Edited by Michael Schütze, Marcel Roche, and Roman Bender

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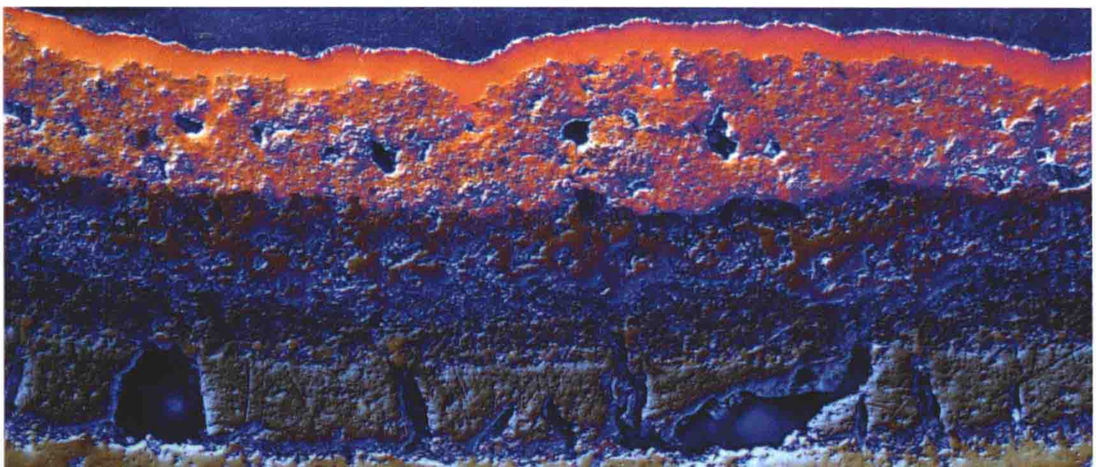
Co[illegible] Resistance of Steels, Nickel Alloys and Zinc in Aqueous Media

Waste Water, Seawater, Drinking Water, High-Purity Water



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Corrosion Resistance of Steels, Nickel Alloys and Zinc in Aqueous Media

DECHEMA

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Preface

Practically all industries face the problem of corrosion – from the micro-scale of components for the electronics industries to the macro-scale of those for the chemical and construction industries. This explains why the overall costs of corrosion still amount to about 2 to 4% of the gross national product of industrialised countries despite the fact that billions of dollars have been spent on corrosion research during the last few decades.

Much of this research was necessary due to the development of new technologies, materials and products, but it is no secret that a considerable number of failures in technology nowadays could, to a significant extent, be avoided if existing knowledge were used properly. This fact is particularly true in the field of corrosion and corrosion protection. Here, a wealth of information exists, but unfortunately in most cases it is scattered over many different information sources. However, as far back as 1953, an initiative was launched in Germany to compile an information system from the existing knowledge of corrosion and to complement this information with commentaries and interpretations by corrosion experts. The information system, entitled "DECHEMA-WERKSTOFF-TABELLE" (DECHEMA Corrosion Data Sheets), grew rapidly in size and content during the following years and soon became an indispensable tool for all engineers and scientists dealing with corrosion problems. This tool is still a living system today: it is continuously revised and updated by corrosion experts and thus represents a unique source of information. Currently, it comprises more than 12,000 pages with approximately 110,000 corrosion systems (i.e., all relevant commercial materials and media), based on the evaluation of over 100,000 scientific and technical articles which are referenced in the database.

Increasing demand for an English version of the DECHEMA WERKSTOFF-TABELLE arose in the 1980's; accordingly the first volume of the DECHEMA Corrosion Handbook was published in 1987. This was a slightly condensed version of the German edition and comprised 12 volumes. Before long, this handbook had spread all over the world and become a standard tool in countless laboratories outside Germany. The second edition of the DECHEMA Corrosion Handbook was published in 2004. Together the two editions covered 24 volumes.

Water is commonly described either in terms of its nature, usage, or origin. The implications in these descriptions range from being highly specific to very general. The present handbook compiles new and updated information on the corrosion behaviour of iron, nickel, zinc and their alloys in contact with the following water grades: drinking water, sea water, industrial and municipal waste water and high purity water.

All water contains some dissolved oxygen and is therefore somewhat corrosive. The rate of corrosion depends on many factors including the water's pH, electrical conductivity, oxygen concentration, and temperature. In addition to corrosion, metals dissolve when the water is extremely low in dissolved salts and in the presence of certain water-borne ions.

Understanding how to improve the corrosion resistance of iron, nickel, zinc and their alloys used in construction, transport and storage vessels and structures against this omnipresent chemical is crucial for all industries involved. This book is therefore an indispensable tool for all mechanical, civil and chemical engineers, material scientists and chemists working with these materials.

This handbook highlights the limitations of iron, nickel, zinc and their alloys in various water grades and provides vital information on corrosion protection measures. The chapters are arranged by the media leading to individual corrosion reactions, and a vast number of alloys are presented in terms of their behaviour in these media. The key information consists of quantitative data on corrosion rates coupled with commentaries on the background and mechanisms of corrosion behind these data, together with the dependencies on secondary parameters, such as flow-rate, pH, temperature, etc. Where necessary this information is complemented by more detailed annotations and by an immense number of references listed at the end of each chapter.

An important feature of this handbook is that the data was compiled for industrial use. Therefore, particularly for those working in industrial laboratories or for industrial clients, the book will be an invaluable source of rapid information for day to day problem solving. The handbook will have fulfilled its task if it helps to avoid the failures and problems caused by corrosion simply by providing a comprehensive source of information summarising the present state of the art. Last but not least, in cases where this knowledge is applied, there is a good chance of decreasing the costs of corrosion significantly.

Finally the editors would like to express their appreciation to Dr. Rick Durham and Dr. Horst Massong for their admirable commitment and meticulous editing of a work that is encyclopaedic in scope.

Michael Schütze, Marcel Roche and Roman Bender

How to use the Handbook

The Handbook provides information on the chemical resistance and the corrosion behaviour of iron, nickel, zinc and their alloys in contact with the following water grades: drinking water, sea water, industrial and municipal waste water and high-purity water.

The user is given information on the range of applications and corrosion protection measures.

Research results and operating experience reported by experts allow recommendations to be made for the selection of materials and to provide assistance in the assessment of damage.

The objective is to offer a comprehensive and concise description of the behaviour of these materials in contact with a particular aqueous medium.

The information on resistance is given as text, tables, and figures. The literature used by the authors is cited at the corresponding point. There is an index of materials as well as a subject index at the end of the book so that the user can quickly find the information given for a particular keyword.

The Handbook is thus a guide that leads the reader to materials that have already been used in certain cases, that can be used or that are not suitable owing to their lack of resistance.

The resistance is labeled with three evaluation symbols in view of concise presentation. Uniform corrosion is evaluated according to the following criteria:

Symbol	*Meaning*	*Area-related mass loss rate* *x*		*Corrosion rate* *y*
		g/m^2 h	g/m^2 d	mm/a
+	resistant	≤ 0.1	≤ 2.4	≤ 0.1
⊕	moderately resistant	> 0.1 to ≤ 1.0	> 2.4 to ≤ 24.0	> 0.1 to ≤ 1.0
–	not resistant	> 1.0	> 24.0	> 1.0

The evaluation of the corrosion resistance of metallic materials is given

- for uniform corrosion or local penetration rate, in: mm/a and mpy
- or if the density of the material is not known, in: g/m^2 h or g/m^2 d.

Pitting corrosion, crevice corrosion, and stress corrosion cracking or non-uniform attack are particularly highlighted.

The following equations are used to convert mass loss rates, x, into the corrosion rate, y:

from x_1 in g/m^2 h

$$\frac{x_1 \cdot 365 \cdot 24}{\rho \cdot 1{,}000} = y\ (mm/a)$$

from x_2 in g/m^2 d

$$\frac{x_2 \cdot 365}{\rho \cdot 1{,}000} = y\ (mm/a)$$

where

x_1: value in g/m^2 h
y: value in mm/a
x_2: value in g/m^2 d
d: days
ρ: density of material in g/cm^3
h: hours

In those media in which uniform corrosion can be expected, if possible, isocorrosion curves (corrosion rate $y = 0.1$ mm/a) are given.

Unless stated otherwise, the data was measured at atmospheric pressure and room temperature.

The resistance data should not be accepted by the user without question, and the materials for a particular purpose should not be regarded as the only ones that are suitable. To avoid wrong conclusions being drawn, it must be always taken into account that the expected material behaviour depends on a variety of factors that are often difficult to recognise individually and which may not have been taken deliberately into account in the investigations upon which the data is based. Under certain circumstances, even slight deviations in the chemical composition of the medium, in the pressure, in the temperature or, for example, in the flow rate are sufficient to have a significant effect on the behaviour of the materials. Furthermore, impurities in the medium or mixed media can result in a considerable increase in corrosion.

The composition or the pretreatment of the material itself can also be of decisive importance for its behaviour. In this respect, welding should be mentioned. The suitability of the component's design with respect to corrosion is a further point which must be taken into account. In case of doubt, the corrosion resistance should be investigated under operating conditions to decide on the suitability of the selected materials.

Contents

Warranty disclaimer

This book has been compiled from literature data with the greatest possible care and attention. The statements made in this book only provide general descriptions and information.

Even for the correct selection of materials and correct processing, corrosive attack cannot be excluded in a corrosion system as it may be caused by previously unknown critical conditions and influencing factors or subsequently modified operating conditions.

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High Purity Water

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Introduction

High purity water is completely demineralised water, which through additional purification processes leads to the removal of remaining electrolytes, organic substances, particles, colloidal components, microbiological impurities and dissolved gases to a very low content. Typical residual contents of electrolytes in high purity water are a few ppt, for microorganisms < 1 CFU/ml and for organic components (TOC) < 10 ppb. Until now there is no generally valid definition for the classification of high purity water, however in various applications guidelines and standards exist in which specifications for high purity water are contained [1–3]. A selection of these guidelines and standards are given in Table 1.

Guideline / Standard	*Application*	*Literature*
DIN ISO 3696	Analytical chemistry	[4]
ASTM D1193	Analytical chemistry	[5]
DAB 10 (German Pharmacopoeia)	Pharmaceuticals, medical products	[6]
EUAB (European Pharmacopoeia)	Pharmaceuticals, medical products, injections	[7]
NCCLS approved guideline C3–A3	Clinical laboratories	[8]
USP 27	Pharmaceuticals	[9]
VDI 2083 Sheet 9 (Draft)	Clean room technology, electronics- and pharmaceuticals industries	[10]

Table 1: Guidelines and standards concerning specifcations for high purity water

To assess the quality of high purity water various parameters for the particular application are used, e.g.:

- Electrical resistance or electrical conductivity
- Cation- and anion content, salt content, silicate content (SiO_2)
- Dissolved organic carbon (DOC), total organic carbon (TOC), oxidisable substances
- microbial impurities, germ number, bacteria (living, total), bacteria endotoxins
- Particles (number, size)
- Dry residue
- pH value
- Dissolved gas content (oxygen, nitrogen, carbon dioxide)

The corrosive attack on materials by high purity water differs far more greatly from that of potable, spring or sea water, whereupon – dependent upon the type of material – both strong attack (e.g. in plastics) and also lighter corrosion attack (e.g. in some metals) by high purity water can be observed.

Physical and chemical properties

High purity water (molar mass 18.015 g/mol) is a clear, odourless and tasteless, colourless liquid, which in thick layers appears blue. Some of the physical properties are listed in Table 2.

Property		
Melting point (at 1013 hPa)	°C K	0 273.15
Enthalpy of fusion (at 0 °C)	kJ/mol	6.010
Boiling point(at 1013 hPa)	°C K	100 373.15
Enthalpy of evaporation (at 100 °C)	kJ/mol	40.651
Enthalpy of sublimation (at 0 °C)	kJ/mol	51.13
Surface tension (at 25 °C/1013 hPa)	N/m	71.96×10^{-3}
Viscosity (at 25 °C/1013 hPa)	MPa s	0.8937
Specific heat capacity	J/g K	4.1855
Dielectric constant (at 25 °C/1013 hPa)		80.18
Electrical conductivity	μS/cm	0.0555–0.0635
Electrical resistance	MΩ · cm	18

Table 2: Physical properties of high purity water [2, 11]

The temperature dependence of density and vapour pressure on high purity water in the temperature range 0–100 °C is reported in Table 3. The sharp rise in vapour pressure above around 50 °C is of particular importance for organic materials, especially for coatings and linings, since increased permeation rates are to be expected above this temperature.

Temperature *°C*	*Vapour pressure* *bar*	*Density*[1] *kg/m*^{3}
0	0.00611	999.84
10	0.01228	999.70
20	0.02338	998.20
30	0.04245	995.65
40	0.07382	992.23
50	0.12346	988.03
60	0.19936	983.19
70	0.31181	977.76
80	0.47379	971.79
90	0.70123	965.31
100	1.01325	958.36

[1] at 1 atm

Table 3: Temperature dependence of water vapour pressure and density [12]

Unalloyed and low alloyed steels/Cast steel

Unalloyed and low alloyed steels are significantly attacked in high purity water at room temperature up to 100 °C, so long as the water is oxygen-rich. The maximum oxygen solubility occurs at 60 °C and this is also associated with the maximum in corrosion attack. At extreme temperatures the formation of a magnetite layer acts as a protective layer. Therefore boiler steels in steam boilers are resistant up to 570 °C, as long as pulsed operation with strongly changing pressure and temperature loads (damage to the protective scale) are avoided. Also, the pH value should be neutral or slightly alkaline and the start up and shut downs should proceed with caution.

Stress corrosion cracking can be avoided is the mechanical stresses of the components remains under the yield strength ($\sigma < Rp_{0,2}$) and no large compensation (yield strength too high) exists and the purity of the water is < 0.2 μS/cm and gaseous impurities are not present. Inhibitors such as hydrazine also greatly improve the behaviour.

Carbon steels or boiler steels are only slightly attacked by distilled or deionised, oxygen free water at room temperature. On the other hand steel in oxygen containing water or at 100 °C has only limited resistance. The corrosion values reach a maximum at about 60 °C in distilled water and are practically the same at room temperature and 100 °C [13]. When iron is exposed to high purity water oxides are produced, which tend to be partly dissolved or can remain on the metal surface, whereby hydrogen will be released:

$$Fe + 2\ H_2O \rightarrow Fe\ (OH)_2 + H_2$$

However, in boiling water Fe(II) hydroxide will be transformed to magnetite:

$$3\ Fe\ (OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2$$

At higher temperatures this reaction occurs instantaneously [14]. The extensively adherent magnetite film inhibits the further attack by water. The prerequisite for good adhesion is a clean and blank metal surface, on which the Fe_3O_4 can grow. However, if the film is formed at a small distance from the metal surface, e.g. in the presence of metallic copper, then it offers no protection [15].

The oxygen content of the water plays a very large role. Thus, one finds the following corrosion rates in distilled water at 25 °C after 9 days duration [16]:

14 mg/dm^2 in water with 8.2 mg/l oxygen
87 mg/dm^2 in water with 37 mg/l oxygen.

Bare iron is only attacked until a flawlessly grown magnetite scale protects the iron underneath. Therefore, one can use deaerated deionised water in non-protected pipes, where the iron uptake is below 0.05 mg/l [17]. In a failure analysis case, after 3 years service life a steel tank used for deionised water (2 mg/l dissolved substances, pH 8.1–8.4, 60–70 °C) with unimpeded access for oxygen and carbon dioxide, a 6 mm thick deposit of a shell like brown rust with undercutting pitting corrosion had formed. In order to reduce the attack of high purity water on boiler steels, additions of hydrazine during downtime are made (27 mg/l) [18]. Further