

Encyclopedia of

Nanotechnology in Water and Wastewater Treatment

Diego Ronaldinho
Editor

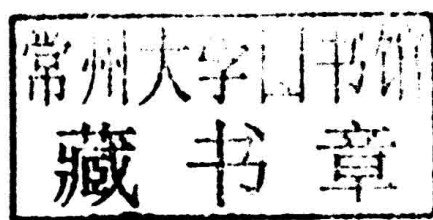
Encyclopedia of Nanotechnology in Water and Wastewater Treatment

**VOLUME 1: CONTROL OF IRON AND MANGANESE
IN DRINKING WATER**

Editor

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Preface

Iron and manganese are minerals commonly found in drinking water supplies. Iron and manganese are considered secondary contaminants. Secondary standards apply to substances in water that cause offensive taste, odor, colour, corrosion, foaming, or staining but have no direct affect on health. The standard Secondary Maximum Contaminant Level (SMCL) for iron is 0.3 milligrams per litre (mg/L or ppm) and 0.05 mg/L for manganese. Private water supplies are not subject to standards, but these standards can be used as guidelines to evaluate the quality of water from wells or tubewells. The presence of iron and manganese in water is one of the most frequent reasons for complaint due to aesthetic issues. These two metals can be removed fairly readily by physico-chemical treatment.

The four forms of iron and manganese commonly found in drinking water are ferrous, ferric, organic and iron bacteria. Normally, water appears clear when first drawn from the cold water faucet. If it is not, it may contain ferric iron or organic iron. Both colour the water. Ferric iron precipitates or settles out. Organic iron does not settle out. In well water, insoluble iron oxide is converted to a soluble form of ferrous (dissolved) iron. Ferrous iron is colourless, but when in contact with air, it oxidizes readily, creating reddish- brown, solid particles that then settle out as ferric oxide. Manganese is similar to iron but forms a brownish-black precipitate and stains. Manganese is less commonly found in groundwater than iron, rarely found alone in a water source, and generally found with dissolved iron.

The presence of iron in a water distribution system may also be caused by corrosion of metal pipes in the system. In this case, the problem must be corrected by corrosion control. If a disinfectant is added to the water, or if iron and manganese are fully or partially oxidized by any means before entering the distribution system, the oxidized iron and manganese will precipitate in the distribution system.

The presence of iron and manganese in the distribution system, in either the dissolved or oxidized state, can also provide a food source for bacterial growth in the system. The bacterial slimes that form can have the following detrimental effects - Reduction in pipeline flow capacity, clogging of meters and valves, further discoloration of the water as a result of the bacterial growth, increased chlorine demand. These bacteria obtain energy for growth from the chemical reaction that occurs when iron and manganese mix with dissolved oxygen. These bacteria form thick slime growths on the walls of the piping system and on well screens. These slimes tend to be a rust-coloured from iron and black-coloured from manganese. Variations in flow can cause these slime growths to separate from pipe walls, resulting in dirty water in the system. The growth of iron bacteria can be controlled by chlorination. However, when water containing iron is chlorinated, the iron is converted from the ferrous state to the ferric state—in other words, rust—and manganese is converted into black manganese dioxide. These materials form a coating on the inside of the water main and, when they break loose, makes the water dirty. Iron bacteria are considered harmless to health, however, they may give water an off taste or colour, cause splotchy yellow stains on laundry, and clog water systems.

The objective of this book is first to evaluate the occurrence, chemistry, and treatment methods associated with iron and manganese in ground and surface waters. Building upon these findings, a further goal was to study problems associated with these minerals in specific water distribution systems. This book will be of interest to water utility practitioners, health agencies and policy makers, as well as students on civil engineering and environmental engineering courses.

—*Editor*

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Chapter 1

Introduction

Iron

Iron is a chemical element with the symbol Fe (from Latin: *ferrum*) and atomic number 26. It is a metal in the first transition series. It is the most common element (by mass) forming the planet Earth as a whole, forming much of Earth's outer and inner core. It is the fourth most common element in the Earth's crust. Iron's very common presence in rocky planets like Earth is due to its abundant production as a result of fusion in high-mass stars, where the production of nickel-56 (which decays to the most common isotope of iron) is the last nuclear fusion reaction that is exothermic. This causes radioactive nickel to become the last element to be produced before collapse of a supernova leads to the explosive events that scatter this precursor radionuclide of iron abundantly into space.

Like other group 8 elements, iron exists in a wide range of oxidation states, -2 to $+6$, although $+2$ and $+3$ are the most common. Elemental iron occurs in meteoroids and other low oxygen environments, but is reactive to oxygen and water. Fresh iron surfaces appear lustrous silvery-gray, but oxidize in normal air to give hydrated iron oxides, commonly known as rust. Unlike many other metals which form passivating oxide layers, iron oxides occupy more volume than iron metal, and thus iron oxides flake off and expose fresh surfaces for corrosion.

Iron metal has been used since ancient times, though copper alloys, which have lower melting temperatures, were used first in history. Pure iron is soft (softer than aluminium), but is unobtainable by smelting. The material is significantly hardened and strengthened by impurities from the smelting process, such as carbon. A certain

proportion of carbon (between 0.002% and 2.1%) produces steel, which may be up to 1000 times harder than pure iron. Crude iron metal is produced in blast furnaces, where ore is reduced by coke to pig iron, which has a high carbon content. Further refinement with oxygen reduces the carbon content to the correct proportion to make steel. Steels and low carbon iron alloys with other metals (alloy steels) are by far the most common metals in industrial use, due to their great range of desirable properties and the abundance of iron.

Iron chemical compounds, which include ferrous and ferric compounds, have many uses. Iron oxide mixed with aluminium powder can be ignited to create a thermite reaction, used in welding and purifying ores. It forms binary compounds with the halogens and the chalcogens. Among its organometallic compounds is ferrocene, the first sandwich compound discovered.

Iron plays an important role in biology, forming complexes with molecular oxygen in hemoglobin and myoglobin; these two compounds are common oxygen transport proteins in vertebrates. Iron is also the metal used at the active site of many important redoxenzymes dealing with cellular respiration and oxidation and reduction in plants and animals.

Characteristics

Mechanical Properties

Characteristic values of tensile strength (TS) and Brinell hardness (BH) of different forms of iron.

<i>Material</i>	<i>TS (MPa)</i>	<i>BH (Brinell)</i>
Iron whiskers	11000	
Ausformed (hardened)steel	2930	850–1200
Martensitic steel	2070	600
Bainitic steel	1380	400
Pearlitic steel	1200	350
Cold-worked iron	690	200
Small-grain iron	340	100
Carbon-containing iron	140	40
Pure, single-crystal iron	10	3

The mechanical properties of iron and its alloys can be evaluated using a variety of tests, including the Brinell test, Rockwell test and the Vickers hardness test. The data on iron is so consistent that it

is often used to calibrate measurements or to compare tests. However, the mechanical properties of iron are significantly affected by the sample's purity: pure research-purpose single crystals of iron are actually softer than aluminium, and the purest industrially produced iron (99.99%) has a hardness of 20–30 Brinell. An increase in the carbon content of the iron will initially cause a significant corresponding increase in the iron's hardness and tensile strength. Maximum hardness of 65 R_c is achieved with a 0.6% carbon content, although this produces a metal with a low tensile strength.

Phase Diagram and Allotropes

Iron represents an example of allotropy in a metal. There are at least four allotropic forms of iron, known as α , γ , δ , and ϵ ; at very high pressures, some controversial experimental evidence exists for a phase β stable at very high pressures and temperatures.

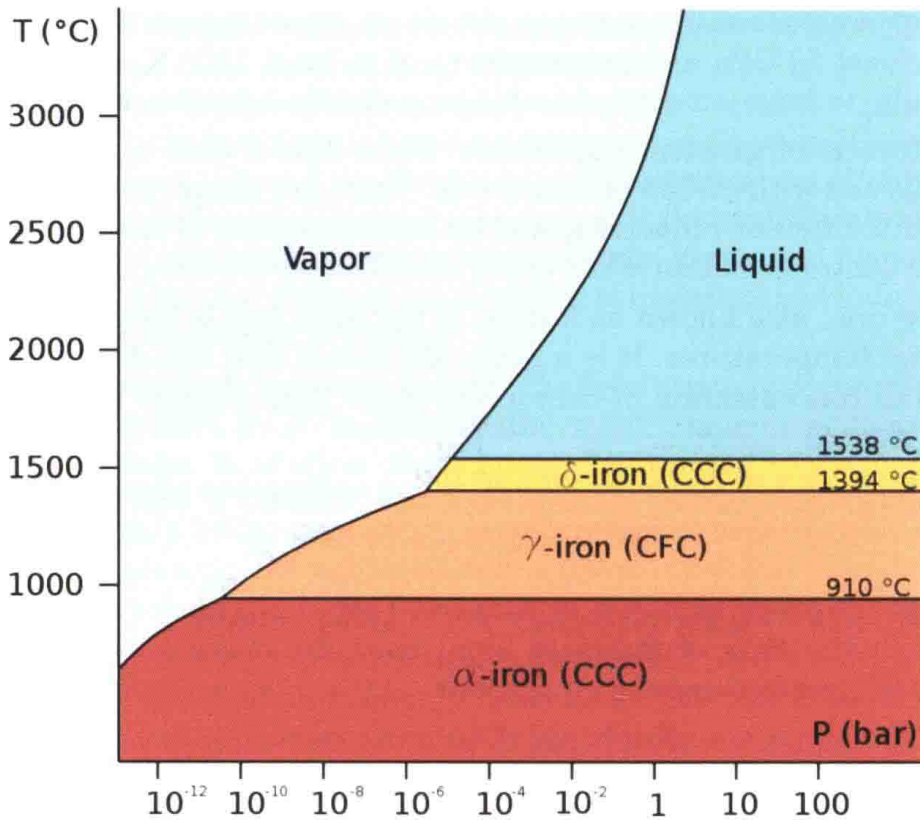


Figure: Low-pressure phase diagram of pure iron

As molten iron cools down it crystallizes at 1538 °C into its δ allotrope, which has a body-centred cubic (bcc) crystal structure. As it cools further its crystal structure changes to face-centred cubic (fcc) at 1394 °C, when it is known as γ -iron, or austenite. At 912 °C the

crystal structure again becomes bcc as α -iron, or ferrite, is formed, and at 770 °C (the Curie point, T_c) iron becomes magnetic. As the iron passes through the Curie temperature there is no change in crystalline structure, but there is a change in “domain structure”, where each domain contains iron atoms with a particular electronic spin. In unmagnetized iron, all the electronic spins of the atoms within one domain are in the same direction; the neighbouring domains point in various directions and thus cancel out. In magnetized iron, the electronic spins of all the domains are aligned, so that the magnetic effects of neighbouring domains reinforce each other. Although each domain contains billions of atoms, they are very small, about 10 micrometres across. At pressures above approximately 10 GPa and temperatures of a few hundred kelvin or less, α -iron changes into a hexagonal close-packed (hcp) structure, which is also known as ϵ -iron; the higher-temperature γ -phase also changes into ϵ -iron, but does so at higher pressure. The β -phase, if it exists, would appear at pressures of at least 50 GPa and temperatures of at least 1500 K; it has been thought to have an orthorhombic or a double hcp structure.

Iron is of greatest importance when mixed with certain other metals and with carbon to form steels. There are many types of steels, all with different properties, and an understanding of the properties of the allotropes of iron is key to the manufacture of good quality steels.

α -iron, also known as ferrite, is the most stable form of iron at normal temperatures. It is a fairly soft metal that can dissolve only a small concentration of carbon (no more than 0.021% by mass at 910 °C).

Above 912 °C and up to 1400 °C α -iron undergoes a phase transition from bcc to the fcc configuration of γ -iron, also called austenite. This is similarly soft and metallic but can dissolve considerably more carbon (as much as 2.04% by mass at 1146 °C). This form of iron is used in the type of stainless steel used for making cutlery, and hospital and food-service equipment.

The high-pressure phases of iron are important as endmember models for the solid parts of planetary cores. The inner core of the Earth is generally assumed to consist essentially of an iron-nickel alloy with ϵ (or β) structure.

The melting point of iron is experimentally well defined for pressures up to approximately 50 GPa. For higher pressures, different studies placed the γ - ϵ -liquid triple point at pressures differing by tens of gigapascals and yielded differences of more than 1000 K for the

melting point. Generally speaking, molecular dynamics computer simulations of iron melting and shock wave experiments suggest higher melting points and a much steeper slope of the melting curve than static experiments carried out in diamond anvil cells.

Isotopes

Naturally occurring iron consists of four stable isotopes: 5.845% of ^{54}Fe , 91.754% of ^{56}Fe , 2.119% of ^{57}Fe and 0.282% of ^{58}Fe . Of these stable isotopes, only ^{57}Fe has a nuclear spin ($-1/2$). The nuclide ^{54}Fe is predicted to undergo double beta decay, but this process had never been observed experimentally for these nuclei, and only the lower limit on the half-life was established: $t_{1/2} > 3.1 \times 10^{22}$ years.

^{60}Fe is an extinct radionuclide of long half-life (2.6 million years). It is not found on Earth, but its ultimate decay product is the stable nuclide nickel-60.

Much of the past work on measuring the isotopic composition of Fe has focused on determining ^{60}Fe variations due to processes accompanying nucleosynthesis (i.e., meteorite studies) and ore formation. In the last decade however, advances in mass spectrometry technology have allowed the detection and quantification of minute, naturally occurring variations in the ratios of the stable isotopes of iron. Much of this work has been driven by the Earth and planetary science communities, although applications to biological and industrial systems are beginning to emerge.

The most abundant iron isotope ^{56}Fe is of particular interest to nuclear scientists as it represents the most common endpoint of nucleosynthesis. It is often cited, falsely, as the isotope of highest binding energy, a distinction which actually belongs to nickel-62. Since ^{56}Ni is easily produced from lighter nuclei in the alpha process in nuclear reactions in supernovae, nickel-56 (14 alpha particles) is the endpoint of fusion chains inside extremely massive stars, since addition of another alpha particle would result in zinc-60, which requires a great deal more energy. This nickel-56, which has a half-life of about 6 days, is therefore made in quantity in these stars, but soon decays by two successive positron emissions within supernova decay products in the supernova remnant gas cloud, first to radioactive cobalt-56, and then stable iron-56. This last nuclide is therefore common in the universe, relative to other stable metals of approximately the same atomic weight.

In phases of the meteorites *Semarkona* and *Chervony Kut* a correlation between the concentration of ^{60}Ni , the daughter product

of ^{60}Fe , and the abundance of the stable iron isotopes could be found which is evidence for the existence of ^{60}Fe at the time of formation of the Solar System. Possibly the energy released by the decay of ^{60}Fe contributed, together with the energy released by decay of the radionuclide ^{26}Al , to the remelting and differentiation of asteroids after their formation 4.6 billion years ago. The abundance of ^{60}Ni present in extraterrestrial material may also provide further insight into the origin of the Solar System and its early history.

Nuclei of iron atoms have some of the highest binding energies per nucleon, surpassed only by the nickel isotope ^{62}Ni . This is formed by nuclear fusion in stars. Although a further tiny energy gain could be extracted by synthesizing ^{62}Ni , conditions in stars are unsuitable for this process to be favoured. Elemental distribution on Earth greatly favours iron over nickel, and also presumably in supernova element production. Iron-56 is the heaviest stable isotope produced by the alpha process in stellar nucleosynthesis; elements heavier than iron and nickel require a supernova for their formation. Iron is the most abundant element in the core of red giants, and is the most abundant metal in iron meteorites and in the dense metal cores of planets such as Earth.

Nucleosynthesis

Iron is created by extremely large, extremely hot (over 2.5 billion kelvin) stars through the silicon burning process. It is the heaviest stable element to be produced in this manner. The process starts with the second largest stable nucleus created by silicon burning, which is calcium. One stable nucleus of calcium fuses with one helium nucleus, creating unstable titanium. Before the titanium decays, it can fuse with another helium nucleus, creating unstable chromium. Before the chromium decays, it can fuse with another helium nucleus, creating unstable iron. Before the iron decays, it can fuse with another helium nucleus, creating unstable nickel-56. Any further fusion of nickel-56 consumes energy instead of producing energy, so after the production of nickel-56, the star does not produce the energy necessary to keep the core from collapsing. Eventually, the nickel-56 decays to unstable cobalt-56, which in turn decays to stable iron-56. When the core of the star collapses, it creates a supernova. Supernovas also create additional forms of stable iron via the r-process.

Planetary Occurrence

Iron is the sixth most abundant element in the Universe, and the most common refractory element. It is formed as the final exothermic stage of stellar nucleosynthesis, by silicon fusion in massive stars.

Metallic or native iron is rarely found on the surface of the Earth because it tends to oxidize, but its oxides are pervasive and represent the primary ores. While it makes up about 5% of the Earth's crust, both the Earth's inner and outer core are believed to consist largely of an iron-nickel alloy constituting 35% of the mass of the Earth as a whole. Iron is consequently the most abundant element on Earth, but only the fourth most abundant element in the Earth's crust. Most of the iron in the crust is found combined with oxygen as iron oxide minerals such as hematite and magnetite. Large deposits of iron are found in banded iron formations. These geological formations are a type of rock consisting of repeated thin layers of iron oxides, either magnetite (Fe_3O_4) or hematite (Fe_2O_3), alternating with bands of iron-poor shale and chert. The banded iron formations were laid down in the time between 3,700 million years ago and 1,800 million years ago.

About 1 in 20 meteorites consist of the unique iron-nickel minerals taenite (35–80% iron) and kamacite (90–95% iron). Although rare, iron meteorites are the main form of natural metallic iron on the Earth's surface. It was proven by Mössbauer spectroscopy that the red colour of the surface of Mars is derived from an iron oxide-rich regolith.

Stocks in Use in Society

According to the International Resource Panel's Metal Stocks in Society report, the global per capita stock of iron in use in society is 2200 kg. Much of this is in more-developed countries (7000–14000 kg per capita) rather than less-developed countries (2000 kg per capita).

Chemistry and Compounds

<i>Oxidationstate</i>	<i>Representative Compound</i>
–2	Disodium tetracarbonylferrate (Collman's reagent)
–1	
0	Iron pentacarbonyl
1	Cyclopentadienyliron dicarbonyl dimer ("Fp ₂ ")
2	Ferrous sulfate, ferrocene
3	Ferric chloride, ferrocenium tetrafluoroborate
4	Barium ferrate(IV)
5	
6	Potassium ferrate

Iron forms compounds mainly in the +2 and +3 oxidation states. Traditionally, iron(II) compounds are called ferrous, and iron(III) compounds ferric. Iron also occurs in higher oxidation states, an

example being the purple potassium ferrate (K_2FeO_4) which contains iron in its +6 oxidation state. Iron(IV) is a common intermediate in many biochemical oxidation reactions. Numerous organometallic compounds contain formal oxidation states of +1, 0, “1, or even “2. The oxidation states and other bonding properties are often assessed using the technique of Mössbauer spectroscopy. There are also many mixed valence compounds that contain both iron(II) and iron(III) centres, such as magnetite and Prussian blue ($Fe_4(Fe[CN]_6)_3$). The latter is used as the traditional “blue” in blueprints.

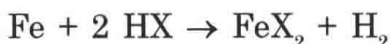
The iron compounds produced on the largest scale in industry are iron(II) sulfate ($FeSO_4 \cdot 7H_2O$) and iron(III) chloride ($FeCl_3$). The former is one of the most readily available sources of iron(II), but is less stable to aerial oxidation than Mohr's salt ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$). Iron(II) compounds tend to be oxidized to iron(III) compounds in the air.

Unlike many other metals, iron does not form amalgams with mercury. As a result, mercury is traded in standardized 76 pound flasks (34 kg) made of iron.

Binary Compounds

Iron reacts with oxygen in the air to form various oxide and hydroxide compounds; the most common are iron(II,III) oxide (Fe_3O_4), and iron(III) oxide (Fe_2O_3). Iron(II) oxide also exists, though it is unstable at room temperature. These oxides are the principal ores for the production of iron. They are also used in the production of ferrites, useful magnetic storage media in computers, and pigments. The best known sulfide is iron pyrite (FeS_2), also known as fool's gold owing to its golden luster.

The binary ferrous and ferric halides are well known, with the exception of ferric iodide. The ferrous halides typically arise from treating iron metal with the corresponding binary halogen acid to give the corresponding hydrated salts.



Iron reacts with fluorine, chlorine, and bromine to give the corresponding ferric halides, ferric chloride being the most common:



Coordination and Organometallic Compounds

Several cyanide complexes are known. The most famous example is Prussian blue, ($Fe_4(Fe[CN]_6)_3$). Potassium ferricyanide and potassium ferrocyanide are also known; the formation of Prussian blue upon

reaction with iron(II) and iron(III) respectively forms the basis of a “wet” chemical test. Prussian blue is also used as an antidote for thallium and radioactive caesium poisoning. Prussian blue can be used in laundry bluing to correct the yellowish tint left by ferrous salts in water.

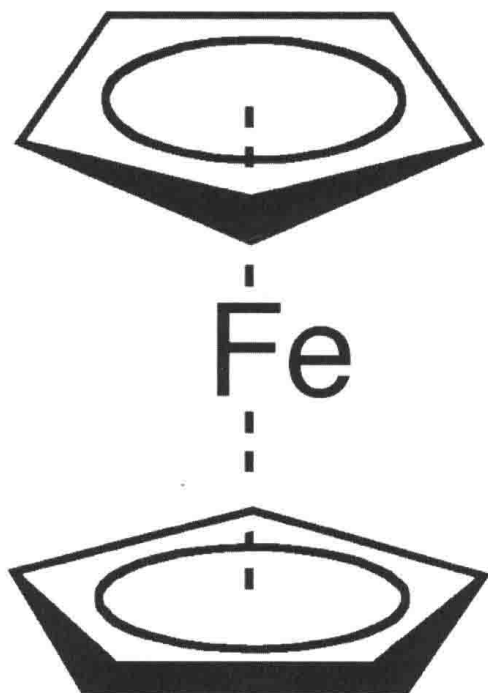


Figure: Ferrocene

Several carbonyl compounds of iron are known. The premier iron(0) compound is iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, which is used to produce carbonyl iron powder, a highly reactive form of metallic iron. Thermolysis of iron pentacarbonyl gives the trinuclear cluster, triiron dodecacarbonyl. Collman's reagent, disodium tetracarbonylferrate, is a useful reagent for organic chemistry; it contains iron in the -2 oxidation state. Cyclopentadienyliron dicarbonyl dimer contains iron in the rare $+1$ oxidation state.

Ferrocene is an extremely stable complex. The first sandwich compound, it contains an iron(II) centre with two cyclopentadienyl ligands bonded through all ten carbon atoms. This arrangement was a shocking novelty when it was first discovered, but the discovery of ferrocene has led to a new branch of organometallic chemistry. Ferrocene itself can be used as the backbone of a ligand, e.g. dppf. Ferrocene can itself be oxidized to the ferrocenium cation (Fc^+); the ferrocene/ferrocenium couple is often used as a reference in electrochemistry.