

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.

<i>Guideline / Standard</i>	<i>Application</i>	<i>Literature</i>
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 specifications 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.

<i>Property</i>		
Melting point (at 1013 hPa)	°C	0
	K	273.15
Enthalpy of fusion (at 0 °C)	kJ/mol	6.010
Boiling point(at 1013 hPa)	°C	100
	K	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

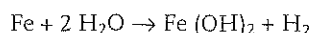
Table 3: Temperature dependence of water vapour pressure and density [12]

Unalloyed and low alloyed steels/Cast steel

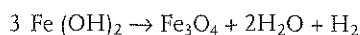
Unalloyed and low alloyed steels are significantly attacked in high purity water at room temperature up to 100 °C, so long as the water is oxygen-rich. The maximum oxygen solubility occurs at 60 °C and this is also associated with the maximum in corrosion attack. At extreme temperatures the formation 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 if the mechanical stresses of the components remains under the yield strength ($\sigma < R_{p0.2}$) and no large compensation (yield strength too high) exists and the purity of the water is $< 0.2 \mu\text{S}/\text{cm}$ 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:



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



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

inhibitors recommended include: 0.1 g $\text{Na}_2\text{Cr}_2\text{O}_7 \times \text{H}_2\text{O}$, 0.2 g $\text{K}_2\text{Cr}_2\text{O}_7$, 0.2 g KNO_2 , 0.2 g KCrO_4 or 0.2 g LiOH (per litre respectively) [19, 20].

The already mentioned transformation of Fe(II) hydroxide into magnetite is particularly active between 120 and 570 °C [15]. All boiler and pipe walls become covered with a uniform protective scale of magnetite during exposure, which relative to the standard hydrogen electrode shows a very noble potential from +400 to +500 mV, while for bare iron a potential of -440 mV was measured [21]. The scale thickness on the pipes reached about 0.05 mm [22], on the boiler walls up to 0.2 mm. The interior of the vessel which is protected by magnetite is practically immune to corrosion when the following conditions are filled:

- Uniform temperature, tailored to the material
- Avoidance of pulsed operation, extremely alternating loads and temperature swings (to avoid spallation of protective scale)
- Adherence of a pH value in the vessel water between neutral and slightly alkaline
- Exclusion of oxygen, chlorides and salts
- Caution with start ups and shut down

The Pourbaix diagram for iron in high purity water (for the temperatures 25, 100, 200 and 300 °C) is discussed in [23]. It shows for the dissolution quantities 10^{-6} and 10^{-8} M, that

- $\text{Fe}(\text{OH})_2$ (crystalline) is stable up to 85 °C and therefore the Schikorr reaction is thermodynamically not possible above 85 °C
- $\text{Fe}(\text{OH})_3$ (crystalline) and goethite are not stable at any temperature
- Haematite is the most stable solid product of Fe (III)
- $\text{Fe}^{3+}(\text{aq})$ is only stable at 25–100 °C and $\text{pH} > 0$
- In high purity water (10^{-8} M) due to the hydrolysis step of Fe (II), a corrosion area between iron and magnetite exists

The corrosion behaviour of steel in the cooling water of coal fired power stations was reported [24]. Hereby, aspects of the application of demineralised water with low phosphate additions (40–60 mg/l) and mechanical deaeration were summarised. The optimum conditions exist when the pH value is > 9.5 , the chloride content is < 5 mg/l and some oxygen (about 1% air saturation, which means about 0.1 mg/l) is present, thus completely anaerobic conditions should be avoided. Without giving corrosion rates, a pH value adjusted to 8.5–9.5 is expected to show very little to negligible attack (operating life at least 25 years).

The behaviour of a low alloyed steel in a test loop trial with regard to iron dissolution as well as scale formation under the conditions, such as in a pre-heater in a power station, was examined in [25]. Iron dissolution is particularly higher in de-ionised water at 150–160 °C under oxygen free conditions than with an oxygen content of 200 µg/l. Evidently in the presence of oxygen the steel exists in the passive condition, which is also concluded from the very noble potential values.

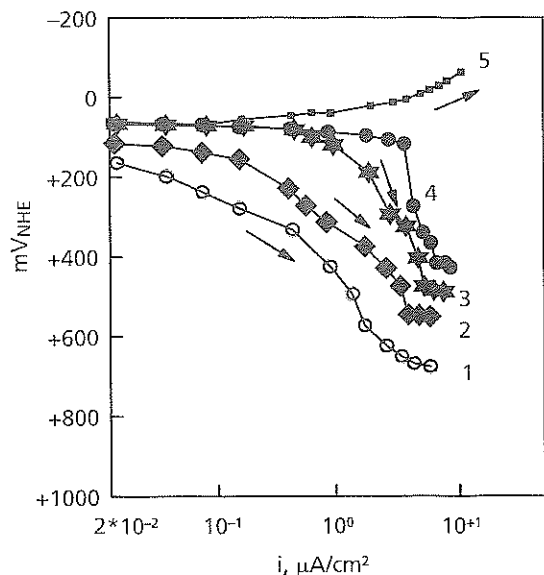


Figure 1: Anodic (1-4) and cathodic (5) polarisation curves of iron in high purity water (about 5 mg/l O₂) [28]

- 1) 25 °C
- 2) 78 °C
- 3) 118 °C
- 4) 139 °C
- 5) 140 °C

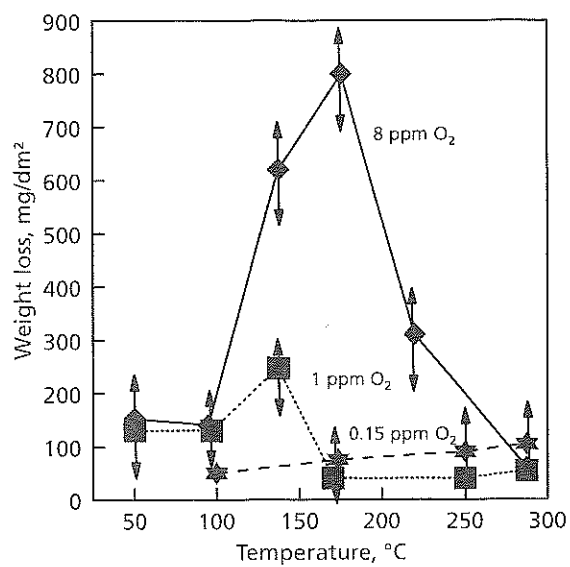


Figure 2: Weight loss of carbon steel in high purity water at 288 °C [30]