially important. Hard waters –natural fresh waters containing large amounts of calcium salts– are less corrosive than soft waters, which contain lesser amounts. Deposits of calcium salts provide a protective film of calcium carbonate, which retards corrosion by shielding oxygen from the cathodic areas. The Table below shows simplified water-hardness classifications expressed as ppm CaCO_3 . A full description of water hardness requires calculating a Saturation Index, which is described in Section C, Chapter 2.

Simplified water-hardness classifications

Table IX

Hardness rating	CaCO_3 , ppm	Corrosiveness*
Very soft	1-3	Severe
Soft	31-60	↑
Medium hard	61-120	
Hard	121-180	
Very hard	> 181	Mild

*Assuming normal oxygen and pH levels

Seawater provides a convenient example of corrosive salt solutions. Seawater contains about 3.4% NaCl and is slightly alkaline, at a pH of 8. The corrosion of steel pilings varies with the depth in seawater. Some distance below the surface, the corrosion rate in normal flow is about 3-4 mpy. At the splash zone, the rate reaches a maximum of about 15-17 mpy. The pitting rate of steel in quiet seawater is about 15-45 mpy. If more sodium chloride is added, the corrosion rate decreases more or less linearly until at saturation (about 26% NaCl), the rate falls below the rate for distilled water. The decrease in corrosion is due to dropping oxygen solubility as NaCl is added.

Although carbon steel is fine for service in low-velocity seawater at ambient temperatures, the corrosion rate increases rapidly with temperature and agitation. At 50°C (122°F) and above, the corrosion rate in agitated seawater is greater than 50 mpy. The Figure in the next section depicts alloy suitability for chloride-containing water. Carbon steel is accordingly approved for percent-level chlorides at temperatures up to 50°C (122°F).

Warning – When you consider carbon steel for service in aqueous salt solutions, do not forget that nitrate solutions cause stress-corrosion cracking in carbon steel at elevated temperatures.

Warning – Sodium hypochlorite at concentrations above about 0.1% is very corrosive not only to carbon steel but also to 304/316 stainless steels and nickel.

Solution velocity – In general, increasing the solution velocity increases corrosion rates, especially if corrosive salts such as NaCl are present.

In natural water, velocity effects can be grouped into five categories, according to velocity ranges:

- * Slight motion (less than 0.3 m/s) may stop localized attack such as pitting.
- * At about 0.3 m/s, the flow may increase the oxygen supply to a level that raises the corrosion rate to as much as 40 mpy. Increased flow also accelerates the cathodic reaction by thinning the liquid film at the steel's surface.
- * Higher velocities may then provide enough oxygen to put the steel in a passive state so that it is protected by an oxide film. Corrosion rates will be about 10 to 30 mpy, depending on the surface finish.
- * At velocities over 5 m/s, turbulence may greatly accelerate the corrosion rate by eroding away the protective film. This occurs frequently at heat-exchanger tubing inlets, U-bends and piping elbows.
- * At more extreme velocities, erosion-corrosion will occur. At e.g. 13 m/s the corrosion rate reaches over 200 mpy.
- * In seawater, passivation of steel cannot occur because chlorides destroy the protective film. In this environment, the corrosion rate of steel increases continuously with velocity. At 3 m/s, the corrosion rate is 25-50 mpy.

2.4.1.b. Chloride attack on 304/316 SS in water

2.4.1.b.i. General

Whenever considering Type 304/316 stainless steels for service in water, always determine the chloride content of the water – even to ppm levels. Otherwise, in considering carbon steel versus 304/316 stainless steels, one may choose a stainless steel (which costs more) and end up with poorer service. The author has seen 304 stainless steel selected to replace carbon steel, after the carbon steel had survived 15 years' service in chloride-containing water. The goal was to avoid the maintenance problems associated with the general corrosion (rusting) of the carbon steel – e.g., yearly cleaning and repainting the steel. However, the 304 stainless steel failed by chloride stress-corrosion cracking or pitting within two years.

Chloride attack of stainless steel by water includes chloride stress corrosion cracking (SCC), pitting, and crevice corrosion. This chloride attack can be disturbing, because 304/316 stainless steels are relatively inexpensive and therefore very popular choices when upgrading from the general rusting problems of carbon steel. Plant people often are willing to pay for these stainless steels, but are often unwilling to consider more-expensive alloys. The fact that chloride contents as low as 40 ppm, or even lower can cause serious problems with 304/316 stainless steels can come as unwelcome news.

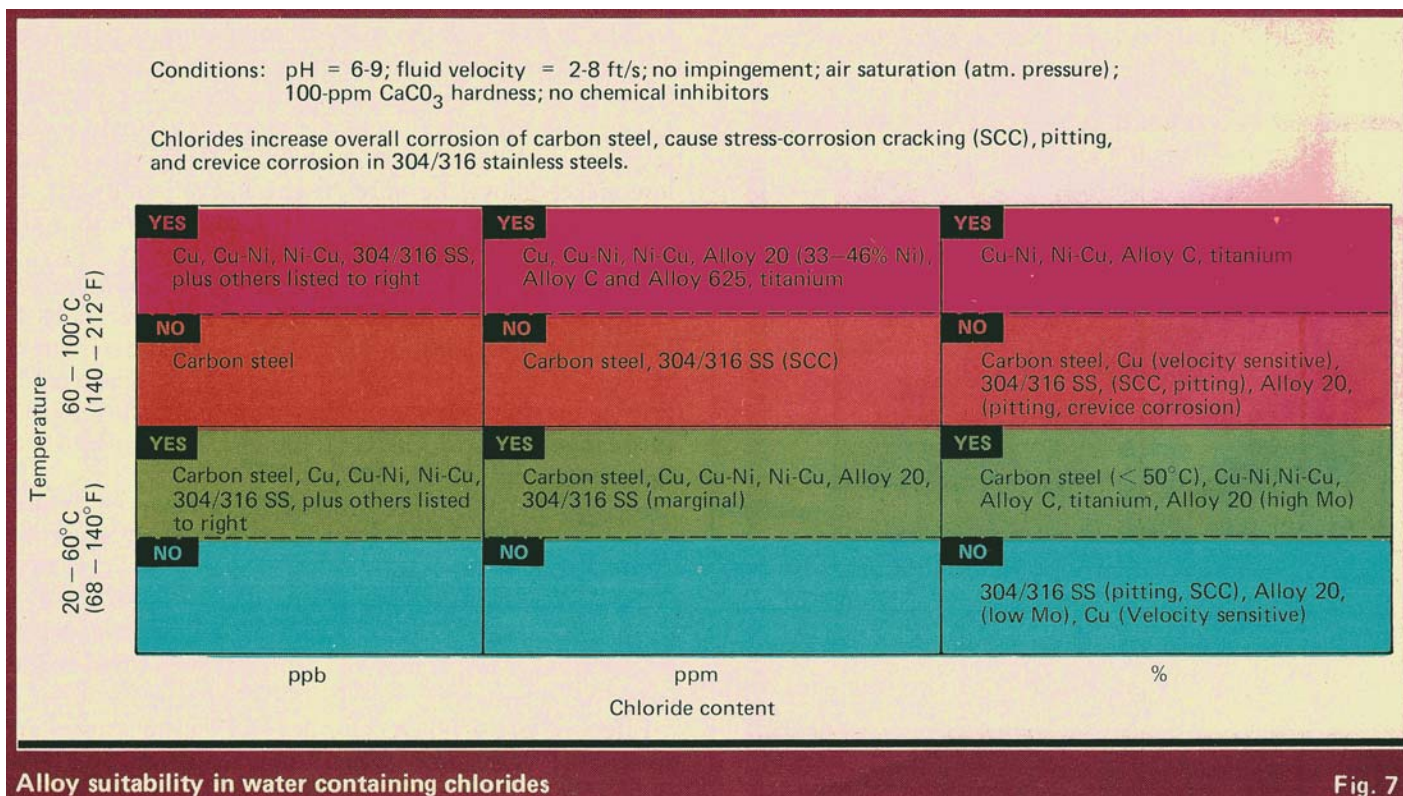


Fig. 7

Stress-corrosion cracking is especially insidious. Even after one or two years of troublefree service, a 304 or 316 stainless steel can suddenly crack without any warning or deformation.

When do SCC problems become significant? The three key determinants are temperature, chloride content and chloride concentration. Unfortunately, their interrelationship is complex, so the present state of understanding is limited to examples of SCC to generate rough working guides:

- #### 2.4.1.b.iii. Chloride pitting

Pits in these alloys are deep and, once started, progress rapidly though the metal. This is because the tip of the pit is anodic to all the surrounding metal, and its corrosive action is thus driven by a huge cathodic area.

Pitting may not begin immediately, showing an incubation period of up to several years. This makes pitting corrosion tests somewhat arbitrary.

Pitting occurs more readily in stagnant conditions. If there is marginal resistance to chloride pitting, do not leave the chloride solution in the equipment over long periods. Pitting tends to occur downward. The author has inspected several 316 stainless steel vessels that had bottom dished heads profusely scarred with spot repair welds where pitting had occurred.

Temperature accelerates pitting. For a given set of pitting conditions, a given alloy can be said to have a “Critical Pitting Temperature” (CPT), which is the temperature below which pitting does not occur.

Molybdenum additions raise this CPT. Thus, the chloride pitting resistance increases in the following progression of austenitic alloys:

Alloy	% Mo
304 SS	nil
316 SS	2-3
Alloy 825	2.5 – 3.5
317 SS	3 – 4
Alloy G	5.5 – 7.5
Alloy 625	8 – 10
Alloy C	14.5 – 16.5

Inhibitors such as chromates, hydroxides or silicates can retard pitting if present in sufficient amounts. In lesser amounts, these chemicals tend to accelerate pitting.

2.4.1.b.iv. Crevice corrosion

Chlorides can cause deep localized corrosion where there are crevices in stainless steels. Good equipment design minimizes the number of crevices. In welding, specify full-penetration welds with minimum porosity, to avoid crevices.

As with pitting, temperature accelerates crevice corrosion, and molybdenum inhibits it.

2.4.1.b.v. Other halides

Bromides and fluorides have been reported to cause SCC of stainless steels, but apparently iodides do not. There is some evidence that iodides inhibit SCC of Type 304 stainless steel in boiling MgCl_2 .

Bromides cause pitting, while fluorides and iodides have comparatively few pitting tendencies.

2.4.1.c. Water and nonmetals

For nonmetals, just water alone can cause serious problems. For example:

* Outdoors, unglazed tile or concrete may absorb water, which can freeze in cold weather to cause cracking or spalling.

* Organic coatings, applied on uncured concrete, may blister off as water works its way out from the interior of the concrete. Allow at least 28 days for the concrete to cure. If in doubt,

* Water solutions in services above about 60°C (140°F) can blister thin-film organic coatings on steel, since water molecules permeate the coatings. The author has seen this with a phenol formaldehyde coating on a drying-oven door after less than a year's service. The driving force for the permeation includes the temperature gradient across the coated wall, so insulating the cold outside of the steel wall will help. However, the insulation cost must be added to the coating cost in any economic evaluation.

* Water (or any solvent) that has permeated a polymer can cause failure by blistering if there are severe cycling fluctuations of temperature or pressure.

Concentrated chemical solutions

Tantalum, glass and phenolic resins resist many strong acids, but they can be severely attacked by strong alkalis.

Highly resistant resins such as furan, phenolics or epoxy cannot withstand highly oxidizing crevices such as oleum or highly concentrated sulfuric acid.

2.4.2.a. Concentrated alkalis

If discoloration from iron contamination is not a problem, then even NaOH and KOH can be handled in carbon steel at concentrations up to about 50%. Temperatures must be kept low enough to avoid stress-corrosion cracking. However, at elevated temperatures, NaOH can cause SCC in carbon steel, 304/316 stainless steels, Alloy 400 (65 Ni - 32 Cu) and Alloy 600 (76 Ni -15 Cr - 8 Fe).

graphitization and possible intergranular attack. Nickel is highly resistant to SCC, but if mercury is present as an impurity, the nickel can crack.

Whenever nickel is used in sodium hydroxide services containing other chemicals, look out for the presence of oxidizable sulfur compounds. The corrosive effects of sulfur contaminants are high for an oxidizable sulfur compound such as sodium sulfide but negligible for a highly oxidized compound such as sodium sulfate.

Amphoteric metals (capable of acting as an acid or a base) such as Aluminum and zinc corrode severely in caustic. For alloys that resist corrosion, the principal problems are metal-ion contamination of the caustic, and stress-corrosion cracking. Types 304/316 stainless steels have low corrosion rates but crack in caustic service (see Fig. 14 and Ref. 40). These stainless steels are limited to caustic concentrations up to 50% and to temperatures up to about 93°C (200°F). The Alloy 20 variations with increased nickel and chromium contents also show low corrosion rates and low susceptibility to SCC

Titanium, zirconium and Alloy 400 are also suitable. In addition to caustic resistance, titanium resists sodium hypochlorite and wet chlorine gas. It is used for caustic scrubbers handling wet chlorine and generating sodium hypochlorite. Alloy 400 should be stress-relieved if used in high-temperature caustic service.

To avoid iron pickup in steel tanks handling 50-73 % caustic, a 20-mil neoprene latex lining is used. Epoxy and epoxy-phenolic coatings are also suitable, although their flexibility is somewhat limited. The neoprene latex coating is less suitable for dilute caustic, which is a much more penetrating liquid than the concentrated solutions. FRP construction using a bisphenol-A fumarate polyester or a vinyl ester can withstand strong caustic and also strong acids. This combination makes fiberglass-reinforced plastic a good material for caustic scrubbers handling strong, nonoxidizing acids.

Materials that may develop problems with caustic and other strong alkalis include phenolic resins, tantalum, and glass. The alkali-resistant glasses on steel may be used up to pH 14 at 65.5°C (150°F), up to pH 13 at 82°C (180°F), and on an intermittent basis up to pH 13 at 100°C (212°F). The older acid/alkali-resistant glasses have a limit of pH 11 at 82 °C (180 °F).

2.4.2.b. Concentrated salt solutions

Salt solutions are generally more of a corrosion problem for metals than for plastics, elastomers or silicates. Exceptions include acid fluorides, which attack silicates, and hypochlorites, which can attack polyesters. Concrete is also attacked by salts.

The corrosiveness of salt solutions to metals depends upon the following solution characteristics (see Table XIII, Section F):

- *The presence of halides.* Chloride solutions (and some other halides) attack carbon steel. With stainless steels, halides penetrate passive oxide films and induce pitting and other forms of localized attack.
- *Acidic, neutral or alkaline pH.* Acid salts such as aluminum chloride, ferrous chloride, nickel sulfate, ammonium bromide and ammonium chloride severely attack carbon steel.

The molybdenum in Type 316 stainless steel makes it perform better than Type 304 stainless in some acid salt solutions. For example, a manganese sulfate solution at pH 1-2 and 60°C (140°F) destroyed a 304 stainless steel sample in eight days, but corroded a 316 stainless steel sample at the low rate of only 2.9 mpy.

Alkaline salts hydrolyze to produce a basic pH. They sometimes inhibit the corrosion of carbon steel. Examples include trisodium phosphate, sodium tetraborate, sodium silicate and sodium carbonate. The 304/316 stainless steels are practically free from corrosion by alkaline salts, including those of a strongly oxidizing nature (nonhalides).

- *Oxidizing versus reducing character.* For carbon steel, chloride-containing oxidizing salts are extremely corrosive (ferric chloride, cupric chloride, mercuric chloride, sodium hypochlorite)—see Table XIII. Other oxidizing salts are corrosion inhibitors (sodium chromate, sodium nitrite, potassium permanganate). For 304/316 stainless steels, oxidizing acid salts tend to cause pitting, while the reducing acid salts favor high overall attack. Oxidizing salts can have a disastrous effect upon nickel, Alloy B (70 Ni - 28 Mo) or Alloy 400 in acid systems.
- *Solution parameters.* Unless a corrosive such as sodium hypochlorite decomposes at higher temperatures, temperature accelerates corrosive attack. Sodium hypo-chlorite can be added at high temperatures to solutions in cast iron kettles because it reacts or decomposes in very short order. Also, the heavy wall thickness of cast iron provides a built-in corrosion allowance.

Velocity accelerates corrosion by stripping off protective films and by accelerating the supply of corrosive to the metal surface.

2.4.2.c. Concentrated inorganic acids

The common inorganic (mineral) acids include sulfuric, nitric, hydrochloric, hydrofluoric and phosphoric acids. Tables XIV and XV (Section F) list common materials for these strong acids. The suitability of materials of construction for such acid service depends upon the following solution characteristics: oxidizing versus reducing character, chloride and/or fluoride concentrations, dilute versus concentrated acid strength, service conditions (such as temperature and solution velocity), and size of the acid molecule.

More details have been discussed in Section C.

2.4.3. Miscellaneous warnings

Here are some useful reminders :

- *Never pair dissimilar metals or a metal-plus-graphite in contact with conducting solutions. This can cause rapid galvanic corrosion of the more active metal. Insulate the two metals, or add a sacrificial third metal that is even more active. If you must paint, paint both metals. Pinholes in the coating of the active metal would cause very rapid corrosion if the large, more-noble cathodic metal were left uncoated.*

□ *Avoid the following disastrous material/environment combinations:*

- *Copper/copper alloys with ammonia and amines, or with mercury and mercury compounds.*
- *Nickel/nickel alloys with sulfur and sulfides at high temperatures .*
- *Titanium with dry chlorine, dry red fuming nitric acid, or high-pressure oxygen. Titanium can ignite in these services.*
- *Type 304 stainless steels in chloride solutions.*
- *Gray cast iron in oleum service. The cast iron may split open from oleum penetration along the graphite flakes.*
- *Tantalum in hot oleum.*
- *Glass or silicate mortars and bricks in an acid fluoride solution.*

□ *Never specify plastics just to save money. Use each material where it is best suited. FRP products require expert engineering design, quality fabrication and careful installation, otherwise dramatic failures can result. Make sure that a prospective FRP fabricator or installation contractor has done the required work many times within the exact scope and specifications you require.*

3. High Temperatures

*Hot gas environments,
normally using specialty alloys ...*

3.1. Introduction

With metals, high temperatures commonly cause degradation through:

Reaction with gaseous environments – Such gases include hydrogen, oxygen, water vapor, carbon monoxide, methane, sulfur compounds, chlorine, and hydrogen chloride.

Mechanical effects – Table XVII lists approximate temperature thresholds, above which elevated-temperature behavior begins for common alloy systems. The effects include creep/rupture deformation effects under load; thermal fatigue; and alloy phase changes. The alloy phase changes can hurt mechanical properties at the high temperatures, or when the alloy is at ambient temperatures.

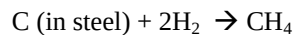
Generally, in air, the iron-, nickel- and cobalt-base alloys are more limited by mechanical strength requirements than by oxidation problems. For ultrahigh temperatures, where only the exotic refractory metals have sufficient strength, oxidation problems will become the limiting factor.

Approximate temperature thresholds for elevated temperature		Table XVII
Alloy system	Temperature	
	°C	°F
Aluminum	205	400
Titanium	315	600
Low-alloy steels	370	700
Series 300 stainless steels	540	1,000
Nickel-base alloys	650	1,200
Cobalt-base alloys	650	1,200
Refractory metals and alloys	980-1,540	1,800-2,800

3.2. Reaction of metals with gases

3.2.1. Hydrogen

In addition to the ambient-temperature effects discussed earlier, hydrogen at high temperatures can degrade alloy properties by decarburization. For carbon steels and low-alloy steels, carbon content is the prime determinant of maximum strength and hardness. For these steels, alloy performance can be severely limited by decarburization, involving the reaction:



Alloying steels with carbide stabilizers, such as chromium or molybdenum, alleviates hydrogen problems, since the carbon is more strongly tied up, thus making decarburization more difficult. 300-series Cr-Ni stainless steels, such as Types 304, 316, 309 or 310, which contain from 16 to 26% chromium, are resistant to high-temperature hydrogen damage.

3.2.2. Oxygen

The normal ambient-temperature surface oxidation of metals is accelerated at elevated temperatures. Most of the useful alloys develop protective oxides that permit their use up to fairly high temperatures. Table XVIII lists the threshold scaling temperatures for several common steels, stainless steels and nickel-base alloys. Below these temperatures, oxide scaling in air or similar oxidizing atmospheres is not a significant problem.

Table XVIII

Alloy	Above temperature	
	°C	°F
1010 carbon steel (0.10% C)	480	900
5 Cr - 0.5 Mo hardenable steel	620	1,150
7 Cr - 0.3 Mo hardenable steel	650	1,200
9 Cr - 1.0 Mo hardenable steel	675	1,250
403, 410 martensitic stainless (12% Cr)	705	1,300
430 ferritic stainless (17 Cr)	845	1,550
442 ferritic stainless (21% Cr)	955	1,750
446 ferritic stainless (25% Cr)	1,095	2,000
302, 304, 18 Cr - 8 Ni stainless	900	1,650
321, 347 stabilized 18 Cr - 8 Ni stainless	900	1,650
316, 18 Cr - 8 Ni - 2.5 Mo stainless	900	1,650
309, 23 Cr - 13 Ni stainless	1,095	2,000
310, 25 Cr - 20 Ni stainless	1,150	2,100
Alloy B (70 Ni - 28 Mo)	760	1,400
Alloy C (59 Ni - 16 Cr - 16 Mo)	1,150	2,100

Excessive oxide scaling in air or similar oxidizing atmospheres

3.2.3. Water vapor

Steam or water vapor is only slightly more corrosive than air. The oxidation temperature limits for steels and stainless steels in steam service are only about 28-50°C (50-100°F) below the limits for these alloys in air. The oxidation temperature limit for carbon steel in air is about 480°C (900°F); in steam, the limit is 427°C (800°F).

For 18 Cr-8 Ni stainless steels such as Types 304, 316 or 321, the limits are 900°C (1,650°F) in air, and 870°C (1,600°F) in steam. For Type 410 stainless steel (12% Cr), the limits are 705°C (1,300°F) in air, and 650°C (1,200°F) in steam.

However, as described above, the high-temperature oxidation of 18 Cr - 8 Ni stainless steel in air is much more severe if the air is contaminated by levels of water in the percent range.

3.2.4. Carbon monoxide and methane

Hydrocarbons such as carbon monoxide and methane can carburize alloys at temperatures above about 705°C (1,300°F). Small amounts of surface carburization are not significant, but heavily carburized steels lose their ductility and become brittle. They may fail under shock at lower temperatures, or by cracking because of stresses set up by thermal cycling.

Stainless steels can also be damaged by carburization. The 400-series types, with their body-centered crystal structures, also have their toughness impaired by the increased carbon content. The 300-series types, with a face-centered-cubic structure, can tolerate a greater increase in carbon content without a significant loss in toughness.

However, the added carbon can tie up the chromium in the alloy, in the form of carbides such as Cr_{23}C_6 , Cr_3C_2 or Cr_7C_3 . If adjacent alloy-matrix areas are depleted in chromium, the resulting structure will be vulnerable to corrosion in acid media such as nitric or sulfuric acid. If a 300-series stainless steel is carburized enough, it can develop brittle surface cracking through continuous grain-boundary carbide networks developed by the carburizing.

Increasing the alloy nickel-content improves resistance to carburizing, possibly because nickel doesn't form a stable carbide. In one carburizing test, run for 25 h at 1,095°C (2,000°F), nickel-base alloys such as Alloy 600 (76% Ni- 15.5% Cr) gained only about 19% of the weight gained by Types 309 and 310 stainless steels (13.5 and 20.5% Ni, respectively). This meant that the nickel-base alloys formed fewer carbides. Another advantage of the high-nickel contents was that the nickel-base alloys tended to form irregularly shaped, *separate* carbide precipitate particles. The 309/310 stainless steels tended to form a more harmful continuous network of grain boundary carbides.

Silicon alloy additions also retard carburization.

CO/CO₂ mixtures can carburize or decarburize steels, depending upon the gas composition.

3.2.5. Sulfur and its compounds

Even in small amounts, sulfur in various forms can accelerate corrosion at high temperatures. Hydrogen sulfide and sulfur vapor are especially corrosive.

Sulfur attack is more severe than oxidation for two reasons. First, metal sulfides are low-melting and may actually be molten during high-temperature service. Second, the sulfides adhere poorly to metal surfaces and are less likely than oxides to form tenacious, continuous, protective films.

Nickel-base and high-nickel alloys generally have poor resistance to sulfur. In reducing atmospheres such as H_2S , sulfur forms a molten-nickel/nickel-sulfide eutectic above about 644°C ($1,190^\circ\text{F}$). This induces rapid failure by liquid penetration along the alloy grain boundaries. Even sulfur-containing crayons that are used to mark high-nickel alloy plate during fabrication can induce local failure during subsequent heat treatment. Keep sulfur and sulfides away from high-nickel alloys at high temperature.

On the positive side, chromium alloy additions contribute good sulfur resistance. In general, a minimum of about 11% chromium is required in stainless steels to prevent sulfur scaling in hydrogen sulfide service. The 18 Cr - 8 Ni stainless steels have been used extensively in H_2S service. Fig 24 shows the corrosion resistance of low-Cr (0-5%) steels and Cr-Ni (300-series) stainless steels to H_2S at elevated temperatures.

Aluminum also has excellent sulfur resistance. It can be diffusion-bonded to steels, stainless steels or nickel alloys by vaporizing the aluminum onto the alloy surface at temperatures above about 927°C ($1,700^\circ\text{F}$). The resulting surface coating is used primarily in sulfur-bearing gas streams, not in low-temperature liquid-phase environments. Alloy additions of aluminum can also help.

3.2.6. Chlorine and hydrogen chloride

The critical aspect here is water content. Dry gaseous chlorine and hydrogen can be handled in many metals and alloys. However, there are significant corrosion rates that increase with increasing temperatures. Moisture has much more effect on the corrosiveness of chlorine. Wet chlorine requires quite expensive alloys such as Alloy C (59 Ni- 16 Cr- 16 Mo) or titanium (titanium ignites in dry chlorine). This is why FRP is used for chlorine headers and diaphragm cell covers. For hydrogen chloride, small amounts of moisture are not significant so long as operations are above the dewpoint.

Use 18 Cr - 8 Ni stainless steels in dry chlorine or hydrogen chloride service with caution. Any accidental or upset introduction of water can cause very rapid localized failures by pitting or stress-corrosion cracking. Accidental water intrusions in carbon steel systems will result in general corrosion that is a more gradual function of exposure time. Also, the damage to carbon steel is clearly evident due to the bright ferric chloride corrosion product.

3.3. Mechanical effects on metals

At elevated temperatures, creep and rupture properties begin to govern design. These concerns become important above about 370°C (700°F) for carbon- and low-alloy steels, above 540°C (1,000°F) for 300-series stainless steels, and above 650°C (1,200°F) for nickel-base alloys.

A secondary mechanical effect involves alloy phase changes that occur during long-term service at elevated temperatures. If desirable phases, such as strengthening carbides, change in morphology or are dissolved, an alloy may be weakened. Conversely, some new phases may precipitate as brittle platelets, needles or grain-boundary networks and can weaken or embrittle the alloy.

4. Low Temperatures

*The cryogenic environments ...
Low temperatures slow down corrosion rates,
but Embrittlement is the problem ...*

4.1. General

The major materials problem at low temperatures is brittleness. Brittle fracture is a sudden, low-energy fracture, usually without significant prior deformation. The classic metals example of brittle fracture involved the cracking of steel plates in welded ships during and immediately after World War II. Polymers can also be brittle – witness the rubber ball that shatters instead of bouncing after being chilled in liquid nitrogen.

4.2. Metals

4.2.1. Introduction

All metals can fail catastrophically, but the most important problem involves ferritic steels becoming brittle as the temperature drops below ambient. Ferritic steels have a body-centered-cubic crystal structure that starts to fail by cleavage under impact loads as the temperature drops below ambient. Cleavage is a low-energy, transcrystalline fracture along specific crystallographic planes.

4.2.2. Guidelines

Studies of earlier steel low-temperature cracking problems have led to these guidelines:

- * High carbon content raises strength, but hurts notch toughness. A mild steel for a pressure vessel will be tougher at 0.20% carbon than at 0.30%. The Charpy vee-notch transition temperature rises about 5°F (2.8°C) per 0.01% increase in carbon up to 0.30% carbon.

- * A fully “killed” steel, deoxidized by small silicon and aluminum additions, will be tougher than “rimmed” or “semi-killed” steels.

* A fine-grained steel will be tougher than a coarse-grained one. Aluminum addition helps refine the grains by introducing aluminum nitride particles that pin the grain boundaries.

* The coarse grains that are generally present in hot-rolled steel usually require a subsequent heat treatment called normalizing. For good toughness in a low-carbon steel, specify a normalized steel, not a hot-rolled steel. For low-alloy steels, a quenched-and-tempered structure may also have good toughness.

* The addition of manganese up to about 1.5% is beneficial and lowers the Charpy transition temperature at a rate of about 10 °F(5.6°C) per 0.10% increase.

* In low-alloy steels, *nickel* is beneficial in maintaining notch toughness at subnormal temperatures. When enough nickel is added to make the steel essentially austenitic (face-centered-cubic), a Charpy transition temperature showing a sudden tough-to-brittle transition is virtually eliminated.

4.3. Organic polymers at low temperatures

Table XXVII shows approximate low-temperature limits for some common polymers. Note that natural rubber starts to be of concern at about -20°F (-29°C). Most other polymers are satisfactory down to the lower limit of severe climatic conditions. Fluoropolymers can be used at cryogenic temperatures.

Table XXVII

Polymer	Low-temperature limit, °F
Acrylonitrile-butadiene-styrene	- 40
Amino	- 70
Epoxy (Biphenol-A)	- 320
FEP	Low cryogenic temperatures
Nylon 6/6	- 85
Phenolic, baked	- 40
Polycarbonate	- 65
Polyester FRP	- 50
Polyethylene	- 100
Polypropylene	0
Polyvinyl chloride	0
Polyvinylidene fluoride	- 110
PTFE	Low cryogenic temperatures
Rubber, natural	- 20
Silicone	- 100

Approximate low-temperature limits for some common organic polymers

E. Materials Protection Techniques

Including Corrosion Control ...

Economic alternatives to the ‘Gold Plating’ solution...

1.1. Corrosion Control Methods

- ☐ A change in the material of construction;
- ☐ A change in the nature of the environment;
- ☐ Placing a barrier film or coating between the material and the environment;
- ☐ Application of an electrochemical potential to the material; and
- ☐ A change in the equipment design.

2. Coatings

Anticorrosion Barriers ...

2.1. General

These comprise some of the metallic and organic or inorganic barriers, as well as paints and coatings. Usually, these are less than 1/8 in. (3.2 mm) thick, as distinct from heavy-duty metal liner applications.

2.2. See Video EFC (European Federation of Corrosion)

<http://www.corrosion.tv>

propensity of austenitic stainless steels. As previously described, a high pH is conducive to the development of protective films for some alloy and solution combinations, such as calcareous deposits on steel in certain waters. Dilute acids, as in waste water or aqueous process streams, may be brought into some degree of control by neutralizing to a pH of 6 to 8, in many cases.

In organic liquids, both acid and alkaline constituents may function only in their proportion to contained or dissolved water (as opposed to their nominal weight per cent). In such cases, corrosion may be greater than anticipated from the percentage value, and partial or complete neutralization of either contained caustic or contained acid may be necessary.

3.3.3. Scavenging

Dissolved oxygen (DO) is frequently scavenged from water through treatment with sodium or ammonium sulfite, or hydrazine. As described in Chapter 19, catalyzed sulfite or hydrazine is available to hasten the speed of reaction.

Organic peroxides may be scavenged by reaction with sodium nitrite in some hydrocarbon applications, reducing the oxidizing capacity of the process environment.

Not so widely known is the capability of propylene oxide and butylene oxide for scavenging traces of HCl from wet organic media, converting the HCl from the corrosive form to the noncorrosive propylene chlorhydrin.

3.3.4. Inhibitors

An inhibitor is a substance that reduces corrosion rates when relatively small amounts are added to the environment. Strictly speaking, an inhibitor should not be a major reactant, as in adjusting pH or scavenging oxygen.

3.4. Electrochemical Techniques

Cathodic protection (CP) and anodic protection (AP) have been mentioned in previous discussion. A fuller treatment is given in a dedicated publication.

There are growing applications of techniques for holding process equipment at some predetermined potential for the alleviation of pitting, crevice corrosion, or environmental cracking. These are really field applications of the laboratory potentiostat, and are different from conventional CP or AP techniques in that current is applied in either direction, as required by the metal's response to process changes.

3.5. More: see Video EFC (European Federation of Corrosion)

<http://www.corrosion.tv>

including websites ...

1. The 10 Most Important Books & Information Tools

- NN. *Metals Handbook* Vol.13 'Corrosion', ASM International (1987 & regular updates).
- B.J. Moniz & W.I. Pollock (Eds.). *Process Industries Corrosion - The theory and practice*. 1st Ed., NACE International (1986).
- W.F. Bogaerts & K. Agema. *Active Library on Corrosion*. version 1.3, CD-ROM, Elsevier Science Publishers (1996); version 2.0 (2000).
- D. Behrens, G. Kreysa & R. Eckerman (Eds.) *Corrosion Handbook* ("Werkstoffstabelle") - 12 Volumes & Supplement. DECHEMA (1987-1993 & regular updates).
- S.L. Chawla & R.K. Gupta. *Materials Selection for Corrosion Control*. ASM International (1993).
- C. P. Dillon. *Corrosion Control in the Chemical Process Industries*. 2nd Ed., Materials Technology Institute of the Chemical Process Industries / Nickel Development Institute (1994).
- L.L. Shreir, R.A. Jarman & G.T. Burstein. *Corrosion*. 3rd Ed., Butterworth Heinemann (1994).
- NN. *CHEM*COR*. Expert System Modules 1-12, NACE International / Materials Technology Institute of the Chemical Process Industries (1990 - 1995).
- NN. *PRIME - Process Industries' Materials Expert*. AI-based Materials Selection Tool, METALogic (1996).
- NN. *COR*AB*. Corrosion Abstracts CD-ROM. NACE International (quarterly updated).

OTHER SOURCES OF INTEREST

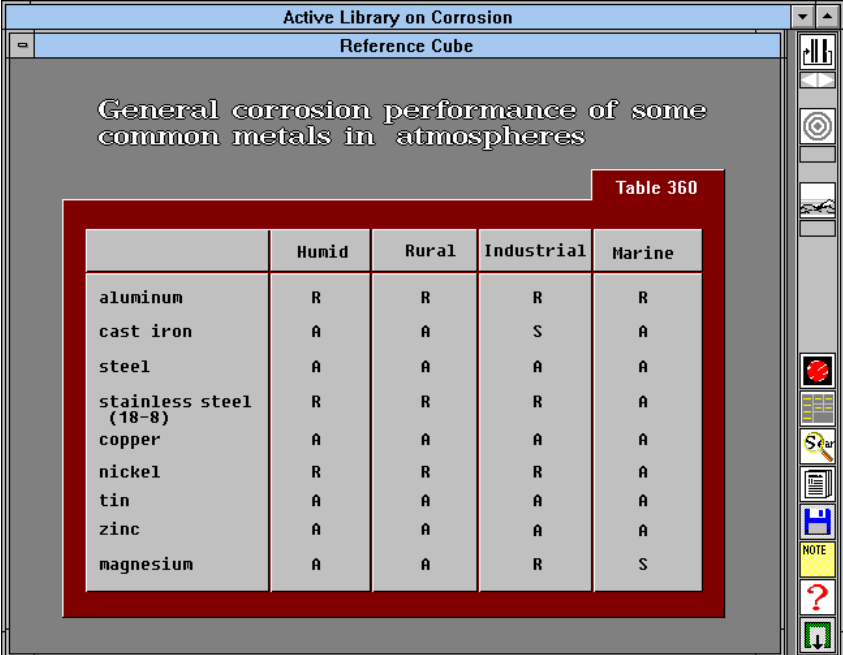
- E.H. Cornish. *Materials and the Designer*. Cambridge University Press (1990).
- M. Ashby. *Materials Selector*. Cambridge University Press.

2. Materials Performance Charts, Tables & Figures

and Websites ...

See e.g.: 'Active Library on Corrosion' CD-ROM

Example :



Active Library on Corrosion
Reference Cube

General corrosion performance of some common metals in atmospheres

Table 360

	Humid	Rural	Industrial	Marine
aluminum	R	R	R	R
cast iron	A	A	S	A
steel	A	A	A	A
stainless steel (18-8)	R	R	R	A
copper	A	A	A	A
nickel	R	R	R	A
tin	A	A	A	A
zinc	A	A	A	A
magnesium	A	A	R	S

Some corrosion-resistant materials for concentrated aqueous solutions

Table XII

Material (with references)	Oxidizing			Acids			Organic		Alkalies		Salts (Aqueous solutions)			Organic solvents		Not recommended for
	Oleum	70-100% H ₂ SO ₄	HNO ₃ (conc.)	0-70% H ₂ SO ₄	0-37% HCl	0-80% HF	Acetic acid	Formic acid	NaOH (caustic)	NH ₄ OH (ammonia)	NaCl	NaOCl	FeCl ₃	Aliphatics	Aromatics	
Alloy C (Ref. 2, 32)	L	L	L	R	L	L	R	R	R	R	R	R	L	R	R	Acid services over 65° C (150° F), especially hydrochloric acid or acid solutions with high chloride contents.
Tantalum (Ref. 2, 33)	V	R	R	L	R	N	R	R	N	N	R	R	R	R	R	Hot oleum (over 50° C), strong alkalis, fluoride solutions, sulfur trioxide.
Glass/silicates (Ref. 3, 34, 35, 36)	R	R	R	R	R	N	R	R	L	L	R	R	R	R	R	Strong alkalis, especially above 54° C, distilled water above 82° C (180° F), hydrofluoric acid, acid fluorides, hot, concentrated phosphoric acid, lithium compounds above 177° C, severe shock or impact applications.
Carbon, impreg. with furan (Ref. 3, 37)	N	L	L	—	—	L	—	—	R	R	R	R	R	—	—	Strong oxidizers, very strong solvents.
Carbon, impreg. with phenolic (Ref. 3, 37)	N	L	L	R	R	L	R	R	N	R	R	R	R	R	R	Strong alkalis, very strong oxidizers.
FEP/TFE	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R*	Molten alkali metals, elemental fluorine, strong fluorinating agents.
Furan resin (Ref. 3, 27, 38)	N	N	V	R	L	N	L	L	R	R	R	V	R	R	L*	Strongly oxidizing solutions, liquid bromine, pyridine.
Phenolic resin (Ref. 3, 27)	N	L	V	R	R	L	L	R	N	N	R	N	L	R	L*	Strong alkalis or alkali salts, very strong oxidizers.
Epoxy resin** (Ref. 3, 27)	N	N	V	L	R	—	L	N	R	L	R	N	R	L	L*	Strong oxidizing conditions, very strong organic solvents.

* See Table VI for detailed polymer resistance to organic solvents
 **Epoxy hardener will strongly affect chemical resistance
 Key: R = Recommended for full range of concentrations up to boiling or to temperature limit of (nonmetallic) product form
 L = Generally good service but limited in concentration and/or temperature
 V = Very limited in concentration and/or temperature for service
 N = Not recommended

Alloy corrosion by salt solutions

Table XIII

Salts (Type and examples)	Corrosion rates for listed alloys				
	Carbon steel	304 SS	316 SS	Alloy 400 (65Ni-32Cu)	Nickel 200
Nonoxidizing nonhalides					
Alkaline (pH > 10) e.g., Sodium carbonate	L	L	L	L	L
Neutral e.g., Sodium sulfate	M	L-M; SCC	L-M	L	L
Sodium nitrate	L-M; SCC	L; pits	L; pits	L	L
Acid e.g., Nickel sulfate	S	L-M	L-M	M	M; pits
Nonoxidizing halides					
Neutral e.g., Sodium chloride	M; pits	M; SCC; pits	M; SCC; pits	M	M
Acid e.g., Zinc chloride	S	S; SCC; pits	S; SCC; pits	M	M
Ammonium chloride	S	S; SCC; pits	M; SCC; pits	M	M-S
Oxidizing nonhalides					
Neutral e.g., Sodium chromate	L*	L	L	L	L
Sodium nitrite	L*	L	L	L	L
Potassium permanganate	M	M	M	M	M
Acid e.g., Ferric sulfate	S	L	L	S	—
Silver nitrate	S SCC	M	M	S	S
Oxidizing halides					
Alkaline e.g., Sodium hypochlorite	S	S; pits	S; pits	M-S; pits	M-S; pits
Acid e.g., Ferric chloride	S; SCC	S; pits	S; pits	S	S
Cupric chloride	S	S; pits	S; pits	S	S
Mercuric chloride	S	S; SCC; pits	S; SCC; pits	S; SCC	S

Key: L = Low — less than 5 mpy; for all concentrations and temperatures below boiling.
M = Moderate — less than 20 mpy; perhaps limited to lower concentrations and/or temperatures.
S = Severe — more than 50 mpy.

*Chemical acts as corrosion inhibitor if present in sufficient amounts, but may cause pitting if in lower amounts.

Common materials of construction for strong acids

Table XIV

Acid	Material	Concerns
Acetic	316L stainless steel	Excess acetic anhydride in glacial acetic acid can accelerate corrosion; chloride impurities (ppm levels) can cause pitting and stress-corrosion cracking.
	Copper/copper alloys	Not for highly oxidizing conditions; cost and availability.
	Aluminum alloys	Sensitive to contaminants; fewer experienced fabricators than for stainless steel; requires very clean welding; attacked very rapidly in concentrations near 100% or with excess acetic anhydride.
Formic	304L stainless steel	For ambient temperatures only.
	Copper/copper alloys	Not for oxidizing conditions, including air.
Hydrochloric	Rubber-lined steel (natural rubber)	Low tolerance for organic solvent impurities; temperature limited according to hardness of rubber; steel fabrication must be properly done.
	Alloy C	Not for hot concentrated HCl.
	Alloy B	Not for oxidizing conditions, <i>must</i> be tested if reducing conditions are in doubt.
	Tantalum	Cost; not for fluoride impurities.
	Impervious graphite	Fragile.
	FRP	HCl may attack or permeate laminate; temperature limited (below 65.5°C/150°F); requires excellent engineering design and fabrication quality.
Hydrofluoric	Alloy 400	Not for oxidizing conditions (test if in doubt).
	Copper	Not for oxidizing conditions (test if in doubt); below 65.5°C (150°F) only; cost and availability.
	Cupro-nickel	Not for oxidizing conditions (test if in doubt); concentration and temperature slightly limited.
	Carbon steel	Not below 60% or 65% concentration, depending on impurities.
	Impervious graphite	Fragile; limited to below 60% concentration.
	Polyvinylidene fluoride	—
Nitric	304L stainless steel	Must use low-carbon (or stabilized grade) if welded; not for fuming acid concentrations above 65.5°C (150°F).
	High-silicon iron	Castings only; limited shock resistance; only for concentrations above 45% if temperatures over 71°C (160°F).
	Aluminum (e.g., 3003, 5052)	Mostly for over 95% concentration, not for below 85% concentration; fewer experienced fabricators than for stainless steel, requires very clean welding.
	Titanium	May ignite in red fuming nitric acid if water is below 1.5% and nitrogen dioxide is above 2.5%; scarcity of experienced fabricators; cost and availability.
Oleum	Carbon steel	Not for 100-101% H ₂ SO ₄ concentration; limited in temperature.
	304L stainless steel	Cost relative to carbon steel.
	Glass-lined steel	Limited shock resistance.
Phosphoric	316 L stainless steel	Must use low-carbon or stabilized grade if welded, up to 85% concentration and 93°C (200°F).
	Alloy 20 variations	Cost.
Sulfuric	Carbon steel	Not for below 70% concentration; ambient temperatures only; velocities below 2 to 4 ft/s.
	Alloy 20 variations	Limited temperature at 65-75% concentration; cost.
	High-silicon iron	Castings only; limited shock resistance.
	Chemical lead	Experienced lead "burners" are scarce; soft and suffers from erosion; creeps at room temperature; limited to below 90% concentration.
	Glass	Limited shock resistance.
	Alloy C	Better for reducing acid strengths (<60% concentration); cost.
	Rubber-lined steel	For dilute not concentrated (oxidizing) strengths; temperature limited according to rubber hardness and acid concentration; steel fabrication must be properly done.
	Brick linings with silicate mortar	Experienced tradesmen required; high initial cost; absorption of the corrosive by the masonry (use membrane substrate); poor properties in tension or shear (use in compression); many brick linings "grow" in service but if used in archlike contours, growth merely increases compression.

Concentration and temperature limits in acids for some nonmetallics

Table XV

Nonmetallic	Hydrochloric acid (reducing)	Hydrofluoric acid (reducing)	Nitric acid (oxidizing)	Sulfuric acid (oxidizing above 60%)
Polypropylene	20% at 79° C (175° F) 38% at 52° C (125° F)	60% at 38° C (100° F) Not recommended over 60%	30% at 52° C (125° F) 60% at 25° C (77° F)	60% at 93° C (200° F) 93% at 79° C (175° F) 98% at 52° C (125° F)
Polyvinylidene fluoride	38% at 134° C (275° F)	70% at 100° C (212° F) 100% at 66° C (150° F)	10% at 93° C (200° F) 50% at 79° C (175° F) 100% at 52° C (125° F)	60% at 110° C (230° F) 85% at 66° C (150° F) 98% at 49° C (120° F)
PVC*	38% at 60° C (140° F)	60% at 49° C (120° F) Not recommended over 60%	40% at 60° C (140° F) 60% at 25° C (77° F)	70% at 60° C (140° F) 93% at 25° C (77° F)
Impervious graphite	38% at 100° C (212° F)	48% at boiling 60% at 85° C (185° F) Not recommended over 60%	10% at 85° C (185° F) 20% at 60° C (140° F) 30% at 25° C (77° F)	93% at 71° C (160° F) 96% at 25° C (77° F)
Hard natural rubber	38% at 85° C (185° F)	20% at 49° C (120° F) Not recommended over 20%	Not recommended	30% at 85° C (185° F) 50% at 66° C (150° F) Not recommended over 50%
FEP/TFE	100% at temperature limit for material	100% at temperature limit for material	100% at temperature limit for material	100% at temperature limit for material

*Resistance will vary with plasticizer additions.

Environments that may cause stress-corrosion cracking

Table X

Material	Environment
Aluminum alloys	NaCl/H ₂ O ₂ solutions NaCl solutions Seawater Air Water vapor
Carbon steels	NaOH solutions Nitrate solutions H ₂ SO ₄ /HNO ₃ HCN solutions Acidic H ₂ S solutions Molten Na/Pb alloys
Copper alloys	Ammonia vapors and solutions Amines Water, water vapor
Gold alloys	FeCl ₃ solutions Acetic-acid/salt solutions
Alloy 600	NaOH solutions
Lead	Lead acetate solutions
Alloy 400	Fused NaOH Hydrofluoric acid Hydrofluosilicic acid Boiling NaOH solutions
Nickel	Mercury Sulfur
304/316 SS	Chloride solutions H ₂ S NaOH solutions
Titanium alloys	Red fuming nitric acid Seawater N ₂ O ₄ Methanol/HCl

Upper temperature limits for some
common nonmetallic materials

Table XXV

<u>Material</u>	Upper temperature limit (approx.)	
	<u>°C</u>	<u>°F</u>
Mortars		
2-Component potassium silicate (refractory filler)	1,370	2,500
2-Component silica	1,093	2,000
2-Component potassium silicate	900-1,010	1,650-1,850
Sodium silicates	400	750
Furans	177-220	350-428
Phenolics	177-190	350-375
Polyester or epoxy	107	225
Sulfur	93	200
Ceramics		
Porcelain	815	1,500
Coatings and linings		
Gun-applied cement linings	538	1,000
Inorganic zinc primer (silicate)	538	1,000
Silicone aluminum paint	538	1,000
Silicone-acrylic or silicone-alkyd paint	260	500
Organic polymers		
PTFE	260	500
FEP	205	400
FRP (polyester)	150-177	300-350
FRP (epoxy)	150-260	300-500
Polyvinylidene fluoride	121-135	250-275

Websites :

- ☐ http://sirius.mtm.kuleuven.be/Research/CBA-Arenberg/Corrosion_Control
- ☐ <http://www.corrosion.tv>