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Iron

Contents

1 . Introduction :

Iron is a chemical element with the symbol **Fe** (Latin : *ferrum*) and atomic number 26. Iron is a group 8 and period 4 element. Iron and iron alloys (steels) are by far the most common metals and the most common ferromagnetic materials in everyday use. Fresh iron surfaces are lustrous and silvery - grey in colour, but oxidise in air to form a red or brown coating of ferrous oxide or rust. Pure single crystals of iron are soft (softer than aluminium) , and the addition of minute amounts of impurities, such as carbon, significantly strengthens them. Alloying iron with appropriate small amounts (up to a few per cent) of other metals and carbon produces steel, which can be 1,000 times harder than pure iron.

Iron - 56 is the heaviest stable isotope produced by the alpha process in stellar nucleosynthesis; heavier elements than iron and

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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.

Name , Symbol , Number	Iron , Fe , 26
Element Category	Transition metal
Group , period , block	8 , 4 , d
Standard atomic weight	56 g · mol^{-1}
Electron configuration	[Ar] 3d^{6} 4s^{2}
Electrons per shell	2 , 8 , 14, 2
Phase	Solid
Density	7.874 g·cm^{-3}
Liquid density at m.p.	6.98 g·cm^{-3}
Melting Point	1538 ° C
Boiling Point	2862 °C
Heat of Fusion	13.81 kJ · mol^{-1}
Heat of Vaporization	340 kJ · mol^{-1}
Specific heat capacity	(25 °C) 25.10 J·mol^{-1}·K^{-1}
Electronegativity	1.83 (Pauling scale)
Ionization energies (more)	1st : 762.5 kJ · mol^{-1}
	2nd : 1561.9 kJ · mol^{-1}
	3rd : 2957 kJ · mol^{-1}
Atomic radius	126 pm
Covalent radius	132± 3 (low spin) pm 152 ± 6 (high spin) pm
Magnetic ordering	ferro magnetic
Electrical resistivity	(20 °C) 96.1 nΩ ·m
Thermal conductivity	(300 K) 80.4 W · m^{-1} ·K^{-1}
Thermal expansion	(25 °C) 11.8 µm·m^{-1} · K^{-1}
Speed of sound	5120 m · s^{-1}
Mohs hardness	4.0

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2 . Characteristics :

Pure iron is a metal but is rarely found in this form on the surface of the earth because it oxidizes readily in the presence of oxygen and moisture. In order to obtain metallic iron, oxygen must be removed from naturally occurring ores by chemical reduction – mainly of the iron ore hematite (Fe_2O_3) by carbon at high temperature. The properties of iron can be modified by alloying it with various other metals (and some non – metals , notably carbon and silicon) to form steels.

Nuclei of iron atoms have some of the highest binding energies per nucleon, surpassed only by the nickel isotope ^{62}Ni. The universally most abundant of the highly stable nuclides is, however, ^{56}Fe. 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 (as Fe^{2+} , ferrous ion) is a necessary trace element used by almost all living organisms. The only exceptions are several organisms that live in iron-poor environments and have evolved to use different elements in their metabolic processes, such as manganese instead of iron for catalysis, or hemocyanin instead of hemoglobin. Iron - containing enzymes, usually containing heme prosthetic groups, participate in catalysis of oxidation reactions in biology, and in transport of a number of soluble gases. hemoglobin , cytochrome , and catalyze.

3 . Mechanical properties

Mechanical properties of iron and its alloys are traditionally evaluated using various measurements, such as Brinell test, Rockwell test, tensile strength and other; their results are so much consistent among each other that universal relations are often used to relate results of one measurement to another.[3][4] Those measurements reveal that mechanical properties of iron crucially depend on purity: Purest research - purpose single crystals of iron are softer than

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aluminium. Addition of only 10 parts per million of carbon doubles their strength . The hardness increases rapidly with carbon content up to 0.2 % and saturates at ~ 0.6 % . The purest industrially produced iron (about 99.99 % purity) has hardness of 20 - 30 Brinell .

3 . 1 . Allotropes of Iron

Iron represents perhaps the best - known example of allotropy in a metal. There are three allotropic forms of iron, known as α , γ and δ

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) the 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; however, in neighbouring domains they point in various directions and thus cancel out. In magnetized iron, the electronic spins of all the domains are all 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 microns across.

Iron is of most 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 .

Alpha 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 body - centred cubic to the face-centred cubic

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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.

3 . 2 . Occurrence

Iron is the sixth most abundant element in the Universe, formed as the final act of nucleosynthesis, by silicon fusing in massive stars. While it makes up about 5 % of the Earth's crust, the Earth's core is 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.

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 major form of natural metallic iron on the Earth's surface .

The red colour of the surface of Mars is thought to derive from an iron oxide-rich regolith.

3 . 3 . Isotopes of Iron ;

Naturally occurring iron consists of four isotopes : 5.845 % of radioactive ^{54}Fe (half –life : $>3.1\times10^{22}$ years) , 91.754 % of stable ^{56}Fe , 2.119 % of stable ^{57}Fe and 0.282 % of stable ^{58}Fe. ^{60}Fe is an extinct radionuclide of long half - life (1.5 million years) .

Much of the past work on measuring the isotopic composition of Fe has centred 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

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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. A common misconception is that this isotope represents the most stable nucleus possible, and that it thus would be impossible to perform fission or fusion on ^{56}Fe and still liberate energy. This is not true, as both ^{62}Ni and ^{58}Fe are more stable, being the most stable nuclei. However, since ^{56}Ni is much more 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 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, to first 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. Of the stable isotopes, only ^{57}Fe has a nuclear spin ($-1/2$) .

4 . Chemistry and compounds

Iron forms compounds mainly in the +2 and +3 oxidation states. Traditionally, iron (II) compounds have been called ferrous, and iron

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(III) compounds ferric. There are many compounds in each of the oxidation states . representative examples would include iron (II) sulfate ($FeSO_4$) and iron (III) chloride ($FeCl_3$) . There are also numerous examples of compounds that contain iron atoms in both of these oxidation states, such as magnetite and prussian blue. The ferrate anion [FeO_4 $]^{2-}$ contains an iron(VI) centre, its highest known oxidation state, and is present, for example in potassium ferrate (K_2FeO_4) . There are numerous organometallic compounds (such as iron pentacarbonyl) that contain formally zerovalent (or lower) iron.

5 . History

The first wrought iron used by mankind during prehistory came from meteors. The smelting of iron in bloomeries began in the second millennium BC . Artefacts from smelted iron occur in India from 1800 - 1200 BC . in the Levant from about 1500 BC (suggesting smelting in Anatolia or the Caucasus) .

Cast iron was first produced in China about 550 BC,[13] but not in Europe until the medieval period . During the medieval period, means were found in Europe of producing wrought iron from cast iron (in this context known as pig iron) using finery forges. For all these processes, charcoal was required as fuel.

Steel (with smaller carbon content than pig iron but more than wrought iron) was first produced in antiquity. New methods of producing it by carburizing bars of iron in the cementation process were devised in the 17th century AD. In the Industrial Revolution, new methods of producing bar iron without charcoal were devised and these were later applied to produce steel. In the late 1850s, Henry Bessemer invented a new steelmaking process, involving blowing air through molten pig iron, to produce mild steel. This and other 19th century and later processes have led to wrought iron no longer being produced.

6 . Industrial production

The production of iron or steel is a process unless the desired final product is cast iron. The first stage is to produce pig iron in a

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blast furnace. The second is to make wrought iron or steel from pig iron by a further process.

6 . 1 . Blast furnace

Ninety percent of all mining of metallic ores is for the extraction of iron. Industrially, iron is produced starting from iron ores, principally hematite (nominally Fe_2O_3) and magnetite (Fe_3O_4) by a carbothermic reaction (reduction with carbon) in a blast furnace at temperatures of about 2000 °C . In a blast furnace , iron ore , carbon in the form of coke , and a *flux* such as lime stone (which is used to remove impurities in the ore which would otherwise clog the furnace with solid material) are fed into the top of the furnace , while a blast of heated air is forced into the furnace at the bottom.

In the furnace , the coke reacts with oxygen in the air blast to produce carbon monoxide :

$$2\ C + O_2 \rightarrow 2\ CO$$

The carbon monoxide reduces the iron ore (in the chemical equation below , hematite) to molten iron, becoming carbon dioxide in the process:

$$3\ CO + Fe_2O_3 \rightarrow 2\ Fe + 3\ CO_2$$

The flux is present to melt impurities in the ore, principally silicon dioxide sand and other silicates. Common fluxes include lime stone (principally calcium carbonate) and dolomite (calcium - magnesium carbonate) . Other fluxes may be used depending on the impurities that need to be removed from the ore . In the heat of the furnace the lime stone flux decomposes to calcium oxide :

$$CaCO_3 \rightarrow Ca\ O + CO_2$$

Then calcium oxide combines with silicon dioxide to form a *slag* :

$$Ca\ O + SiO_2 \rightarrow Ca\ SiO_3$$

The slag melts in the heat of the furnace . In the bottom of the furnace, the molten slag floats on top of the denser molten iron, and

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apertures in the side of the furnace are opened to run off the iron and the slag separately. The iron once cooled , is called pig iron , while the slag can be used as a material in road construction or to improve mineral - poor soils for agriculture .

In 2005, approximately 1,544 million metric tons of iron ore were produced world wide . China was the top producer of iron ore with at least one-fourth world share followed by Brazil, Australia and India .

6 . 2 . Further processes (Steelmaking and Iron works) :

Pig iron is not pure iron , but has 4 – 5 % carbon dissolved in it with small amounts of other impurities like sulfur , magnesium , phosphorus and manganese. As the carbon is the major impurity, the iron (pig iron) becomes brittle and hard . This form of iron is used to cast articles in foundries such as stoves, pipes, radiators, lamp-posts and rails.

Alternatively pig iron may be made into steel (with up to about 2 % carbon) or wrought iron (commercially pure iron) . Various processes have been used for this, including finery forges, puddling furnaces, Bessemer converters, open hearth furnaces, basic oxygen furnaces, and electric arc furnaces. In all cases, the objective is to oxidize some or all of the carbon, together with other impurities .

On the other hand, other metals may be added to make alloy steels .

The hardness of the steel depends upon its carbon content, the higher the proportion of carbon, the greater the hardness and the lesser the ductility. The properties of the steel can also be changed by tempering it .

To harden the steel, it is heated to red hot and then cooled by quenching it in the water. It becomes harder and more brittle. This steel is then heated to a required temperature and allowed to cool . The steel thus formed is less brittle.

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7 . Applications

7 . 1 . Elemental iron

Iron is the most widely used of all the metals , accounting for 95 % of worldwide metal production. Its low cost and high strength make it indispensable in engineering applications such as the construction of machinery and machine tools , automobiles , the hulls of large ships, and structural components for buildings. Since pure iron is quite soft, it is most commonly used in the form of steel. Some of the forms in which iron is produced commercially include :

- Pig iron has 3.5 – 4.5 % carbon and contains varying amounts of contaminants such as sulfur, silicon and phosphorus. Its only significance is that of an intermediate step on the way from iron ore to cast iron and steel.
- Cast iron contains 2 – 4 % carbon , 1– 6 % silicon, and small amounts of manganese. Contaminants present in pig iron that negatively affect material properties, such as sulfur and phosphorus, have been reduced to an acceptable level. It has a melting point in the range of 1420 – 1470 K, which is lower than either of its two main components, and makes it the first product to be melted when carbon and iron are heated together. Its mechanical properties vary greatly, dependent upon the form carbon takes in the alloy. "White" cast irons contain their carbon in the form of cementite, or iron carbide. This hard, brittle compound dominates the mechanical properties of white cast irons, rendering them hard, but unresistant to shock. The broken surface of a white cast iron is full of fine facets of the broken carbide, a very pale, silvery, shiny material, hence the appellation. In grey iron the carbon exists free as fine flakes of graphite, and also renders the material brittle due to the stress - raising nature of the sharp edged flakes of graphite. A newer variant of grey iron, referred to as ductile iron is specially treated with trace amounts of magnesium to alter the shape of graphite to spheroids , or nodules, vastly increasing the toughness and strength of the material .

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The fining process of smelting iron ore to make wrought iron from pig iron, with the right illustration displaying men working a blast furnace, from the *Tiangong Kaiwu* encyclopedia, published in 1637 by Song Yingxing.

- Wrought iron contains less than 0.25 % carbon . It is a tough, malleable product, but not as fusible as pig iron. If honed to an edge, it loses it quickly. Wrought iron is characterized by the presence of fine fibres of slag entrapped in the metal. Wrought iron is more corrosion resistant than steel. It has been almost completely replaced by mild steel for traditional " wrought iron " products and blacksmithing. Mild steel corrodes more readily that wrought iron, but is cheaper and more widely available.
- Carbon steel contains 2.0 % carbon or less , with small amounts of manganese, sulfur, phosphorus, and silicon.
- Alloy steels contain varying amounts of carbon as well as other metals, such as chromium, vanadium, molybdenum, nickel, tungsten, etc. Their alloy content raises their cost, and so they can usually only be justified for specialist uses. Recent developments in ferrous metallurgy have produced a growing range of microalloyed steels, also termed 'HSLA' or high-strength, low alloy steels, containing tiny additions to produce high strengths and often spectacular toughness at minimal cost .

The main disadvantage of iron and steel is that pure iron, and most of its alloys, suffer badly from rust if not protected in some way. Painting, galvanization, passivation, plastic coating and bluing are some techniques used to protect iron from rust by excluding water and oxygen or by sacrificial protection.

7 . 2 . Iron compounds

- Iron oxides (FeO , Fe_3O_4 , and Fe_2O_3) are ores used for iron production . They are also used as a catalyst in the Space Shuttle Solid Rocket Boosters , and in the production of magnetic storage media in computers . They are often mixed

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with other compounds, and retain their magnetic properties in solution.

- Iron (II) acetate Fe (CH_3CO_2) $_2$ (ferrous acetate) is used as a mordant in the dyeing of cloth and leather , and as a wood preservative.
- Iron (III) ammonium citrate ($C_6H_{5+4y}Fe_xN_yO_7$) is used in blue prints.
- Iron (III) arsenate ($FeAsO_4$) is used in insecticides.
- Iron (III) chloride (Fe Cl_3) is used in water purification and sewage treatment , in the dyeing of cloth , as a colouring agent in paints , as an additive in animal feed , and as an etchant for copper in the manufacture of printed circuit boards.
- Iron (III) chromate $Fe_2(CrO_4)_3$ is a yellow pigment for paints and ceramics.
- Iron (III) hydroxide Fe $(OH)_3$ is used as a brown pigment for rubber and in water purification systems.
- Iron (III) phosphate ($FePO_4$) is used in fertilizers and as an additive in human and animal food.
- Iron (II) gluconate (Fe $(C_6H_{11}O_7)_2$) is used as a dietary supplement in iron pills.
- Iron (II) oxalate (FeC_2O_4) is used as yellow pigment for paints , plastics , glass and ceramics , and in photography.
- Iron (II) sulfate ($FeSO_4$) is used in water purification and sewage treatment systems , as a catalyst in the production of ammonia , as an ingredient in fertilizer , herbicide, and moss killer , as an additive in animal feed , in wood preservative , and as an additive to flour to increase nutritional iron levels . Experimental iron fertilization of areas of the ocean using iron (II) sulfate has proven successful in increasing plankton growth .

The use of iron compounds in organic synthesis is mainly for the reduction of nitro compounds . Additionally, iron has been used for desulfurizations , reduction of aldehydes , and the deoxygenation of amine oxides .

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8 . Biological role (Human iron metabolism) :

Iron is essential to nearly all known organisms. In cells, iron is generally stored in the centre of metalloproteins, because "free" iron (which binds non - specifically to many cellular components) can catalyse production of toxic free radicals. Iron deficiency can lead to iron deficiency anemia.

In animals, plants, and fungi, iron is often the metal ion incorporated into the heme complex. Heme is an essential component of cytochrome proteins, which mediate redox reactions, and of oxygen carrier proteins such as hemoglobin, myoglobin, and leghemoglobin. Inorganic iron also contributes to redox reactions in the iron - sulfur clusters of many enzymes, such as nitrogenase (involved in the synthesis of ammonia from nitrogen and hydrogen) and hydrogenase . Non - heme iron proteins include the enzymes methane mono oxygenase (oxidizes methane to methanol) , ribonucleotide reductase (reduces ribose to deoxyribose ; DNA biosynthesis) , hemerythrins (oxygen transport and fixation in marine invertebrates) and purple acid phosphatase (hydrolysis of phosphate esters) .

Iron distribution is heavily regulated in mammals , partly because iron has a high potential for biological toxicity[24]. Iron distribution is also regulated because many bacteria require iron, so restricting its availability to bacteria (generally by sequestering it inside cells) can help to prevent or limit infections. This is probably the reason for the relatively low amounts of iron in mammalian milk. A major component of this regulation is the protein transferrin, which binds iron absorbed from the duodenum and carries it in the blood to cells .

8 . 1 . Dietary sources

Good sources of dietary iron include red meat , fish , poultry , lentils , beans , leaf vegetables , tofu , chickpeas , black - eyed peas , fortified bread , and fortified breakfast cereals. Iron in low amounts is found in molasses , teff and farina. Iron in meat (haem iron) is more easily absorbed than iron in vegetables , but heme / hemoglobin from

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red meat has effects which may increase the likelihood of colorectal cancer .

Iron provided by dietary supplements is often found as iron (II) fumarate, although iron sulfate is cheaper and is absorbed equally well. Elemental iron, despite being absorbed to a much smaller extent (stomach acid is sufficient to convert some of it to ferrous iron) , is often added to foods such as breakfast cereals or "enriched" wheat flour (where it is listed as "reduced iron" in the list of ingredients). Iron is most available to the body when chelated to amino acids - iron in this form is ten to fifteen times more bioavailable than any other, and is also available for use as a common iron supplement. Often the amino acid chosen for this purpose is the cheapest and most common amino acid, glycine, leading to " iron glycinate " supplements . The RDA for iron varies considerably based on age , gender , and source of dietary iron (heme -based iron has higher bioavailability) . Infants may require iron supplements if they are breast - fed . Blood donors and pregnant women are at special risk of low iron levels and are often advised to supplement their iron intake .

8 . 2 . Regulation of up take

Excessive iron can be toxic, because free ferrous iron reacts with peroxides to produce free radicals, which are highly reactive and can damage DNA, proteins, lipids, and other cellular components. Thus, iron toxicity occurs when there is free iron in the cell, which generally occurs when iron levels exceed the capacity of transferrin to bind the iron.

Iron uptake is tightly regulated by the human body, which has no regulated physiological means of excreting iron. Only small amounts of iron are lost daily due to mucosal and skin epithelial cell sloughing, so control of iron levels is mostly by regulating uptake . However, large amounts of ingested iron can cause excessive levels of iron in the blood because high iron levels can damage the cells of the gastrointestinal tract , preventing them from regulating iron absorption. The resulting high blood concentrations of iron damage

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cells in the heart, liver and elsewhere, which can cause serious problems, including long-term organ damage and even death .

Humans experience iron toxicity above 20 milligrams of iron for every kilogram of mass , and 60 milligrams per kilogram is a lethal dose . Over - consumption of iron, often the result of children eating large quantities of ferrous sulfate tablets intended for adult consumption, is one of the most common toxicological causes of death in children under six . The DRI lists the Tolerable Upper Intake Level (UL) for adults as 45 mg/day. For children under fourteen years old the UL is 40 mg / day.

Regulation of iron uptake is impaired in some people as a result of a genetic defect that maps to the HLA - H gene region on chromosome 6. In these people, excessive iron intake can result in iron overload disorders, such as hemochromatosis. Many people have a genetic susceptibility to iron overload without realizing it or being aware of a family history of the problem. For this reason, it is advised that people do not take iron supplements unless they suffer from iron deficiency and have consulted a doctor. Hemochromatosis is estimated to cause disease in between 0.3 and 0.8 % of Caucasians .

The medical management of iron toxicity is complex, and can include use of a specific chelating agent called deferoxamine to bind and expel excess iron from the body .

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Iron Alloys

Main Iron Alloys Is :

1 – Cast Iron

2 – Pig Iron

3 – Wrought Iron

4 – Stainless Steel

1 - Cast iron

Contents

1 – Introduction :

Cast iron is derived from pig iron, and while it usually refers to gray iron, it also identifies a large group of ferrous alloys which solidify with a eutectic. The colour of a fractured surface can be used to identify an alloy. **White cast iron** is named after its white surface when fractured, due to its carbide impurities which allow cracks to pass straight through. **Grey cast iron** is named after its grey fractured surface, which occurs because the graphitic flakes deflect a passing crack and initiate countless new cracks as the material breaks.

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Carbon (C) and silicon (Si) are the main alloying elements, with the amount ranging from 2.1 to 4 wt % and 1 to 3 wt %, respectively. Iron alloys with less carbon content are known as steel. While this technically makes these base alloys ternary Fe-C-Si alloys, the principle of cast iron solidification is understood from the binary iron-carbon phase diagram. Since the compositions of most cast irons are around the eutectic point of the iron-carbon system, the melting temperatures closely correlate, usually ranging from 1,150 to 1,200 °C , which is about 300 °C lower than the melting point of pure iron.

Cast iron tends to be brittle, except for malleable cast irons. With its relatively low melting point, good fluidity, cast ability, excellent machine ability, resistance to deformation and wear resistance, cast irons have become an engineering material with a wide range of applications and are used in pipes, machines and automotive industry parts, such as cylinder heads (declining usage), cylinder blocks and gearbox cases (declining usage). It is resistant to destruction and weakening by oxidization (rust).

2 - Production :

Cast iron is made by re - melting pig iron , often along with substantial quantities of scrap iron and scrap steel and taking various steps to remove undesirable contaminants such as phosphorus and sulphur. Depending on the application, carbon and silicon content are reduced to the desired levels, which may be anywhere from 2 to 3.5% and 1 to 3 % respectively. Other elements are then added to the melt before the final form is produced by casting .

Iron is sometimes melted in a special type of blast furnace known as a cupola, but more often melted in electric induction furnaces . After melting is complete, the molten iron is poured into a holding furnace or ladle.

Phosphorus and sulphur are undesirable elements to have in iron and steel and need to be burnt out. Unfortunately the desirable carbon burns away first so the carbon then has to be replaced. Allegedly the cheapest steel as used by budget quality car manufacturers has the sulphur and phosphorus left in. This latter allegation will be very

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much a trade secret, however the evidence of excessive corrosion can be found in scrap yards all over the world. Some steels known as "weathering steels" hardly rust at all.

3 – Types :

Cast iron drain, waste and vent piping

3 – 1 - Alloying elements :

Cast iron's properties are changed by adding various alloying elements , or alloy ants . Next to carbon, silicon is the most important alloy ant because it forces carbon out of solution. Instead the carbon forms graphite which results in a softer iron, reduces shrinkage, lowers strength, and decreases density. Sulfur, when added, forms iron sulfide, which prevents the formation of graphite and increases hardness. The problem with sulfur is that it makes molten cast iron sluggish, which causes short run defects. To counter the effects of sulfur, manganese is added because the two form into manganese sulfide instead of iron sulfide. The manganese sulfide is lighter than the melt so it tends to float out of the melt and into the slag. The amount of manganese required to neutralize sulfur is 1.7 × sulfur content + 0.3 %. If more than this amount of manganese is added, then manganese carbide forms, which increases hardness and chilling, except in grey iron, where up to 1% of manganese increases strength and density.

Nickel is one of the most common alloy ants because it refines the pearlite and graphite structure, improves toughness, and evens out hardness differences between section thicknesses. Chromium is added in small amounts to the ladle to reduce free graphite, produce chill, and because it is a powerful carbide stabilizer; nickel is often added in conjunction. A small amount of tin can be added as a substitute for

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0.5 % chromium. Copper is added in the ladle or in the furnace, on the order of 0.5 to 2.5 %, to decrease chill, refine graphite, and increase fluidity. Molybdenum is added on the order of 0.3 to 1% to increase chill and refine the graphite and pearlite structure; it is often added in conjunction with nickel, copper, and chromium to form high strength irons. Titanium is added as a degasser and deoxidizer, but it also increases fluidity. 0.15 to 0.5% vanadium are added to cast iron to stabilize cementite, increase hardness, and increase resistance to wear and heat. 0.1 to 0.3 % zirconium helps to form graphite, deoxidize, and increase fluidity.

In malleable iron melts, bismuth is added, on the scale of 0.002 to 0.01%, to increase how much silicon can be added. In white iron, boron is added to aid in the production of malleable iron; it also reduces the coarsening effect of bismuth.

3 – 2 - Grey cast iron

Grey cast iron is characterized by its graphitic microstructure, which causes fractures of the material to have a grey appearance. It is the most commonly used cast iron and the most widely used cast material based on weight. Most cast irons have a chemical composition of 2.5 to 4.0 % carbon, 1 to 3 % silicon, and the remainder is iron. Grey cast iron has less tensile strength and shock resistance than steel, but its compressive strength is comparable to low and medium carbon steel.

3 – 3 - White cast iron :

It is the iron that displays white fractured surface due to the presence of cementite. With a lower silicon content and faster cooling, the carbon in *white cast iron* precipitates out of the melt as the metastable phase cementite , Fe_3C, rather than graphite. The cementite which precipitates from the melt forms as relatively large particles, usually in a eutectic mixture, where the other phase is austenite (which on cooling might transform to marten site). These eutectic carbides are much too large to provide precipitation hardening (as in some steels, where cementite precipitates might inhibit plastic deformation by impeding the movement of dislocations

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through the ferrite matrix). Rather, they increase the bulk hardness of the cast iron simply by virtue of their own very high hardness and their substantial volume fraction, such that the bulk hardness can be approximated by a rule of mixtures. In any case, they offer hardness at the expense of toughness. Since carbide makes up a large fraction of the material, white cast iron could reasonably be classified as a cermet . White iron is too brittle for use in many structural components, but with good hardness and abrasion resistance and relatively low cost, it finds use in such applications as the wear surfaces (impeller and volute) of slurry pumps, shell liners and lifter bars in ball mills and autogenous grinding mills, balls and rings in coal pulverisers, and the teeth of a backhoe's digging bucket (although cast medium - carbon martensitic steel is more common for this application).

It is difficult to cool thick castings fast enough to solidify the melt as white cast iron all the way through. However, rapid cooling can be used to solidify a shell of white cast iron, after which the remainder cools more slowly to form a core of grey cast iron. The resulting casting, called a *chilled casting*, has the benefits of a hard surface and a somewhat tougher interior.

High - chromium white iron alloys allow massive castings (for example, a 10-tonne impeller) to be sand cast, i.e., a high cooling rate is not required, as well as providing impressive abrasion resistance .

3 – 4 - Malleable cast iron :

Malleable iron starts as a white iron casting that is then heat treated at about 900 °C . Graphite separates out much more slowly in this case, so that surface tension has time to form it into spheroidal particles rather than flakes. Due to their lower aspect ratio, spheroids are relatively short and far from one another, and have a lower cross section vis - a - vis a propagating crack or phonon. They also have blunt boundaries, as opposed to flakes, which alleviates the stress concentration problems faced by grey cast iron. In general, the properties of malleable cast iron are more like mild steel. There is a

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limit to how large a part can be cast in malleable iron, since it is made from white cast iron.

3 – 5 - Ductile cast iron :

A more recent development is *nodular* or *ductile cast iron*. Tiny amounts of magnesium or cerium added to these alloys slow down the growth of graphite precipitates by bonding to the edges of the graphite planes. Along with careful control of other elements and timing, this allows the carbon to separate as spheroidal particles as the material solidifies. The properties are similar to malleable iron, but parts can be cast with larger sections.

4 - Historical uses :

Because cast iron is comparatively brittle, it is not suitable for purposes where a sharp edge or flexibility is required. It is strong under compression, but not under tension. Cast Iron was first invented in China in the 4th century BC and poured into moulds to make ploughshares and pots as well as weapons and pagodas . In the west, where it did not become available till the late 14th century, its earliest uses included cannon and shot. Henry VIII initiated the casting of cannon in England. Soon, English iron workers using blast furnaces developed the technique of producing cast iron cannons, which, while heavier than the prevailing bronze cannons, were much cheaper and enabled England to arm her navy better. The ironmasters of the Weald continued producing cast irons until the 1760s and armament was one of the main uses of irons after the Restoration.

Cast iron pots were made at many English blast furnaces at the time. In 1707, Abraham Darby patented a method of making pots (and kettles) thinner and hence cheaper than his rivals could. This meant that his Coalbrookdale furnaces became dominant as suppliers of pots, an activity in which they were joined in the 1720s and 1730s by a small number of other coke - fired blast furnaces.

The development of the steam engine by Thomas Newcomen provided further market for cast iron, since cast iron was considerably cheaper than the brass of which the engine cylinders were originally

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made. John Wilkinson was a great exponent of cast iron, who, amongst other things, cast the cylinders for many of James Watt's improved steam engines until the establishment of the Soho Foundry in 1795.

4 – 1 - Cast iron bridges :

The use of cast iron for structural purposes began in the late 1770s, when Abraham Darby III built the Iron Bridge, although short beams had already been used, such as in the blast furnaces at Coalbrookdale. Other inventions followed, including one patented by Thomas Paine. Cast iron bridges became commonplace as the Industrial Revolution gathered pace. Thomas Telford adopted the material for his bridge upstream at Buildwas , and then for a canal trough aqueduct at Longdon - on -Tern on the Shrewsbury Canal.

It was followed by the Chirk Aqueduct and the Pontcysyllte Aqueduct, both of which remain in use following the recent restorations. Cast iron beam bridges were used widely by the early railways, such as the Water Street Bridge at the Manchester terminus of the Liverpool and Manchester Railway. Problems arose when a new bridge carrying the Chester and Holy head Railway across the River Dee in Chester collapsed in May 1847, less than a year after it was opened. The Dee bridge disaster was caused by excessive loading at the centre of the beam by a passing train, and many similar bridges had to be demolished and rebuilt, often in wrought iron. The bridge had been erroneously designed, being trussed with wrought iron straps, which were wrongly thought to reinforce the structure. The centres of the beams were put into bending, with the lower edge in tension, where cast iron, like masonry, is very weak.

The best way of using cast iron for bridge construction was by using arches, so that all the material is in compression. Cast iron, again like masonry, is very strong in compression. Wrought iron, like most other kinds of iron and indeed like most metals in general, is strong in tension, and also tough - resistant to fracturing. The relationship between wrought iron and cast iron, for structural

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purposes, may be thought of as analogous to the relationship between wood and stone.

Nevertheless, cast iron continued to be used in inappropriate structural ways, until the Tay Rail Bridge disaster of 1879 cast serious doubt on the use of the material. Crucial lugs for holding tie bars and struts in the Tay Bridge had been cast integral with the columns and they failed in the early stages of the accident. In addition, the bolt holes were also cast and not drilled, so that all the tension from the tie bars was placed on a corner, rather than being spread over the length of the hole. The replacement bridge was built in wrought iron and steel.

Further bridge collapses occurred, however, culminating in the Norwood Junction rail accident of 1891. Thousands of cast iron rail under bridges were eventually replaced by steel equivalents.

The iron bridge over the River Severn at Coalbrookdale, England

4 – 2 - Buildings :

Cast iron columns enabled architects to build tall buildings without the enormously thick walls required to construct masonry buildings of any height. Such flexibility allowed tall buildings to have large windows. In urban centers like SoHo - Cast Iron Historic District in New York City, manufacturing buildings and early department stores were built with cast iron columns to allow daylight to enter. Slender cast iron columns could also support the weight that would otherwise require thick masonry columns or piers, opening up floor spaces in factories, and sight lines in churches and auditoriums. The historic Iron Building in Water vliet , New York, is a cast iron building.

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4 – 3 - Textile mills :

Another important use was in textile mills. The air in the mills contained flammable fibres from the cotton, hemp, or wool being spun. As a result, textile mills had an alarming propensity to burn down. The solution was to build them completely of non-combustible materials, and it was found convenient to provide the building with an iron frame, largely of cast iron, replacing flammable wood. The first such building was at Ditherington in Shrewsbury, Shropshire. Many other warehouses were built using cast iron columns and beams, although faulty designs, flawed beams or overloading sometimes caused building collapses and structural failures.

During the Industrial Revolution, cast iron was also widely used for frame and other fixed parts of machinery, including spinning and later weaving machines in textile mills. Cast iron became widely used, and many towns had foundries producing industrial and agricultural machinery.

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2 - Pig iron

Pig Iron of a type used to make ductile iron, stored in a bin

Contents

1 – Introduction :

Pig iron is the intermediate product of smelting iron ore with a high-carbon fuel such as coke, usually with limestone as a flux. Charcoal and anthracite have also been used as fuel. Pig iron has a very high carbon content, typically 3.5 – 4.5 % , which makes it very brittle and not useful directly as a material except for limited applications.

The traditional shape of the molds used for these ingots was a branching structure formed in sand, with many individual ingots at right angles to a central channel or *runner*. Such a configuration is similar in appearance to a litter of piglets suckling on a sow . When the metal had cooled and hardened, the smaller ingots (the *pigs*) were simply broken from the much thinner runner (the *sow*), hence the name *pig iron*. As pig iron is intended for remelting , the uneven size of the ingots and the inclusion of small amounts of sand caused only insignificant problems considering the ease of casting and handling them.

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2 - History :

Casting pig iron, Iroquois smelter, Chicago, between 1890 and 1901.

The Chinese were making pig iron by the later Zhou Dynasty (1122 – 256 BC) . In Europe , the process was not invented until the Late Middle Ages (1350 – 1500) . Actually the phase transition of the iron into liquid phase in the furnace was an *avoided* phenomenon, as decarburizing the pig iron into steel was an extremely tedious process with medieval technology.

3 - Uses :

Traditionally pig iron would be worked into wrought iron in finery forges, and later puddling furnaces, more recently into steel. In these processes, pig iron is melted and a strong current of air is directed over it while it is being stirred or agitated. This causes the dissolved impurities (such as silicon) to be thoroughly oxidized. An intermediate product of puddling is known as *refined pig iron*, *finers metal*, or *refined iron*.

Pig iron can also be used to produce gray iron. This is achieved by remelting pig iron, often along with substantial quantities of steel and scrap iron, removing undesirable contaminants, adding alloys, and adjusting the carbon content. Some pig iron grades are suitable for producing ductile iron. These are high purity pig irons and depending on the grade of ductile iron being produced these pig irons may be low in the elements silicon, manganese, sulfur and phosphorus. These types of pig irons are useful to dilute all elements in a ductile iron charge (except carbon) which may be harmful to the ductile iron process.

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3 – 1 - Modern uses :

Today, pig iron is typically poured directly out of the bottom of the blast furnace through a trough into a ladle car for transfer to the steel mill in mostly liquid form; in this state, the pig iron is referred to as *hot metal*. The hot metal is then charged into a steelmaking vessel to produce steel, typically with an electric arc furnace or basic oxygen furnace, by burning off the excess carbon in a controlled fashion and adjusting the alloy composition. Earlier processes for this included the finery forge, the puddling furnace, the Bessemer process, and the open hearth furnace.

Modern steel mills and direct - reduction iron plants transfer the molten iron to a ladle for immediate use in the steel making furnaces or cast it into pigs on a pig - casting machine for reuse or resale. Modern pig casting machines produce stick pigs, which break into smaller 4 –10 kg pieces at discharge.

Pig iron was used as ballast on NASA Boeing 747 Shuttle Carrier Aircraft .

3 – 2 - Cultural Note :

It is common, particularly in country music, to refer to cheap iron used in certain cheap firearms, and more recently in the engine of cheap muscle cars, as pig iron. It is important to note that this is slang and not actually pig iron. Pig iron features prominently in the country song Rock Island Line .

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3 - Wrought iron

	
Iron pillar at Delhi, India, containing 98 % wrought iron	*The Eiffel tower is constructed from puddle iron, a form of wrought iron*

Contents

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1 – Introduction :

Wrought iron is an iron alloy with a very low carbon content, in comparison to steel, and has fibrous inclusions, known as slag. This is what gives it a "grain" resembling wood, which is visible when it is etched or bent to the point of failure. Wrought iron is tough, malleable, ductile and easily welded. Historically, it was known as "commercially pure iron" ; however, it no longer qualifies because current standards for commercially pure iron require a carbon content of less than 0.008 wt %.

Before the development of effective methods of steelmaking and the availability of large quantities of steel, wrought iron was the most common form of malleable iron. A modest amount of wrought iron was used as a raw material for manufacturing of steel, which was mainly to produce swords , cutlery, chisels, axes and other edge tools as well as springs and files. Demand for wrought iron reached its peak in the 1860s with the adaptation of ironclad warships and rail ways, but then declined as mild steel became more available.

Before they came to be made of mild steel, items produced from wrought iron included rivets, nails, wire, chains, rail way couplings, water and steam pipes, nuts, bolts, horse shoes, handrails , straps for timber roof trusses, and ornamental iron work.

Wrought iron is no longer produced on a commercial scale. Many products described as wrought iron, such as guard rails, garden furniture and gates , are made of mild steel . They retain that description because they are wrought (worked) by hand.

2 – Terminology :

The word "wrought" is an archaic past tense form of the verb "to work," and so "wrought iron" literally means "worked iron". Wrought iron is a general term for the commodity, but is also used more specifically for finished iron goods, as manufactured by a blacksmith or other smith. It was used in this narrower sense in British Customs records, such manufactured iron being subject to a higher rate of duty than what might be called "unwrought" iron. Cast iron, unlike

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wrought iron, is brittle and cannot be worked either hot or cold. Cast iron can break if struck with a hammer.

In the 17th, 18th and 19th centuries, wrought iron went by a wide variety of terms according to its form, origin, or quality.

While the bloomery process produced wrought iron directly from ore, cast iron or pig iron were the starting materials used in the finery forge and puddling furnace. Pig iron and cast iron have high carbon content which make them very brittle, but they have a lower melting point than iron or steel. Cast and especially pig iron have excess slag which must be at least partially removed to produce quality wrought iron. Another difference is that steel can be hardened by heat treating.

For several years after the introduction of Bessemer and open hearth steel there were different opinions as to what differentiated iron from steel, some thinking it was the chemical composition and others believing it was whether the iron heated sufficiently to melt and "fuse". Fusion eventually became generally accepted as relatively more important than composition below a given low carbon concentration.

2 – 1 - Form or shapes :

- Bar iron — iron in bars, which are the usual product of the finery forge, but not necessarily made by that process. These might be square or flat, and flat bars might be narrow or broad.
- Rod iron — cut from flat bar iron in a slitting mill to provide the raw material for nails.
- Hoop iron — suitable for the hoops of barrels, made by passing rod iron through flat rolls.
- Plate iron — sheets of iron suitable for use as boiler plate.
- Black plate — sheets of iron, perhaps thinner than plate iron, from the black rolling stage of tinplate production.
- Voyage iron — narrow flat bar iron, made or cut into bars of a particular weight, a commodity for sale in Africa for the Atlantic slave trade . The number of bars per ton gradually

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increased from 70 per ton in the 1660s to 75–80 per ton in 1685 and "near 92 to the ton" in 1731.

2 – 2 – Origin :

- Charcoal Iron — Until the end of the eighteenth century, wrought iron was smelted from ore using charcoal, by the bloomery process. Wrought iron was also produced from pig iron using a finery forge or from the industrial revolution in a Lancashire hearth. The resulting metal was highly variable, both in chemistry and slag content.
- Puddled Iron — By the late eighteenth century there was a demand from pig iron, an impure form of cast iron, to be refined with coal as fuel. This resulted in 'puddled iron', which contained less slag, sulfur and had a very low carbon content. The iron was kept separate from the fire in a reverberatory furnace to prevent harmful sulphur and phosphorus from entering the finished iron. Puddled iron, although also variable in its properties, was generally more consistent than the earlier irons, and the method lent itself to the production of far greater quantities. By 1876, annual production of puddled iron in the UK alone was over 4 million tons.
- Oregrounds iron — a particularly pure grade of bar iron made ultimately from iron ore from the Dannemora mine in Sweden. Its most important use was as the raw material for the cementation process of steelmaking.
- Danks iron — originally iron imported to Great Britain from Gdańsk, but in the 18th century more probably the kind of iron (from eastern Sweden) that once came from Gdańsk.
- Forest iron — iron from the English Forest of Dean, where haematite ore enabled tough iron to be produced.
- Lukes iron — iron imported from Liège , whose Dutch name is "Luik " .
- Ames iron or amys iron — another variety of iron imported to England from northern Europe. Its origin has been suggested to be Amiens, but it seems to have been imported from Flanders in the 15th century and Holland later, suggesting an origin in the Rhine valley. Its origins remain controversial.[11]

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- Botolf iron or Boutall iron — from Bytów (Polish Pomerania) or Bytom (Polish Silesia) .
- Sable iron (or Old Sable) — iron bearing the mark (a sable) of the Demidov family of Russian ironmasters, one of the better brands of Russian iron.

2 – 3 – Quality :

Tough iron

Tough iron, also spelled "tuf", is not brittle and strong enough to be used for tools.

Blend iron

Blend iron is made using a mixture of different types of pig iron.

Best iron

Best iron is iron that had gone through several stages of piling and rolling, might reach the stage of being best iron (in the 19th century).

Marked bar iron

This is iron made by members of the Marked Bar Association and marked with the maker's brand mark as a sign of its quality.

2 – 4 - Defects

Wrought iron is *redshort* if it contains sulfur in excess quantity. It has sufficient tenacity when cold, but cracks when bent or finished at a red heat. It is therefore useless for welding or forging.

Coldshort iron, also known as *coldshear*, *colshire* or *bloodshot*, contains excessive phosphorus. It is very brittle when it is cold. It cracks if bent. It may, however, be worked at high temperature. Historically, cold short iron was considered good enough for nails.

Nevertheless , phosphorus is not necessarily detrimental to iron. Ancient Indian smiths did not add lime to their furnaces ; the absence of Ca O in the slag , and the deliberate use of wood with high phosphorus content during the smelting , induces a *higher P content*

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(> 0.1 %, average 0.25 %) than in modern iron. Analysis of the Iron Pillar of Delhi gives 0.10 % in the slags for .18 % in the iron itself, for a total P content of 0.28% in the metal and accounts for much of its corrosion resistance. Furthermore, the presence of phosphorus (without carbon) produces a ductile iron suitable for wire drawing, for piano wire .

3 - History

The puddling process of smelting iron ore to make wrought iron from pig iron, the right half of the illustration (not shown) displays men working a blast furnace, Tiangong Kaiwu encyclopedia published in 1637, written by Song Yingxing (1587 – 1666) .

Wrought iron has been used for many centuries, and is the "iron" that is referred to throughout western history. The other form of iron, cast iron, was not introduced into Western Europe until the 15th century; even then, due to its brittleness, it could only be used for a limited number of purposes. Throughout much of the Middle Ages iron was produced by the direct reduction of ore in manually operated bloomeries , although water power had begun to be employed by 1104.

The raw material produced by all indirect processes is pig iron. It has a high carbon content and as a consequence it is brittle and

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could not be used to make hardware. The osmond process was the first of the indirect processes, developed by 1203, but bloomery production continued in many places. The process depended on the development of the blast furnace, of which medieval examples have been discovered at Lapphyttan, Sweden and in Germany.

The bloomery and osmond processes were gradually replaced from the 15th century by finery processes, of which there were two versions, the German and Walloon. They were in turn replaced from the late 18th century by puddling, with certain variants such as the Swedish Lancashire process. These too are now obsolete, and wrought iron is no longer manufactured commercially.

3 – 1 - Bloomery process

Wrought iron was originally produced by a variety of smelting processes, all described today as bloomeries. Different forms of bloomery were used at different places and times. The bloomery was charged with charcoal and iron ore and then lit. Air was blown in through a tuyere to heat the bloomery to a temperature somewhat below the melting point of iron. In the course of the smelt, slag would melt and run out, and carbon monoxide from the charcoal would reduce the ore to iron, which formed a spongy mass. The iron remained in the solid state. If the bloomery was allowed to become hot enough to melt the iron, carbon would dissolve into it and form pig or cast iron, but that was not the intention.

After smelting was complete, the bloom was removed, and the process could then be started again. It was thus a batch process, rather than a continuous one. The spongy mass contained iron and also silicate (slag) from the ore; this was iron bloom from which the technique got its name. The bloom had to be forged mechanically to consolidate it and shape it into a bar, expelling slag in the process.

During the Middle Ages , water - power was applied to the process, probably initially for powering bellows, and only later to hammers for forging the blooms. However, while it is certain that water-power was used, the details of this remain uncertain . This was the culmination of the direct process of iron making . It survived in

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Spain and southern France as Catalan Forges to the mid 19th century, in Austria as the *stuckofen* to 1775 , and near Garstang in England until about 1770 ; it was still in use with hot blast in New York State in the 1880s .

3 – 2 - Osmond process

Osmond iron consisted of balls of wrought iron, produced by melting pig iron and catching the droplets on a staff, which was spun in front of a blast of air so as to expose as much of it as possible to the air and oxidise its carbon content. The resultant ball was often forged into bar iron in a hammer mill.

3 – 2 - Finery process

In the 15th century, the blast furnace spread into what is now Belgium and was improved. From there, it spread via the Pays de Bray on the boundary of Normandy and then to the Weald in England. With it, the finery forge spread. These remelted the pig iron and (in effect) burnt out the carbon, producing a bloom, which was then forged into a bar iron. If rod iron was required, a slitting mill was used.

The finery process existed in two slightly different forms. In Great Britain, France, and parts of Sweden, only the Walloon process was used. This employed two different hearths, a finery hearth for fining the iron and a chafery hearth for reheating it in the course of drawing the bloom out into a bar. The finery always burnt charcoal, but the chafery could be fired with mineral coal, since its impurities would not harm the iron when it was in the solid state. On the other hand, the German process, used in Germany, Russia, and most of Sweden used a single hearth for all stages.

The introduction of coke for use in the blast furnace by Abraham Darby in 1709 (or perhaps others a little earlier) initially had little effect on wrought iron production. Only in the 1750s was coke pig iron used on any significant scale as the feedstock of finery forges. However, charcoal continued to be the fuel for the finery.

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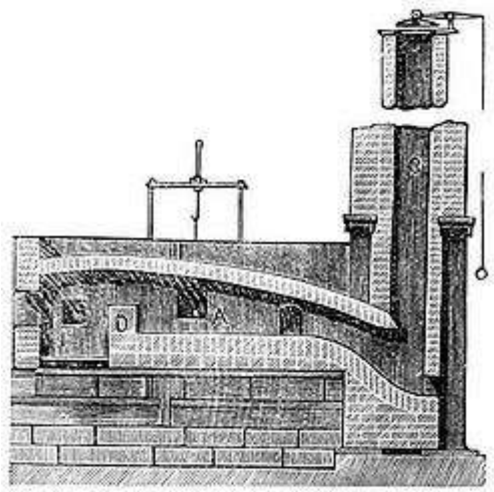
3 – 4 - Potting and stamping

From the late 1750s, ironmasters began to develop processes for making bar iron without charcoal. There were a number of patented processes for this, which are referred to today as potting and stamping. The earliest were developed by John Wood of Wednesbury and his brother Charles Wood of Low Mill at Egremont , patented in 1763 . Another was developed for the Coalbrookdale Company by the Cranage brothers . Another important one was that of John Wright and Joseph Jesson of West Bromwich .

3 – 5 - Puddling process



Schematic drawing of a puddling furnace

A number of processes for making wrought iron with out charcoal were devised as the Industrial Revolution began during the latter half of the 18th century. The most successful of these was puddling, using a puddling furnace (a variety of the rever beratory furnace) . This was invented by Henry Cort in 1784. It was later improved by others including Joseph Hall. In this type of furnace, the metal does not come into contact with the fuel, and so is not contaminated by impurities in it. The flame from the fire is reverberated or sent back down onto the metal on the fire bridge of the furnace.

Unless the raw material used is white cast iron, the pig iron or other raw material first had to be refined into refined iron or finers metal. This would be done in a refinery where raw coal is used to

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remove silicon and convert carbon from a graphitic form to a combined form.

This metal was placed into the hearth of the puddling furnace where it was melted. The hearth was lined with oxidizing agents such as haematite and iron oxide . This mixture is subjected to a strong current of air and stirred with long bars, called puddling bars or rabbles , through working doors . The air, stirring, and "boiling" action of the metal help the oxidizing agents to oxidize the impurities and carbon out of the pig iron to their maximum capability. As the impurities oxidize, they form a molten slag while the retaining iron particles solidify into spongy wrought iron balls, called puddle balls.

3 – 5 – 1 - Shingling

There is still some slag left in the puddle balls, so while they are still hot they must be shingled to remove the remaining slag and cinder . It may be achieved by forging the balls under a power hammer, or by squeezing the bloom in a machine. The material obtained at the end of shingling is known as bloom and it is still red-hot . The blooms are not useful in this form, so they must be rolled into a final product.

Some times European ironworks would skip this step completely and roll the puddle balls. The only drawback to this is that the edges of the rough bars are not as well compressed. When the rough bar is reheated, the edges may separate and be lost into the furnace .

3 – 5 – 2 - Rolling

The bloom is passed through grooved rollers and flat bars were produced. These bars of wrought iron were of poor quality, called muck bars or puddle bars . To improve the quality of wrought iron, these bars were cut up, piled and tied together by wires, a process known as faggoting or piling . They were then reheated and rolled again in merchant rolls. This process may be repeated several times to get wrought iron of desired quality. Wrought iron that has been rolled multiple times is called merchant bar or merchant iron .

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3 – 6 – Lancashire process

The advantage of puddling was that it used coal, not charcoal as fuel. However this was little advantage in Sweden, which lacks coal. Gustaf Ekman observed charcoal fineries at Ulverstone , which were quite different from any in Sweden. After his return to Sweden in the 1830s, he experimented and developed a process similar to puddling but using forewood and charcoal, which was widely adopted in the Bergslagen in the following decades.

3 – 7 – The Aston process

In 1925, James Aston of the United States developed a process for manufacturing wrought iron quickly and economically. It involves taking molten steel from a Bessemer converter and pouring it into cooler liquid slag. The temperature of the steel is about 1500 °C and the liquid slag is maintained at approximately 1200 °C. The molten steel contains a large amount of dissolved gases so when the liquid steel hits the cooler surfaces of the liquid slag the gases are liberated. The molten steel then freezes to yield a spongy mass having a temperature of about 1370 °C . This spongy mass must then be finished by being shingled and rolled as described under puddling (above). Three to four tons can be converted per batch with this method.

3 – 8 – Wrought iron as Pure Iron

Dr Gerry McDonnell in 2010 England , demonstrated by analysis that a wrought iron bloom, from a traditional smelt, could be worked into 99.7 % pure iron with no evidence of carbon. It was found that the stringers common to other wrought irons were not present thus making it very malleable for the smith to work hot and cold. A commercial source of pure iron is available and is used by smiths as an alternative to traditional wrought iron and other new generation ferrous metals.

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3 – 9 – The end of wrought iron

Steel began to replace iron for rails as soon as Bessemer production began (ca. 1860s). Iron remained dominant for structural applications until the 1880s because of problems with brittle steel, caused by high carbon, excess phosphorous or excessive temperature during rolling or too rapid rolling . By 1890 steel had largely replaced iron for structural applications.

Sheet iron (Armco 99.97 % pure iron) had good properties for use in appliances including being well suited for enameling and welding and being rust resistant.

In the 1960s the price of steel production was dropping due to recycling and even using the Aston process wrought iron production was a labor-intensive process. It has been estimated that the production of wrought iron costs approximately twice as much as the production of low carbon steel . In the United States the last plant closed in 1969 . The last in Great Britain (and the world) was the Atlas Ironworks of Thomas Walmsley Ltd in Bolton, which closed in 1973. Its equipment, of a type dating from the 1860s, was moved to the Blists Hill site of Iron bridge Gorge Museum for preservation.[38] Some wrought iron is still being produced for heritage restoration purposes, but only by recycling scrap.

4 - Properties

The slag inclusions, or stringers, in wrought iron give it properties not found in other forms of ferrous metal. There are approximately 250,000 inclusions per square inch . A fresh fracture shows a clear bluish color with a high silky luster and fibrous appearance.

Wrought iron lacks the carbon content necessary for hardening through heat treatment, but in areas where steel was uncommon or unknown, tools were sometimes cold - worked (hence cold iron) in order to harden them. An advantage of its low carbon content is its excellent weld ability . Furthermore, sheet wrought iron cannot bend as much as steel sheet metal (when cold worked) . Wrought iron can

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be cast, however there is no engineering advantage as compared to cast iron; cast iron is much easier to produce and thus cheaper, so it is exclusively chosen over wrought iron .

Due to the variations in iron ore origin and iron manufacture, wrought iron can be inferior or superior in corrosion resistance compared to other iron alloys . There are many mechanisms behind this corrosion resistance. Chilton and Evans found that nickel enrichment bands reduce corrosion . They also found that in puddled and forged and piled the working over of the iron spread out copper, nickel and tin impurities, which produce electrochemical conditions that slow down corrosion . The slag inclusions have been shown to disperse corrosion in to an even film to resist pitting . Another study has shown that slag inclusions are pathways to corrosion . Other studies show that sulfur impurities in the wrought iron decrease corrosion resistance , but phosphorus increase corrosion resistance . Environments with a high concentration of chlorine ions also decreases wrought iron's corrosion resistance .

Wrought iron may be welded in the same manner as mild steel, but the presence of oxide or inclusions will give defective results . The material has a rough surface so it can hold platings and coatings better. For instance, a galvanic zinc finish is approximately 25–40% thicker than the same finish on steel . In Table 1, the chemical composition of wrought iron is compared to that of pig iron and carbon steel. Although it appears that wrought iron and plain carbon steel have similar chemical compositions, this is deceiving. Most of the manganese, sulfur, phosphorus, and silicon are incorporated into the slag fibers present in the wrought iron, so wrought iron really is purer than plain carbon steel.

Table 1: Chemical composition comparison of :
pig iron , plain carbon steel , and wrought iron

Material	Iron	Carbon	Manganese	Sulfur	Phosphorus	Silicon
Pig iron	91–94	3.5–4.5	0.5–2.5	0.018–0.1	0.03–0.1	0.25–3.5
Carbon steel	98 –99.5	0.07–1.3	0.3–1.0	0.02–0.06	0.002–0.1	0.005–0.5
Wrought iron	99 –99.8	0.05–0.25	0.01–0.1	0.02–0.1	0.05–0.2	0.02–0.2
All units are percent weight						

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Amongst its other properties, wrought iron becomes soft at red heat, and can be easily forged and forge welded . It can be used to form temporary magnets, but cannot be magnetized permanently, and is ductile , malleable and tough .

4 – 1 - The importance of ductility :

For most purposes, ductility is a more important measure of the quality of wrought iron than tensile strength. In tensile testing, the best irons are able to undergo considerable elongation before failure. Higher tensile wrought iron is brittle.

Because of the large number of boiler explosions on steamboats, the U.S. Congress passed legislation in 1830 which approved funds for correcting the problem. The treasury awarded a $1500 contract to the Franklin Institute to conduct a study. As part of the study Walter R. Johnson and Benjamin Reeves conducted strength tests on various boiler iron using a tester they had built in 1832 based on the design of one by Lagerhjelm in Sweden. Unfortunately, because of the misunderstanding of tensile strength and ductility, this work did little to reduce failures .

The importance of ductility was recognized by some very early in the development of tube boilers , such as Thurston's comment :

‘ If made of such good iron as the makers claimed to have put into them “which worked like lead,” they would, as also claimed, when ruptured, open by tearing, and discharge their contents without producing the usual disastrous consequences of a boiler explosion ’ .

By the late 19 th century when metallurgy was able to better understand what properties and processes made good iron, it was being displaced by steel.

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5 - Applications

Wrought iron furniture has a long history, dating back to Roman times. There are thirteenth century wrought iron gates in Westminster Abbey in London, and wrought iron furniture appeared to reach its peak popularity (in Britain) in the seventeenth century during the reign of William and Mary · How ever, cast iron and cheaper steel caused a gradual decline in wrought iron manufacture, with the last wrought ironworks in Britain closing in 1974 .

It is also used to make home decor items such as baker's racks, wine racks, pot racks, etageres, table bases, desks, gates, beds, candle holders, curtain rods, bars and bar stools.

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4 - Stainless steel

Contents

1 – Introduction :

In metallurgy, **stainless steel**, also known as **inox steel** or **inox** from French "*inoxydable*", is defined as a steel alloy with a minimum of 10.5 or 11 % chromium content by mass .

Stainless steel does not stain, corrode, or rust as easily as ordinary steel, but it is not stain - proof. It is also called **corrosion-resistant steel** or **CRES** when the alloy type and grade are not detailed, particularly in the aviation industry. There are different grades and surface finishes of stainless steel to suit the environment the alloy must endure. Stainless steel is used where both the properties of steel and resistance to corrosion are required.

Stainless steel differs from carbon steel by the amount of chromium present. Unprotected carbon steel rusts readily when exposed to air and moisture. This iron oxide film (the rust) is active and accelerates corrosion by forming more iron oxide. Stainless steels contain sufficient chromium to form a passive film of chromium

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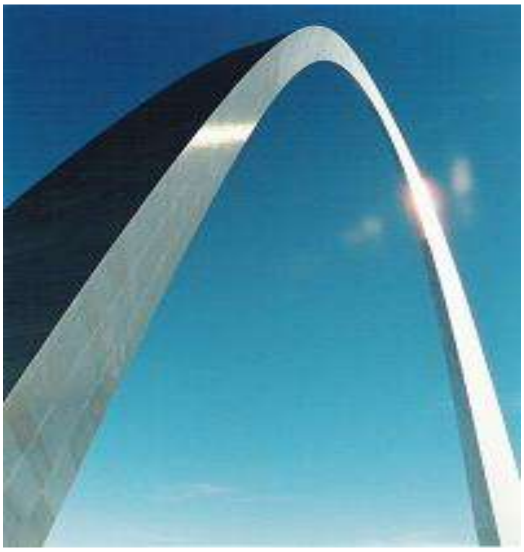
oxide, which prevents further surface corrosion and blocks corrosion from spreading into the metal's internal structure.

Passivation only occurs if the proportion of chromium is high enough.



The 192 m high, stainless - clad (type 304) Gateway Arch defines St. Louis's skyline.

2 - History :

A few corrosion-resistant iron artifacts survive from antiquity. A famous example is the Iron Pillar of Delhi, erected by order of Kumara Gupta I around AD 400. Unlike stainless steel, however, these artifacts owe their durability not to chromium but to their high phosphorus content, which, together with favorable local weather conditions, promotes the formation of a solid protective passivation layer of iron oxides and phosphates, rather than the non-protective cracked rust layer that develops on most ironwork.

The corrosion resistance of iron - chromium alloys was first recognized in 1821 by French metallurgist Pierre Berthier, who noted their resistance against attack by some acids and suggested their use in cutlery. Metallurgists of the 19th century were unable to produce the combination of low carbon and high chromium found in most modern stainless steels, and the high-chromium alloys they could produce were too brittle to be practical.

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In the late 1890s Hans Goldschmidt of Germany developed an aluminothermic (thermite) process for producing carbon - free chromium. Between 1904 and 1911 several researchers, particularly Leon Guillet of France, prepared alloys that would today be considered stainless steel.

Friedrich Krupp Germaniawerft built the 366-ton sailing yacht *Germania* featuring a chrome-nickel steel hull in Germany in 1908. In 1911, Philip Monnartz reported on the relationship between chromium content and corrosion resistance. On October 17, 1912, Krupp engineers Benno Strauss and Eduard Maurer patented austenitic stainless steel as ThyssenKrupp Nirosta.

Similar developments were taking place contemporaneously in the United States, where Christian Dantsizen and Frederick Becket were industrializing ferritic stainless steel. In 1912, Elwood Haynes applied for a US patent on a martensitic stainless steel alloy, which was not granted until 1919.

Also in 1912, Harry Brearley of the Brown-Firth research laboratory in Sheffield, England, while seeking a corrosion-resistant alloy for gun barrels, discovered and subsequently industrialized a martensitic stainless steel alloy. The discovery was announced two years later in a January 1915 newspaper article in *The New York Times*.[4] The metal was later marketed under the 'Staybrite' brand by Firth Vickers in England and was used for the new entrance canopy for the Savoy Hotel in London in 1929.]

Brearley applied for a US patent during 1915 only to find that Haynes had already registered a patent. Brearley and Haynes pooled their funding and with a group of investors formed the American Stainless Steel Corporation, with headquarters in Pittsburgh, Pennsylvania.[9] In the beginning stainless steel was sold in the US under different brand names like 'Allegheny metal' and 'Nirosta steel'. In 1929 before the Great Depression hit, over 25,000 tons of stainless steel was manufactured and sold in the US.

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3 - Properties :

High oxidation - resistance in air at ambient temperature is normally achieved with additions of a minimum of 13 % (by weight) chromium, and up to 26 % is used for harsh environments . The chromium forms a passivation layer of chromium (III) oxide (Cr_2O_3) when exposed to oxygen. The layer is too thin to be visible, and the metal remains lustrous. The layer is impervious to water and air, protecting the metal beneath. Also, this layer quickly reforms when the surface is scratched. This phenomenon is called passivation and is seen in other metals, such as aluminium and titanium. Corrosion-resistance can be adversely affected if the component is used in a non-oxygenated environment, a typical example being underwater keel bolts buried in timber.

When stainless steel parts such as nuts and bolts are forced together, the oxide layer can be scraped off, causing the parts to weld together. When disassembled, the welded material may be torn and pitted, an effect known as galling. This destructive galling can be best avoided by the use of dissimilar materials for the parts forced together, for example bronze and stainless steel, or even different types of stainless steels (martensitic against austenitic), when metal-to-metal wear is a concern. Nitronic alloys reduce the tendency to gall through selective alloying with manganese and nitrogen. In addition, threaded joints may be lubricated to prevent galling.

4 - Applications :

Stainless steel’s resistance to corrosion and staining, low maintenance and familiar luster make it an ideal material for many applications. There are over 150 grades of stainless steel, of which fifteen are most commonly used. The alloy is milled into coils, sheets, plates, bars, wire, and tubing to be used in cookware, cutlery, hardware, surgical instruments, major appliances, industrial equipment (for example, in sugar refineries) and as an automotive and aerospace structural alloy and construction material in large buildings. Storage tanks and tankers used to transport orange juice and other food are often made of stainless steel, because of its corrosion

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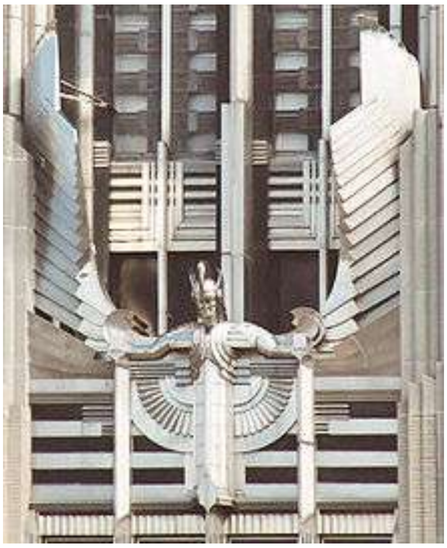
resistance and antibacterial properties. This also influences its use in commercial kitchens and food processing plants, as it can be steam-cleaned and sterilized and does not need paint or other surface finishes.



An art deco sculpture on the Niagara - Mohawk Power building in Syracuse, New York.

Stainless steel is used for jewellery and watches with 316L being the type commonly used for such applications. It can be re-finished by any jeweler and will not oxidize or turn black.

Some firearms incorporate stainless steel components as an alternative to blued or parkerized steel. Some handgun models, such as the Smith & Wesson Model 60 and the Colt M1911 pistol, can be made entirely from stainless steel. This gives a high - luster finish similar in appearance to nickel plating. Unlike plating, the finish is not subject to flaking, peeling, wear-off from rubbing (as when repeatedly removed from a holster), or rust when scratched.

Some automotive manufacturers use stainless steel as decorative highlights in their vehicles.

4 – 1 – Architectural :

Stainless steel is used for buildings for both practical and aesthetic reasons. Stainless steel was in vogue during the art deco period. The most famous example of this is the upper portion of the

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Chrysler Building (pictured). Some diners and fast-food restaurants use large ornamental panels and stainless fixtures and furniture. Because of the durability of the material, many of these buildings retain their original appearance.

The forging of stainless steel has given rise to a fresh approach to architectural blacksmithing in recent years.

Type 316 stainless is used on the exterior of both the Petronas Twin Towers and the Jin Mao Building, two of the world's tallest skyscrapers.

The Parliament House of Australia in Canberra has a stainless steel flagpole weighing over 220 tons (200 metric tonnes).

The aeration building in the Edmonton Composting Facility, the size of 14 hockey rinks, is the largest stainless steel building in North America.

4 – 2 – Bridges :

- Minorca Road Bridge (Spain) is the first stainless steel road bridge.
- Sant Fruitos Pedestrian Bridge (Catalonia, Spain), arch pedestrian bridge.
- Padre Arrupe Bridge (Bilbao, Spain) links the Guggenheim museum to the University of Deusto .

4 – 3 – Monuments and sculptures :

- The Unisphere, constructed as the theme symbol of the 1964-5 World's Fair in New York City, is the world's largest globe-shaped structure.
- The Gateway Arch (pictured) is clad entirely in stainless steel : 804 metric tones of 6.4 mm plate , # 3 finish , type 304 stainless steel.
- The United States Air Force Memorial has an austenitic stainless steel structural skin.

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- The Atomium in Brussels, Belgium was renovated with stainless-steel cladding in a renovation completed in 2006; previously the spheres and tubes of the structure were clad in aluminium.
- The Cloud Gate sculpture by Anish Kapoor, in Chicago US.
- The Sibelius monument in Helsinki, Finland, is made entirely of stainless steel tubes.

4 – 4 – Other :

- The DeLorean DMC-12 automobile used stainless steel body panels over a glass-reinforced plastic monocoque.

5 - Recycling and reuse :

Stainless steel is 100 % recyclable. An average stainless steel object is composed of about 60 % recycled material of which approximately 40 % originates from end - of - life products and about 60 % comes from manufacturing processes . According to the International Resource Panel's Metal Stocks in Society report , the per capita stock of stainless steel in use in society is 80 – 180 kg in more developed countries and 15kg in less-developed countries.

There is a secondary market that recycles usable scrap for many stainless steel markets. The product is mostly coil, sheet and blanks. This material is purchased at a less-than-prime price and sold to commercial quality stampers and sheet metal houses. The material may have scratches, pits and dents but is made to the current specifications.

6 - Types of stainless steel :

There are different types of stainless steels: when nickel is added, for instance, the austenite structure of iron is stabilized. This crystal structure makes such steels virtually non - magnetic and less brittle at low temperatures. For greater hardness and strength, more carbon is added. With proper heat treatment, these steels are used for such things as razor blades, cutlery, and tools.

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Pipes and fittings made of stainless steel.

Significant quantities of manganese have been used in many stainless steel compositions. Manganese preserves an austenitic structure in the steel as does nickel, but at a lower cost.

Stainless steels are also classified by their crystalline structure :

- *Austenitic*, or 300 series, stainless steels make up over 70 % of total stainless steel production. They contain a maximum of 0.15 % carbon, a minimum of 16% chromium and sufficient nickel and / or manganese to retain an austenitic structure at all temperatures from the cryogenic region to the melting point of the alloy. A typical composition of 18 % chromium and 10% nickel, commonly known as *18/10 stainless*, is often used in flatware. *18/0* and *18/8* are also available. Super austenitic stainless steels, such as alloy AL-6XN and 254SMO, exhibit great resistance to chloride pitting and crevice corrosion because of high molybdenum content (>6%) and nitrogen additions, and the higher nickel content ensures better resistance to stress - corrosion cracking versus the 300 series. The higher alloy content of super austenitic steels makes them more expensive. Other steels can offer similar performance at lower cost and are preferred in certain applications. Low - carbon versions, for example 316L or 304L, are used to avoid corrosion problems caused by welding. Grade 316LVM is preferred where biocompatibility is required (such as body implants and piercings) . The "L" means that the carbon content of the alloy is below 0.03 % , which reduces the sensitization effect (precipitation of chromium carbides at grain boundaries) caused by the high temperatures involved in welding .

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- *Ferritic* stainless steels generally have better engineering properties than austenitic grades, but have reduced corrosion resistance, because of the lower chromium and nickel content. They are also usually less expensive. They contain between 10.5 % and 27 % chromium and very little nickel, if any, but some types can contain lead. Most compositions include molybdenum; some, aluminium or titanium. Common ferritic grades include 18Cr-2Mo, 26 Cr -1 Mo , 29 Cr – 4 Mo , and 29 Cr - 4Mo - 2Ni . These alloys can be degraded by the presence of σ chromium, an inter metallic phase which can precipitate upon welding.

- *Martensitic* stainless steels are not as corrosion-resistant as the other two classes but are extremely strong and tough, as well as highly machinable, and can be hardened by heat treatment. Martensitic stainless steel contains chromium (12 – 14%) , molybdenum (0.2 – 1 %) , nickel (less than 2 %) , and carbon (about 0.1– 1 %) (giving it more hardness but making the material a bit more brittle). It is quenched and magnetic.

- *Precipitation-hardening martensitic* stainless steels have corrosion resistance comparable to austenitic varieties, but can be precipitation hardened to even higher strengths than the other martensitic grades. The most common, 17- 4 PH , uses about 17% chromium and 4% nickel. The Lockheed-Martin Joint Strike Fighter is the first aircraft to use a precipitation - harden able stainless steel — Carpenter Custom 465 — in its airframe.

- *Duplex* stainless steels have a mixed microstructure of austenite and ferrite, the aim usually being to produce a 50/50 mix, although in commercial alloys the ratio may be 40/60. Duplex stainless steels have roughly twice the strength compared to austenitic stainless steels and also improved resistance to localized corrosion, particularly pitting, crevice corrosion and stress corrosion cracking. They are characterized by high chromium (19–32 %) and molybdenum (up to 5 %) and lower nickel contents than austenitic stainless steels. Duplex grades are characterized into groups based on their alloy content and corrosion resistance. Lean duplex refers to grades such as UNS S 32101 (LDX 2101) ,

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S 32304 , and S 32003 . The standard duplex is 22 % chromium with UNS S 31803 / S 32205 known as 2205 being the most widely used. Super duplex is by definition a duplex stainless steel with a pitting corrosion equivalent (PRE) > 40, where PRE = %Cr + 3.3x (% Mo + 0.5x % W) + 16 x % N. Usually super duplex grades have 25 % chromium or more and some common examples are S 32760 (Zeron 100), S 32750 (2507) and S32550 (Ferralium), although not all Ferralium grades are super duplex grades. Hyper duplex refers to duplex grades with a PRE > 48 and at the moment only UNS S 32707 and S 33207 are available on the market. The properties of duplex stainless steels are achieved with an overall lower alloy content than similar - performing super-austenitic grades , making their use cost - effective for many applications.

6 – 1 - Comparison of standardized steels :

EN-standard Steel no. k.h.s DIN	EN-standard Steel name	SAE grade	UNS
		440A	S44002
1.4112	X90CrMoV18	440B	S44003
1.4125		440C	S44004
		440F	S44020
1.4016	X6Cr17	430	S43000
1.4408	G-X 6 Cr Ni Mo 18 -10	316	
1.4512	X6CrTi12	409	S40900
		410	S41000
1.4310	X10 Cr Ni 18 - 8	301	S30100
1.4318	X2CrNiN18-7	301LN	N/A
1.4307	X2CrNi18-9	304L	S30403
1.4306	X2CrNi19-11	304L	S30403
1.4311	X2CrNiN18-10	304LN	S30453
1.4301	X5CrNi18-10	304	S30400
1.4948	X6CrNi18-11	304H	S30409
1.4303	X5CrNi18-12	305	S30500
	X5CrNi30-9	312	
1.4541	X6CrNiTi18-10	321	S32100

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1.4878	X12CrNiTi18-9	321H	S32109
1.4404	X2CrNiMo17-12-2	316L	S31603
1.4401	X5CrNiMo17-12-2	316	S31600
1.4406	X2CrNiMoN17-12-2	316LN	S31653
1.4432	X2CrNiMo17-12-3	316L	S31603
1.4435	X2CrNiMo18-14-3	316L	S31603
1.4436	X3CrNiMo17-13-3	316	S31600
1.4571	X6CrNiMoTi17-12-2	316Ti	S31635
1.4429	X2CrNiMoN17-13-3	316LN	S31653
1.4438	X2CrNiMo18-15-4	317L	S31703
1.4362	X2CrNi23-4	2304	S32304
1.4462	X2CrNiMoN22-5-3	2205	S31803/S32205
1.4539	X1NiCrMoCu25-20-5	904L	N08904
1.4529	X1NiCrMoCuN25-20-7	1925hMo/6MO	N08926
1.4547	X1CrNiMoCuN20-18-7	254SMO	S31254

6 – 2 - Stainless steel grades :

There are a number of different systems for grading stainless and other steels. The article on US SAE steel grades details a large number of grades with their properties.

6 – 3 - Stainless steel in 3D printing :

Some 3D printing providers have developed proprietary stainless steel sintering[18] blends for use in rapid prototyping. Currently available grades do not vary significantly in their properties.

7 - Stainless steel finishes :

Standard mill finishes can be applied to flat rolled stainless steel directly by the rollers and by mechanical abrasives. Steel is first rolled to size and thickness and then annealed to change the properties of the final material. Any oxidation that forms on the surface (mill scale) is removed by pickling, and a passivation layer is created on the surface. A final finish can then be applied to achieve the desired aesthetic appearance.

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- No. 0: Hot rolled, annealed, thicker plates
- No. 1: Hot rolled, annealed and passivated
- No. 2D: Cold rolled, annealed, pickled and passivated
- No. 2B: Same as above with additional pass-through highly polished rollers
- No. 2BA: Bright annealed (BA or 2R) same as above then bright annealed under oxygen-free atmospheric condition
- No. 3: Coarse abrasive finish applied mechanically
- No. 4: Brushed finish
- No. 5: Satin finish
- No. 6: Matte finish
- No. 7: Reflective finish
- No. 8: Mirror finish
- No. 9: Bead blast finish
- No. 10: Heat colored finish-wide range of electropolished and heat colored surfaces

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Iron Carbonate (Siderite)

Siderite from Brazil

Siderite is a mineral composed of iron carbonate $FeCO_3$. It takes its name from the Greek word *sideros*, “iron”. It is a valuable iron mineral, since it is 48 % iron and contains no sulfur or phosphorus. Both magnesium and manganese commonly substitute for the iron.

Siderite has Mohs hardness of 3.75 - 4.25, a specific gravity of 3.96, a white streak and a vitreous lustre or pearly luster.

Its crystals belong to the hexagonal system, and are rhombohedral in shape, typically with curved and striated faces. It also occurs in masses. Color ranges from yellow to dark brown or black , the latter being due to the presence of manganese (some times called manganosiderite).

Siderite is commonly found in hydrothermal veins, and is associated with barite, fluorite, galena, and others. It is also a common diagenetic mineral in shales and sand stones, where it sometimes forms concretions. In sedimentary rocks, siderite commonly forms at shallow burial depths and its elemental composition is often related to the depositional environment of the enclosing sediments. In addition, a number of recent studies have used the oxygen isotopic composition of sphaerosiderite (a type

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associated with soils) as a proxy for the isotopic composition of meteoric water shortly after deposition.

Category	Carbonate Mineral
Chemical Formula	Fe CO_3
Color	Pale yellow to tannish , grey, brown , green , red , black and sometimes nearly colorless
Crystal habit	Tabular crystals, often curved - botryoidal to massive
Crystal system	Trigonal - Hexagonal scalenohedral (3 2 / m)
Mohs scale hardness	3.75 - 4.25
Luster	Vitreous , may be silky to pearly
Streak	White
Diaphaneity	Translucent to sub translucent
Specific gravity	3.96
Optical properties	Uniaxial (-)
Refractive index	nω = 1.875 nε = 1.633

	
Cut siderite from Minas Gerais , Brazil (size : 5 x 3.2 mm)	*Siderite crystals with galena and quartz (size: 6.2 x 4.1 x 3.6 cm)*

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Iron (II) Chloride

Contents

1 . Introduction ;

Iron (II) chloride, also known as **ferrous chloride** , is the chemical compound of formula $FeCl_2$. It has a high melting point, paramagnetic solid, usually obtained as an off-white solid. $FeCl_2$ crystallizes from water as the greenish tetrahydrate, which is the form that is most commonly encountered in commerce and the laboratory. There is also a dihydrate.

Other Names	Ferrous chloride , Rokühnite
Molecular Formula	$Fe Cl_2$
Molar Mass	127 g / mol (anhydrous) 191 g / mol (tetra hydrate)
Appearance	Tan solid (anhydrous) pale green solid (di – tetra hydrate)
Density	3.16 g /cm^3 (anhydrous) 2.30 g / cm^3 (di hydrate) 1.39 g / cm^3 (tetra hydrate)
Melting Point	677 °C (anhydrous) 120 °C (di hydrate) 105 °C (tetra hydrate)
Boiling Point	1023 °C (anhydrous)
Solubility in Water	64.4 g / 100 mL (1 0°C) , 68.5 g / 100 mL (20°C) , 105.7 g / 100 mL (100°C)

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2 . Production

Hydrated forms of ferrous chloride are generated by treatment of wastes from steel production with hydrochloric acid. Such solutions are designated "spent acid," especially when the hydrochloric acid is not completely consumed:

$$Fe + 2\ HCl \rightarrow FeCl_2 + H_2$$

The spent acid requires treatment before its disposal. It is also byproduct from titanium production, since some titanium ores contain iron .

3 . Laboratory preparation

Ferrous chloride is conveniently prepared using a methanol solution of concentrated hydrochloric acid. This reaction gives the methanol solvate, which upon heating in a vacuum at about 160 °C gives anhydrous $FeCl_2$. $FeBr_2$ and FeI_2 can be prepared analogously.

An alternative laboratory synthesis of $Fe\ Cl_2$ entails the reaction of $FeCl_3$ with chloro benzene :

$$2\ Fe\ Cl_3 + C_6H_5\,Cl \rightarrow 2\ Fe\ Cl_2 + C_6H_4\ Cl_2 + H\ Cl$$

$Fe\ Cl_2$ prepared in this way exhibits convenient solubility in tetra hydro furan , a common solvent for chemical reactions. In one of two classic syntheses of ferrocene, Wilkinson generated $Fe\ Cl_2$ by heating $Fe\ Cl_3$ with iron powder . Ferric chloride decomposes to ferrous chloride at high temperatures.

4 . Reactions

$Fe\ Cl_2$ forms complexes with many ligands . It reacts with two molar equivalents of $[\ (\ C_2H_5\ )\ _4N\ ]\ Cl$ to give the salt $[\ (\ C_2H_5\ )\ _4N\ ]_2\ [\ Fe\ Cl\ _4\ ]$. Related compounds that can be prepared similarly include the $[\ Mn\ Cl_4\ ]^{2-}$, $[\ Mn\ Br_4\ ]^{2-}$, $[\ MnI_4\ ]^{2-}$, $[\ Fe\ Br_4\ ]^{2-}$, $[\ Co\ Cl_4\ ]^{2-}$, $[Co\ Br_4\ ]^{2-}$, $[\ Ni\ Cl_4\ ]^{2-}$, and $[\ Cu\ Cl_4\ ]^{2-}$ salts .

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5 . Applications

Ferrous chloride has a variety of niche applications, but the related compounds ferrous sulfate and ferric chloride enjoy more applications. Aside from use in the laboratory synthesis of iron complexes, ferrous chloride serves as a reducing flocculating agent in wastewater treatment, especially for wastes containing chromate. It is the precursor to hydrated iron (III) oxides that are magnetic pigments . Ferrous chloride employed as a reducing agent in organic synthesis.

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Iron (III) Chloride

Contents

1 . Introduction ;

Iron(III) chloride, also called **ferric chloride**, is an industrial scale commodity chemical compound, with the formula $FeCl_3$. The colour of iron (III) chloride crystals depends on the viewing angle: by reflected light the crystals appear dark green, but by transmitted light they appear purple-red. Anhydrous iron (III) chloride is deliquescent, forming hydrated hydrogen chloride mists in moist air. It is rarely observed in its natural form, mineral molysite , known mainly from some fumaroles.

When dissolved in water, iron (III) chloride undergoes hydrolysis and gives off heat in an exothermic reaction. The resulting brown, acidic, and corrosive solution is used as a coagulant in sewage treatment and drinking water production, and as an etchant for copper - based metals in printed circuit boards. Anhydrous iron (III) chloride is a fairly strong Lewis acid, and it is used as a catalyst in organic synthesis.

Other names	Ferric chloride Molysite Flores martis
Molecular Formula	$Fe\ Cl_3$

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Molar Mass	162 g / mol (anhydrous) 270 g / mol (hexa hydrate)
Appearance	Green - black by reflected light ; purple - red by transmitted light hexa hydrate : yellow solid aq. Solutions : brown
Density	2.898 g / cm^3 (anhydrous)
Melting point	306 °C (anhydrous) 37 °C (hexa hydrate)
Boiling Point	315 °C (anhydrous , decomp) 280 °C (hexa hydrate , decomp) (partial decomposition to $FeCl_2$ + Cl_2)
Solubility in Water	74.4 g / 100 mL (0 °C) 92 g / 100 mL (20 °C) 92 g / 100 mL (hexa hydrate , 20 °C)
Solubility in acetone	63 g / 100 ml (18 °C)
Methanol	highly soluble
Ethanol	83 g / 100 ml
Diethyl ether	highly soluble
Viscosity	40 % solution : 12 cP

2 . Chemical and physical properties

Iron (III) chloride has a relatively low melting point and boils at around 315 °C. The vapour consists of the dimer Fe_2 Cl_6 (compare aluminium chloride) which increasingly dissociates into the monomeric Fe Cl_3 (D_{3h} point group molecular symmetry) at higher temperature, in competition with its reversible decomposition to give iron (II) chloride and chlorine gas .

2 . 1 . Reactions

Iron (III) chloride is a moderately strong Lewis acid , forming adducts with Lewis bases such as tri phenyl phosphine oxide, e.g. Fe Cl_3 $(OPPh_3)_2$ where Ph = phenyl.

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Iron (III) chloride reacts with other chloride salts to give the yellow tetrahedral $Fe\,Cl_4^-$ ion. Salts of $Fe\,Cl_4^-$ in hydrochloric acid can be extracted into diethyl ether.

When heated with iron (III) oxide at 350 °C , iron (III) chloride gives iron oxy chloride , a layered solid and intercalation host .

$$Fe\,Cl_3 + Fe_2O_3 \rightarrow 3\ Fe\,O\,Cl$$

In the presence of base , alkali metal alk oxides react to give the dimeric complexes :

$$2\ Fe\,Cl_3 + 6\ C_2H_5OH + 6\ NH_3 \rightarrow (\ Fe\,(OC_2H_5)_3\ )_2 + 6\ NH_4Cl$$

Oxalates react rapidly with aqueous iron (III) chloride to give $[\ Fe\ (\ C_2O_4\ )_3\ ]^{3-}$. Other carboxylate salts form complexes, e.g. citrate and tartrate .

Iron (III) chloride is a mild oxidizing agent, for example capable of oxidizing copper (I) chloride to copper (II) chloride. Reducing agents such as hydrazine convert iron (III) chloride to complexes of iron (II).

2 . 2 . Structure

Iron (III) chloride adopts the BiI_3 structure, which features octahedral Fe (III) centers interconnected by two - coordinate chloride ligands .

3 . Preparation and production

Anhydrous iron (III) chloride may be prepared by union of the elements :

$$2\ Fe\,(s) + 3\ Cl_2\,(g) \rightarrow 2\ Fe\,Cl_3\,(s)$$

Solutions of iron (III) chloride are produced industrially both from iron and from ore , in a closed - loop process.

1. Dissolving pure iron in a solution of iron (III) chloride
$Fe\,(s) + 2\ Fe\,Cl_3\,(aq) \rightarrow 3\ Fe\,Cl_2\,(aq)$

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2. Dissolving iron ore in hydrochloric acid

Fe_3O_4 (s) + 8 HCl (aq) → $FeCl_2$(aq) + 2 $FeCl_3$(aq) + 4 H_2O

3. Upgrading the iron (II) chloride with chlorine

2 Fe Cl_2 (aq) + Cl_2 (g) → 2 Fe Cl_3 (aq)

Alternatively, iron (II) chloride can be oxidized with sulfur dioxide :

$$32\ Fe\ Cl_2 + 8\ SO_2 + 32\ HCl \rightarrow 32\ Fe\ Cl_3 + S_8 + 16\ H_2O$$

Like many other hydrated metal chlorides, hydrated iron (III) chloride can be converted to the anhydrous salt by refluxing with thionyl chloride . The hydrate cannot be converted to anhydrous iron (III) chloride by only heat, as instead HCl is evolved and iron oxy chloride forms .

4 . Uses

4 . 1 . Industrial

In industrial application, iron (III) chloride is used in sewage treatment and drinking water production . In this application , $FeCl_3$ in slightly basic water reacts with the hydroxide ion to form a floc of iron (III) hydroxide, or more precisely formulated as FeO $(OH)^-$, that can remove suspended materials :

$$Fe^{3+} + 4\ OH^- \rightarrow Fe\ (OH)_4^- \rightarrow Fe\ O\ (OH)_2^- \cdot H_2O$$

It is also used as a leaching agent in chloride hydro metallurgy , for example in the production of Si from Fe Si (Silgrain process)

Another important application of iron (III) chloride is etching copper in two - step redox reaction to copper (I) chloride and then to copper (II) chloride in the production of printed circuit boards .

$$Fe\ Cl_3 + Cu \rightarrow Fe\ Cl_2 + Cu\ Cl$$
$$Fe\ Cl_3 + Cu\ Cl \rightarrow Fe\ Cl_2 + Cu\ Cl_2$$

Iron (III) chloride is used as catalyst for the reaction of ethylene with chlorine, forming ethylene dichloride (1,2-dichloroethane), an

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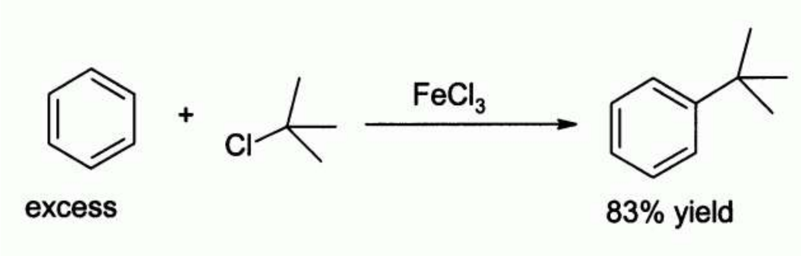
important commodity chemical, which is mainly used for the industrial production of vinyl chloride, the monomer for making PVC.

$$H_2C = CH_2 + Cl_2 \rightarrow ClCH_2\ CH_2Cl$$

4 . 2 . Laboratory use

In the laboratory iron (III) chloride is commonly employed as a Lewis acid for catalyzing reactions such as chlorination of aromatic compounds and Friedel - Crafts reaction of aromatics. It is less powerful than aluminium chloride, but in some cases this mildness leads to higher yields, for example in the alkylation of benzene :



The ferric chloride test is a traditional colorimetric test for phenols, which uses a 1 % iron (III) chloride solution that has been neutralized with sodium hydroxide until a slight precipitate of Fe O (OH) is formed . The mixture is filtered before use. The organic substance is dissolved in water, methanol or ethanol, then the neutralized iron (III) chloride solution is added—a transient or permanent coloration (usually purple, green or blue) indicates the presence of a phenol or enol.

4 . 3 . Other uses

- Anhydrous iron (III) chloride is some times used as a drying reagent in certain reactions.
- Iron (III) chloride is some times used by American coin collectors to identify the dates of Buffalo nickels that are so badly worn that the date is no longer visible.
- Iron (III) chloride is commonly used by knife craftsmen and sword smiths to stain blades, as to give a contrasting effect to the metal, and to view metal layering or imperfections.

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- Iron (III) chloride is often used to etch the widmanstatten pattern in iron meteorites .
- Iron (III) chloride is necessary for the etching of photogravure plates for printing photographic and fine art images in intaglio and for etching rotogravure cylinders used in the printing industry.
- Iron (III) chloride is used in veterinary practice to treat over cropping of an animal's claws, particularly when the over cropping results in bleeding.
- Iron (III) chloride reacts with cyclo penta dienyl magnesium bromide in one preparation of ferrocene, a metal-sandwich complex .
- Iron (III) chloride is sometimes used in the technique of Raku Firing as an additive during the reduction process, turning a pottery piece a burnt orange color due to the iron content present in the reducing atmosphere.
- Iron (III) chloride can be used to test the pitting and crevice corrosion resistance of stainless steels and other alloys.
- Iron (III) chloride can be used in conjunction with Na I in aceto nitrile to mildly reduce organic azides to primary amines .
- Iron (III) chloride is used in an animal thrombosis model .

5 . Safety

Iron (III) chloride is toxic, highly corrosive and acidic. The anhydrous material is a powerful dehydrating agent.

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Iron (II) citrate

Ferrous citrate , or **iron (II) citrate** , is a chemical compound consisting of one atom of iron (Fe^{2+}) and two citrate anions. It has the chemical formula Fe $C_6H_6O_7$.

Iron (II) becomes less soluble at PH > 7 . Citrate is a chelating agent , which results in an easily soluble complex.

It is a common nutritional supplement against iron deficiency.

IUPAC Name : Ferrous 2-hydroxypropanoate ERROR	
Other Names : Iron dicitrate Iron (II) citrate E585	
Molecular Formula	$C_6H_{10}Fe\ O_6\ C_6H_6Fe\ O_7{}^{-2}$
Molar mass	246 g / mol

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Iron (II) hydroxide

1 Introduction :

Iron (II) hydroxide or **ferrous hydroxide** is a compound produced when iron (II) ions , from a compound such as iron (II) sulfate react with hydroxide ions . Iron (II) hydroxide itself is practically white, but even traces of oxygen impart it with a greenish tinge. If the solution was not deoxygenated and the iron reduced, the precipitate can vary in color starting from green to reddish brown depending on the iron (III) content. This precipitate is also known as "green rust" in the crystal lattice of which Fe^{2+} ions are easily substituted by Fe^{3+} ions produced by its progressive oxidation. In the presence of oxygen the color changes quickly. Green rust is a powerful reducing agent and also a layer double hydroxides (LDH) capable to sorb anions because of the presence of positive electrical charges borne on its surface. The mineralogical form of green rust is a recently discovered fougerite . All forms of green rust (including fougerite) does not correspond the ideal $Fe(OH)_2$ compound, as their structure is more complex and variable. The natural analogue of $Fe(OH)_2$ compound is a very rare mineral amakinite , $(Fe, Mg)(OH)_2$.

Iron (II) hydroxide is poorly soluble (1.43×10^{-3} g / L) . It precipitates from the reaction of iron (II) sulfate and hydroxide ions (from a soluble compound containing hydroxide ion) :

$$FeSO_4 + 2OH^{-} \rightarrow Fe(OH)_2 + SO_4^{2-}$$

It is also easily formed as an undesirable by - product of other reactions, a.o., in the synthesis of siderite , an iron carbonate $FeCO_3$.

Other Names	Ferrous hydroxide
Molecular Formula	$Fe(OH)_2$
Molar Mass	90 g / mol
Appearance	brown solid

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Density	3.4 g / cm^3
Solubility in water	0.00015 g / 100 mL (20 ° C)
Solubility product, K_{sp}	8.0 x 10^{-16}

2 . Uses :

Anions such as selenite and selenate can be easily adsorbed on the positively charged surface of green rust where they are subsequently reduced by Fe^{2+}. The resulting products being poorly soluble (Se^0 , Fe Se , or $FeSe_2$) .

Ferrous hydroxide has also been investigated as an agent for the removal of toxic selenate and selenite ions from water systems such as wetlands. The ferrous hydroxide reduces these ions to elemental selenium, which is insoluble in water and precipitates out .

Note : pK_{sp} = 15.097 where p is the -log and K_{sp} is the Solubility Product Constant. This means it has a low tendency to dissolve, but is not entirely insoluble. An acidic solution would allow this to disassociate more because the H^+ would react with the OH^- in the compound.

In a basic solution (potassium hydroxide) , ferrous hydroxide is the electro chemically active material of the negative electrode of the Nickel - iron battery.

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Iron (III) oxide - hydroxide

Contents

1 – Introduction :

A number of species are dubbed **iron (III) oxide - hydroxide**. These chemicals are oxide - hydroxides of iron, and may occur in anhydrous (FeO (OH)) or hydrated (FeO (OH) · nH_2O) forms. The monohydrate (FeO (OH)·H_2O) might otherwise be described as **iron (III) hydroxide** ($Fe(OH)_3$), and is also known as **hydrated iron oxide** or **yellow iron oxide**.

IUPAC Name ; Iron (III) oxide - hydroxide	
Other Names : Ferric acid	
Molecular Formula	H Fe O_2
Molar mass	89 g mol^{-1}
Appearance	Vivid , dark orange , opaque crystals

2 - Natural occurrences :

Iron (III) oxide - hydroxide occurs naturally as the minerals goethite , akaganéite (rarely found in weathered meteorites), lepidocrocite and feroxyhyte, as well as siderogel and limonite, which is a commonly found mixture of mainly goethite, lepidocrocite, quartz and clay minerals. Goethite and lepidocrocite, both crystallizing in orthorhombic system, are the most common forms of iron (III) oxide - hydroxide and the most important mineral carriers of iron in soils. The mineral ferrihydrite , also a soil constituent, is a related compound.

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3 - Uses :

Yellow iron oxide is used as a pigment, e.g. **Pigment Yellow 42** or **C.I. 77492**. Pigment Yellow 42 is Food and Drug Administration (FDA) approved for use in cosmetics and is used in some tattoo inks. Solid material color ranges from yellow through dark-brown to black. Iron oxide - hydroxide is also used in aquarium water treatment as a phosphate binder .

4 - Production

It is obtained by reacting ferric chloride with sodium hydroxide:

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaCl$$

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Iron (III) Nitrate

Contents

1 – Introduction :

Iron (III) nitrate , or **ferric nitrate**, is the chemical compound with the formula $Fe(NO_3)_3$. Since it is deliquescent, it is commonly found in its nona hydrate form $Fe(NO_3)_3 \cdot 9H_2O$ in which it forms colourless to pale violet crystals.

IUPAC name : Iron (III) nitrate	
Other names : Ferric nitrate , Nitric acid iron (3+) salt	
Molecular Formula	$Fe(NO_3)_3$
Molar Mass	242 g / mol (anhydrous) 404 g / mol (nona hydrate)
Appearance	Pale violet crystals , hygroscopic
Density	1.68 g / cm^3 (nona hydrate)
Melting point	47.2 °C (nona hydrate) 125 °C (decomp)
Solubility in water	Very soluble
Solubility in alcohol , Acetone	Soluble

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2 - Preparation :

The compound is prepared by treating iron metal or iron oxides with nitric acid.

$$Fe_2O_3 + 6\ HNO_3 \rightarrow 2\ Fe\ (NO_3)_3 + 3\ H_2O$$

3 - Applications :

3 – 1 - In the chemical laboratory :

Ferric nitrate is the catalyst of choice for the synthesis of sodium amide from a solution of sodium in ammonia :

$$2\ NH_3 + 2\ Na \rightarrow 2\ NaNH_2 + H_2$$

Certain clays impregnated with ferric nitrate have been shown to be useful oxidants in organic synthesis. For example, ferric nitrate on Montmorillonite — a reagent called "Clay fen" — has been employed for the oxidation of alcohols to aldehydes and thiols to disulfides .

3 – 2 - Other applications :

Ferric nitrate solutions are used by jewelers and metal

smiths to etch silver and silver alloys.

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Iron Ore

Contents

1 – Introduction :

Iron ores are rocks and minerals from which metallic iron can be economically extracted. The ores are usually rich in iron oxides and vary in colour from dark grey, bright yellow, deep purple, to rusty red. The iron itself is usually found in the form of magnetite (Fe_3O_4), hematite (Fe_2O_3),(alt spelling: haematite) goethite, limonite or siderite. Hematite is also known as "natural ore". The name refers to the early years of mining, when certain hematite ores contained 66% iron and could be fed directly into iron making blast furnaces. Iron ore is the raw material used to make pig iron, which is one of the main raw materials to make steel. 98 % of the mined iron ore is used to make steel .

2 - Sources :

Pure iron is virtually unknown on the surface of the Earth except as Fe - Ni alloys from meteorites and very rare forms of deep mantle xenoliths. Therefore, all sources of iron used by human industry

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exploit iron oxide minerals, the primary form which is used in industry being hematite.

However, in some situations, more inferior iron ore sources have been used by industrialized societies when access to high - grade hematite ore was not available. This has included utilization of taconite in the United States, particularly during World War II, and goethite or bog ore used during the American Revolution and the Napoleonic wars. Magnetite is often used because it is magnetic and hence easily liberated from the gangue minerals.

Inferior sources of iron ore generally require beneficiation. Due to the high density of hematite relative to silicates, beneficiation usually involves a combination of crushing and milling as well as heavy liquid separation. This is achieved by passing the finely crushed ore over a bath of solution containing bentonite or other agent which increases the density of the solution. When the density of the solution is properly calibrated, the hematite will sink and the silicate mineral fragments will float and can be removed.

Iron ore mining methods vary by the type of ore being mined. There are four main types of iron ore deposits worked currently, depending on the mineralogy and geology of the ore deposits. These are magnetite, titano magnetite , massive hematite and pisolitic ironstone deposits.

2 – 1 - Magnetite banded iron deposits :

Banded iron formations (BIF) are fine grained metamorphosed sedimentary rocks composed predominantly of magnetite and silica (as quartz). Banded Iron formations are locally known as taconite within North America.

Mining of BIF formations involves coarse crushing and screening, followed by rough crushing and fine grinding to comminute the ore to the point where the crystallised magnetite and quartz are fine enough that the quartz is left behind when the resultant powder is passed under a magnetic separator.

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The mining involves moving tremendous amounts of ore and waste. The waste comes in two forms, bedrock in the mine (mullock) that isn't ore, and unwanted minerals which are an intrinsic part of the ore rock itself (gangue) . The mullock is mined and piled in waste dumps, and the gangue is separated during the beneficiation process and is removed as tailings. Taconite tailings are mostly the mineral quartz, which is chemically inert. This material is stored in large, regulated water settling ponds.

The key economic parameters for magnetite ore being economic are the crystallinity of the magnetite, the grade of the iron within the BIF host rock, and the contaminant elements which exist within the magnetite concentrate. The size and strip ratio of most magnetite resources is irrelevant as BIF formations can be hundreds of metres thick, with hundreds of kilo meters of strike, and can easily come to more than 2,500 million tonnes of contained ore.

The typical grade of iron at which a magnetite-bearing banded iron formation becomes economic is roughly 25 % Fe , which can generally yield a 33 % to 40 % recovery of magnetite by weight, to produce a concentrate grading in excess of 64 % Fe by weight. The typical magnetite iron ore concentrate has less than 0.1 % phosphorus, 3 - 7 % silica and less than 3% aluminium.

The grain size of the magnetite and its degree of comingling with the silica groundmass determine the grind size to which the rock must be comminuted to enable efficient magnetic separation to provide a high purity magnetite concentrate. This determines the energy inputs required to run a milling operation. Generally most magnetite BIF deposits must be ground to between 32 and 45 micrometres in order to provide a low-silica magnetite concentrate. Magnetite concentrate grades are generally in excess of 63 % Fe by weight and usually are low phosphorus, low aluminium, low titanium and low silica and demand a premium price.

Currently magnetite iron ore is mined in Minnesota and Michigan in the U.S., and Eastern Canada mine taconite. Magnetite bearing BIF is currently mined extensively in Brazil, which exports

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significant quantities to Asia, and there is a nascent and large magnetite iron ore industry in Australia.

2 – 2 - Magmatic magnetite ore deposits :

Occasionally granite and ultrapotassic igneous rocks segregate magnetite crystals and form masses of magnetite suitable for economic concentration. A few iron ore deposits, notably in Chile, are formed from volcanic flows containing significant accumulations of magnetite phenocrysts. Chilean magnetite iron ore deposits within the Atacama Desert have also formed alluvial accumulations of magnetite in streams leading from these volcanic formations.

Some magnetite skarn and hydrothermal deposits have been worked in the past as high-grade iron ore deposits requiring little beneficiation. There are several granite-associated deposits of this nature in Malaysia and Indonesia.

Other sources of magnetite iron ore include metamorphic accumulations of massive magnetite ore such as at Savage River, Tasmania, formed by shearing of ophiolite ultramafics .

Another, minor, source of iron ores are magmatic accumulations in ultramafic to mafic layered intrusions which contain a typically titanium-bearing magnetite crystal rock (magnetitite) often with vanadium. These ores form a niche market, with specialty smelters used to recover the iron, titanium and vanadium. These ores are beneficiated essentially similar to banded iron formation ores, but usually are more easily upgraded via crushing and screening. The typical titanomagnetite concentrate grades 57 % Fe, 12 % Ti and 0.5 % V2O5.

2 – 3 - Hematite ore :

Hematite iron ore deposits are currently exploited on all continents, with the largest intensity in South America, Australia and Asia. Most large hematite iron ore deposits are sourced from meta somatically altered banded iron formations and rarely igneous accumulations.

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Hematite iron is typically rarer than magnetite bearing BIF or other rocks which form its main source or protolith rock, but it is considerably cheaper and easier to beneficiate the hematite ores and requires considerably less energy to crush and grind. Hematite ores however can contain significantly higher concentrations of penalty elements, typically being higher in phosphorus, water content (especially pisolite sedimentary accumulations) and aluminium (clays within pisolites).

In Australia iron ore is won from three main sources: pisolite "channel iron deposit" ore derived by mechanical erosion of primary banded - iron formations and accumulated in alluvial channels such as at Pannawonica , Western Australia; and the dominant meta somatically - altered banded iron formation related ores such as at Newman, the Chichester Range, the Hamersley Range and Koolyanobbing , Western Australia. Other types of ore are coming to the fore recently, such as oxidised ferruginous hardcaps, for instance laterite iron ore deposits near Lake Argyle in Western Australia.

The total recoverable reserves of iron ore in India are about 9,602 million tones of hematite and 3,408 million tones of magnetite. Madhya Pradesh, Karnataka, Bihar, Orissa, Goa, Maharashtra, Andhra Pradesh, Kerala, Rajasthan and Tamil Nadu are the principal Indian producers of iron ore.

3 - Production and consumption

Iron is the world's most commonly used metal. It is used primarily in structural engineering applications and in maritime purposes, automobiles, and general industrial applications (machinery).

Iron - rich rocks are common worldwide, but ore-grade commercial mining operations are dominated by the countries listed in the table aside. The major constraint to economics for iron ore deposits is not necessarily the grade or size of the deposits, because it is not particularly hard to geologically prove enough tonnage of the rocks exist. The main constraint is the position of the iron ore relative

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to market, the cost of rail infrastructure to get it to market and the energy cost required to do so.

World production averages one billion metric tons of raw ore annually. The world's largest producer of iron ore is the Brazilian mining corporation Vale, followed by Anglo-Australian companies BHP Billiton and Rio Tinto Group. A further Australian supplier, Fortescue Metals Group Ltd may eventually bring Australia's production to second in the world.

World consumption of iron ore grows 10% per annum on average with the main consumers being China, Japan, Korea, the United States and the European Union.

China is currently the largest consumer of iron ore, which translates to be the world's largest steel producing country. China is followed by Japan and Korea, which consume a significant amount of raw iron ore and metallurgical coal. In 2006, China produced 588 million tons of iron ore, with an annual growth of 38 %.

4 - Depletion :

Iron ore reserves at present seem quite vast, but some are starting to suggest that the maths of continual exponential increase in consumption can even make this resource seem quite finite. For instance, Lester Brown of the Worldwatch Institute has suggested iron ore could run out within 64 years based on an *extremely conservative* extrapolation of 2 % growth per year.

5 – Smelting :

Iron ore consists of oxygen and iron atoms bonded together into molecules. To convert it to metallic iron it must be smelted or sent through a direct reduction process to remove the oxygen. Oxygen-iron bonds are strong, and to remove the iron from the oxygen, a stronger elemental bond must be presented to attach to the oxygen. Carbon is used because the strength of a carbon-oxygen bond is greater than that of the iron - oxygen bond, at high temperatures. Thus, the iron ore

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must be powdered and mixed with coke, to be burnt in the smelting process.

However, it is not entirely as simple as that; carbon monoxide is the primary ingredient of chemically stripping oxygen from iron. Thus, the iron and carbon smelting must be kept at an oxygen deficient reduced state to promote burning of carbon to produce CO not CO_2.

Air blast and charcoal (coke): $2C + O_2 \rightarrow 2CO$.
Carbon monoxide (CO) is the principal reduction agent.
Stage One : $3Fe_2 O_3 + CO \rightarrow 2Fe_3 O_4 + CO_2$
Stage Two : $Fe_3 O_4 + CO \rightarrow 3Fe O + CO_2$
Stage Three : $Fe O + CO \rightarrow Fe + CO_2$
Limestone fluxing chemistry : $CaCO_3 \rightarrow Ca O + CO_2$

5 – 1 - Trace Elements : Effects and Remedies :

The inclusion of even small amounts of some elements can have profound effects on the behavioral characteristics of a batch of iron or the operation of a smelter. These effects can be both good and bad. Some catastrophically bad. Some chemicals were deliberately added. The addition of a flux made a blast furnace more efficient. Others were added because they made the iron more fluid, harder, or some other desirable quality. The choice of ore, fuel, and flux determined how the slag behaved and the operational characteristics of the iron produced. Ideally iron ore contains only iron and oxygen. In nature this is rarely the case. Typically, iron ore contains a host of elements which are often unwanted in modern steel.

5 – 1 – 1 - Silicon :

Silica (SiO2) is almost always present in iron ore. Most of it is slagged off during the smelting process. But, at temperatures above 1300 °C some will be reduced and form an alloy with the iron. The hotter the furnace, the more silicon will be present in the iron. It is not uncommon to find up to 1.5 % Si in European cast iron from the 16th to 18th centuries. The major effect of silicon is to promote the

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formation of gray iron. Gray iron is less brittle and easier to finish than white iron..

5 – 1 – 2 – Phosphorus :

Phosphorus (P) has four major effects on iron: increased hardness and strength, lower solidus temperature, increased fluidity, and cold shortness. Depending on the use intended for the iron, these effects are either good or bad. Bog ore often has a high Phosphorus content .

The strength and hardness of iron increases with the concentration of phosphorus. 0.05 % phosphorus in wrought iron makes it as hard as medium carbon steel. High phosphorus iron can also be hardened by cold hammering. The hardening effect is true for any concentration of phosphorus. The more phosphorus, the harder the iron becomes and the more it can be hardened by hammering. Modern steel makers can increase hardness by as much as 30%, without sacrificing shock resistance by maintaining phosphorus levels between 0.07 and 0.12%. It also increases the depth of hardening due to quenching, but at the same time also decreases the solubility of carbon in iron at high temperatures. This would decrease its usefulness in making blister steel (cementation), where the speed and amount of carbon absorption is the overriding consideration.

The addition of phosphorus has a down side. At concentrations higher than 0.2 % iron becomes increasingly cold short, or brittle at low temperatures. Cold short is especially important for bar iron. Although, bar iron is usually worked hot, its uses often require it to be tough, bendable, and resistant to shock at room temperature. A nail that shattered when hit with a hammer or a carriage wheel that broke when it hit a rock would not sell well. High enough concentrations of phosphorus render any iron unusable (Rostoker and Bronson 1990:22). The effects of cold shortness are magnified by temperature. Thus, a piece of iron that is perfectly serviceable in summer, might become extremely brittle in winter. There is some evidence that during the Middle Ages the very wealthy may have had a high phosphorus sword for summer and a low phosphorus sword for winter

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Careful control of phosphorus can be of great benefit in casting operations. Phosphorus depresses the liquidus temperature, allowing the iron to remain molten for longer and increases fluidity. The addition of 1 % can double the distance molten iron will flow . The maximum effect, about 500 °C , is achieved at a concentration of 10.2 % . For foundry work Turner felt the ideal iron had 0.2-0.55% phosphorus. The resulting iron filled molds with fewer voids and also shrank less. In the 19th century some producers of decorative cast iron used iron with up to 5% phosphorus. The extreme fluidity allowed them to make very complex and delicate castings. But, they could not be weight bearing, as they had no strength .

There are two remedies for high phosphorus iron. The oldest, and easiest, was avoidance. If the iron your ore produced was cold short, you found a new source of ore. The second method involves oxidizing the phosphorus during the fining process by adding iron oxide. The technique is usually associated with puddling in the 19th century, and may not have been understood earlier. For instance Isaac Zane, the owner of Marlboro Iron Works did not appear to know about it in 1772. Given Zane's reputation for keeping abreast of the latest developments, the technique was probably unknown to the ironmasters of Virginia and Pennsylvania.

Phosphorus is a deleterious contaminant because it makes steel brittle, even at concentrations of as little as 0.5%. Phosphorus cannot be easily removed by fluxing or smelting, and so iron ores must generally be low in phosphorus to begin with. The iron pillar of India which does not rust is protected by a phosphoric composition. Phosphoric acid is used at a rust converter because phosphoric iron is less susceptible to oxidation.

5 – 1 – 3 – Aluminium

Small amounts of aluminium (Al) are present in many ores (often as clay) and some limestone. The former can be removed by washing the ore prior to smelting. Until the introduction of brick lined furnaces the amounts are small enough that they do not have an effect on either the iron or slag. However, when brick is used for hearths and

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the interior of blast furnaces, the amount of aluminium increases dramatically. This is due to the erosion of the furnace lining by the liquid slag,

Aluminium is very hard to reduce. As a result aluminium contamination of the iron is not a problem. However, it does increase the viscosity of the slag . This will have a number of adverse effects on furnace operation. The thicker slag will slow the descent of the charge, prolonging the process. High aluminium will also make it more difficult to tap off the liquid slag. At the extreme this could lead to a frozen furnace.

There are a number of solutions to a high aluminium slag. the first is avoidance, don't use ore or a lime source with a high aluminium content. Increasing the ratio of lime flux will decrease the viscosity .

5 – 1 – 4 – Sulfur

Sulfur (S) is a frequent contaminant in coal. It is also present in small quantities in many ores, but would be removed by calcining. Sulfur dissolves readily in both liquid and solid iron at the temperatures present in iron smelting. The effects of even small amounts of sulfur are immediate and serious. They were one of the first worked out by iron makers. Sulfur causes iron to be red or hot short .

Hot short iron is brittle when hot. This was a serious problem as most iron used during the 17th and 18th century was bar or wrought iron. Wrought iron is shaped by repeated blows with a hammer while hot. A piece of hot short iron will crack if worked with a hammer. When a piece of hot iron or steel cracks the exposed surface immediately oxidizes. This layer of oxide prevents the mending of the crack by welding. Large cracks cause the iron or steel to break up. Smaller cracks can cause the object to fail during use. The degree of hot shortness is in direct proportion to the amount of sulfur present. Today iron with over 0.03 % sulfur is avoided.

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Hot short iron can be worked, but it has to be worked at low temperatures. Working at lower temperatures requires more physical effort from the smith or forge man . the metal must be struck more often and harder to achieve the same result. A mildly sulfur contaminated bar could be worked, but it required a great deal more time and effort.

In cast iron sulfur promotes the formation of white iron. As little as 0.5% can counteract the effects of slow cooling and a high silicon content . White cast iron is more brittle, but also harder. It was generally avoided, because it was difficult to work. Except in China where high sulfur cast iron, some as high as 0.57%, made with coal and coke, was used to make bells and chimes , good foundry iron should have less than 0.15 % sulfur. In the rest of the world a high sulfur cast iron could be used for making castings, but would make poor wrought iron.

There are a number of remedies for sulfur contamination. The first, and the one most used in historic and prehistoric operations, was avoidance. Coal was not used in Europe (unlike China) as a fuel for smelting because it contained sulfur and caused hot short iron. If an ore resulted in hot short metal, ironmasters found another ore. When mineral coal was first used in European blast furnaces in 1709 (or perhaps earlier), it was coked. Only with the introduction of hot blast from 1829 was raw coal used.

Sulfur can be removed from ores by roasting and washing. Roasting oxidizes sulfur to form sulfur dioxide which either escapes into the atmosphere or can be washed out. In warm climates it was possible to leave pyritic ore out in the rain. The combined action of rain, bacteria, and heat oxidize the sulfides to sulfates, which are water soluble . However, historically (at least) iron sulfide (iron pyrite, FeS_2), though a common iron mineral has not been used an ore for the production of metal. Natural weathering was also used in Sweden. The same process, at geological speed, results in the gossan limonite ores.

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The importance attached to low sulfur iron is demonstrated by the consistently higher prices paid for the iron of Sweden, Russia, and Spain from the 16th to 18th centuries. Today sulfur is no longer a problem. The modern remedy is the addition of manganese. But, the operator must know how much sulfur is in the iron because at least five times as much manganese must be added to neutralize it. Some historic irons display manganese levels, but most are well below the level needed to neutralize sulfur .

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Iron oxide

Contents

1 . Introduction ;

Iron oxides are chemical compounds composed of iron and oxygen. Altogether, there are sixteen known iron oxides and oxy hydroxides .

2 . Oxides

- FeO , iron (II) oxide, (wüstite)
- Fe_3O_4 , iron (II,III) oxide, (magnetite)
- Fe_2O_3 , iron (III) oxide, (Hematite)
  - α - Fe_2O_3 , hematite
  - β - Fe_2O_3
  - γ - Fe_2O_3, maghemite
  - ε - Fe_2O_3

3 . Hydroxides

- iron (II) hydroxide $Fe(OH)_2$
- iron (III) hydroxide $Fe(OH)_3$, (bernalite)

4 . Oxide - hydroxides

- goethite (α - Fe OOH) ,
- akaganéite (β - Fe OOH) ,
- lepidocrocite (γ - Fe OOH) ,
- feroxyhyte (δ – Fe OOH) ,
- ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$ approx)

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- High - pressure Fe OOH
- Schwertmannite

5 . Uses

A prehistorical painting (Lascaux) created with locally-available pigments : red and yellow ochers · The most industrially - important iron ores are chemically iron oxides.

Some iron oxides are widely used in ceramic applications, particularly in glazing. Many metal oxides provide the colors in glazes after being fired at high temperatures.

Iron oxides yield pigments . Natural iron oxides pigments are called ochres. Many classic paint colors, such as raw and burnt siennas and umbers, are iron - oxide pigments. These pigments have been used in art since the earliest prehistoric art known, the cave paintings at Lascaux and nearby sites. Iron (III) oxide is typically used.

Iron pigments are also widely used in the cosmetic field. They are considered to be nontoxic, moisture resistant, and non bleeding . Iron oxides graded safe for cosmetic use are produced synthetically in order to avoid the inclusion of ferrous or ferric oxides, and impurities normally found in naturally occurring iron oxides. Typically, the iron (II) oxide pigment is black, while the iron (III) oxide is red or rust - colored. (Iron compounds other than oxides can have other colors.)

Black oxide converts ferrous materials into magnetite for corrosion resistance purposes . A grade of hematite called MIO (micaceous iron oxide) is used as anti-corrosion paint (many bridges, Eiffel tower) .

Iron oxides are used as contrast agent in Magnetic Resonance Imaging, to shorten proton relaxation times , (T1 , T2 and T2 *). The super paramagnetic contrast agents are composed of a water insoluble crystalline magnetic core, usually magnetite (Fe_3O_4) or maghemite (γ - Fe_2O_3) . The mean core diameter ranges from 4 to 10 nm. This crystalline core is often surrounded by a layer of dextran or starch

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derivatives. The total size of the particle is expressed as the mean hydrated particle diameter. USPIO , Ultra small Super paramagnetic Iron Oxide nano particles , which usually have single crystal cores, have a mean hydrated particle diameter less than 50 nm.

They may also be used in electro chromic paints.

Combined with aluminium powder, iron oxide forms thermite, which is used in demolition and bomb building.

The iron oxide cycle ($Fe_3 O_4$ / Fe O) is a two - step thermo chemical process used for hydrogen production.

6 . Properties

- Iron (II) oxide (Fe O) or ferrous oxide is also known as wüstite in its mineral form. As a powder this black oxide can cause explosions as it readily ignites.

- Iron (III) oxide (Fe_2O_3) or ferric oxide is also known as hematite (alpha form) or maghemite (gamma form) in its mineral form. As an industrial chemical it is commonly called rouge. Purified, it is used as a coating in magnetic audio and computer media. In a dry or alkaline environment, it can cause passivation and inhibit rust, yet it is also a major component of rust and dried blood.

- Iron (II , III) oxide ($Fe_3 O_4$) or ferrous ferric oxide is also known as magnetite or lodestone in its mineral form, a major iron ore. Magnetite forms readily when iron oxidizes underwater, and so is often found inside tanks or below the waterline of ships.

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Iron (II) Oxide

Contents

1 . Introduction :

Iron (II) oxide , also known as **ferrous oxide** , **iron oxide / oxidized iron** or more commonly **rusted iron** , is one of the iron oxides. It is a black-colored powder with the chemical formula Fe O . It consists of the chemical element iron in the oxidation state of 2 bonded to oxygen. Its mineral form is known as wüstite. Iron (II) oxide should not be confused with rust, which usually consists of hydrated iron (III) oxide (ferric oxide). Iron (II) oxide is an example of a non – stoichio metric compound and the ratio of the elements iron and oxygen can vary, samples are typically iron deficient with a compositions ranging from $Fe_{0.84}O$ to $Fe_{0.95}O$.

Other Names	Ferrous oxide
Molecular Formula	Fe O
Molar Mass	72 g / mol
Appearance	Black crystals
Density	5.745 g / cm^3
Melting Point	1377 °C
Boiling point	3414 °C
Solubility in Water	Insoluble
Solubility	insoluble in alkali , dissolves in acid

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2 . Preparation

Fe O can be prepared by heating iron (II) oxalate in vacuo :

$Fe\ C_2O_4 \rightarrow Fe\ O + CO + CO_2$

The black powder can be made less reactive by heating. The heated sample has a more physical change is quenched to prevent disproportionation . Stoichio metric Fe O can be prepared by heating $Fe_{0.95}$ O with metallic iron at 770 °C and 36 k bar .

3 . Reactions

Fe O is thermo dynamically unstable below 575 °C , dispro - portionating to metal and Fe_3O_4 :

$4\ FeO \rightarrow Fe + Fe_3O_4$

4 . Structure

Iron (II) oxide adopts the cubic, rock salt structure, where iron atoms are octahedrally coordinated by oxygen atoms and the oxygen atoms octahedrally coordinated by iron atoms. The non – stoichio metry occurs because of the ease of oxidation of Fe^{II} to Fe^{III} effectively replacing a small portion of Fe^{II} with two thirds their number of Fe^{III} , which take up tetrahedral positions in the close packed oxide lattice .

Below 200 K there is a minor change to the structure which changes the symmetry to rhombohedral and samples become anti ferromagnetic .

5 . Uses

Iron (II) oxide is used as a pigment. It is FDA - approved for use in cosmetics and it is used in some tattoo inks .

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Wüstite

Contents

1 . Introduction :

Wüstite (Fe O) is a mineral form of iron (II) oxide found with meteorites and native iron. It has a gray color with a greenish tint in reflected light. Wüstite crystallizes in the isometric - hexoctahedral crystal system in opaque to translucent metallic grains. It has a Mohs hardness of 5 to 5.5 and a specific gravity of 5.88. Wüstite is a typical example of a non - stoichio metric compound.

Wüstite was named for Fritz Wüst (1860 - 1938) , In addition to the type locality in Germany, it has been reported from Disko Island, Greenland; the Jharia coalfield, Jharkhand, India and as inclusions in diamonds in a number of kimberlite pipes . It also is reported from deep sea manganese nodules.

Chemical Formula	Fe O
Color	Greyish white to yellow or brown ; colourless in thin section
Crystal habit	Pyramidic , prismatic
Crystal system	Cubic
Mohs Scale hardness	5 - 5.5
Specific gravity	5.88 g / cm³
Density	5.7 g / cm³
Refractive index	1.735 to 2.32 in synthetic crystals
Solubility	Soluble in dilute HCl

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2 - Wüstite Redox Buffer :

Wüstite, in geochemistry, defines a *redox buffer* of oxidation within rocks at which point the rock is so reduced that Fe^{3+} and thus hematite is absent.

As the redox state of a rock is further reduced, magnetite is converted to wüstite . This occurs by conversion of the Fe^{3+} ions in magnetite to Fe^{2+} ions. An example reaction is presented below:

$Fe O .Fe_2 O_3$ + C --> 3FeO + CO
magnetite + graphite/diamond --> wüstite + carbon monoxide

The formula for magnetite is more accurately written as $Fe O . Fe_2 O_3$ than as $Fe_3 O_4$. Magnetite is one part Fe O and one part $Fe_2 O_3$, rather than a solid solution of wüstite and hematite. The magnetite is termed a *redox buffer* because until all Fe^{3+} magnetite is converted to Fe^{2+} the oxide mineral assemblage of iron remains wüstite-magnetite, and furthermore the redox state of the rock remains at the same level of oxygen fugacity. This is similar to buffering in the H^+ / OH^- acid - base system of water.

Once the Fe^{3+} is consumed, then oxygen must be stripped from the system to further reduce it and wüstite is converted to native iron. The oxide mineral equilibrium assemblage of the rock becomes wüstite-magnetite - iron.

In nature, the only natural systems which are chemically reduced enough to even attain a wüstite - magnetite composition are rare, including carbonate - rich skarns , meteorites and perhaps the mantle where reduced carbon is present, exemplified by the presence of diamond and/or graphite.

2 . 1 . Effects upon silicate minerals

The ratio of Fe^{2+} to Fe^{3+} within a rock determines, in part, the silicate mineral assemblage of the rock. Within a rock of a given chemical composition , iron enters minerals based on the bulk chemical composition and the mineral phases which are stable at that

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temperature and pressure. Iron may only enter minerals such as pyroxene and olivine if it is present as Fe^{2+}; Fe^{3+} cannot enter the lattice of fayalite olivine and thus for every two Fe^{3+} ions, one Fe^{2+} is used and one molecule of magnetite is created.

In chemically reduced rocks, magnetite may be absent due to the propensity of iron to enter olivine , and wüstite may only be present if there is an excess of iron above what can be used by silica. Thus, wüstite may only be found in silica – under saturated compositions which are also heavily chemically reduced, satisfying both the need to remove all Fe^{3+} and to maintain iron outside of silicate minerals.

In nature, carbonate rocks, potentially carbonatite , kimberlites , carbonate - bearing melilitic rocks and other rare alkaline rocks may satisfy these criteria. However, wüstite is not reported in most of these rocks in nature, potentially because the redox state necessary to drive magnetite to wüstite is so rare.

3 . Related minerals

Wüstite forms a solid solution with periclase (Mg O) , and Fe substitutes for Mg. Periclase, when hydrated, forms brucite ($Mg(OH)_2$) , a common product of serpentinite metamorphic reactions . Zinc, aluminium and other transition metals may substitute for Fe in wüstite.

Wüstite in dolomite skarns may be related to siderite (Fe – carbonate) , wollastonite, enstatite , diopside and magnesite.

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Iron (III) Oxide

Contents

1 . Introduction :

Iron (III) oxide—also known as **ferric oxide** , **hematite** , **red iron oxide** , **synthetic maghemite** , **colcothar** , or simply rust—is one of the several oxide compounds of iron, and has paramagnetic properties. Its chemical formula is Fe_2O_3.

Other names	Ferric oxide Hematite
Molecular Formula	$Fe_2\ O_3$
Molar mass	160 g / mol
Appearance	Red - brown solid
Odor	Odorless
Density	5.242 g / cm^3 , solid
Melting point	1566 °C (1838 K) *decomp* .
Solubility in water	Insoluble
Crystal structure	rhombohedral

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2 . Different forms

2 . 1 . Alpha phase

A - Fe_2O_3 has the rhombohedral , corundum (α - Al_2O_3) structure and is the most common form. It occurs naturally as the mineral hematite which is mined as the main ore of iron. It is antiferro- magnetic below ~260 K (Morin transition temperature) , and weak ferromagnetic between 260 K and 950 K . It is easy to prepare using both thermal decomposition and precipitation in the liquid phase. Its magnetic properties are dependent on many factors, e.g. pressure, particle size, and magnetic field intensity.

2 . 2 . Beta phase

Cubic face centered, meta stable , at temperatures above 500 °C converts to alpha phase. It can be prepared by reduction of hematite by carbon, pyrolysis of iron (III) chloride solution, or thermal decomposition of iron (III) sulfate.

2 . 3 . Gamma phase

Cubic, meta stable , converts to the alpha phase at high temperatures. Occurs naturally as the mineral maghemite. Ferrimagnetic. Ultrafine particles smaller than 10 nanometers are super paramagnetic . Can be prepared by thermal dehydratation of gamma iron (III) oxide - hydroxide, careful oxidation of iron (II , III) oxide. The ultrafine particles can be prepared by thermal decomposition of iron (III) oxalate.

2 . 4 . Epsilon phase

Rhombic, shows properties intermediate between alpha and gamma. So far has not been prepared in pure form; it is always mixed with the alpha phase or gamma phases. Material with a high proportion of epsilon phase can be prepared by thermal transformation of the gamma phase. The epsilon phase is metastable, transforming to the alpha phase at between 500 and 750 °C. Can also

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be prepared by oxidation of iron in an electric arc or by sol-gel precipitation from iron (III) nitrate.

3 . Uses

3 . 1 . Magnetic storage

The magnetic iron (III) oxides are often used in magnetic storage, for example in the magnetic layer of floppy disks. These consist of a thin sheet of PET film, coated with iron (III) oxide. The particles can be magnetized to represent binary data. MICR (Magnetic Ink Character Recognition) also uses iron (III) oxide compounds, suspended in an ink which can be read by special scanning hardware.

The majority of recorded information on earth (such as text and photographs) is stored in the form of magnetization patterns on a thin layer of iron (III) oxide. This is probably because the cost per bit of iron-based magnetic media is currently far less than the cost per bit of any known alternative, such as optical discs, paper books, or microfilm. More text and photos are stored on magnetic media than all the paper books and paper photographs in the world .

3 . 2 . Polishing

A very fine powder of ferric oxide is known as **jeweller ' s rouge** , **red rouge** , or simply **rouge** . It is used to put the final polish on metallic jewellery and lenses, and historically as a cosmetic.

Rouge cuts more slowly than some modern polishes, such as cerium (IV) oxide, but is still used in optics fabrication and by jewelers for the superior finish it can produce. When polishing gold, the rouge slightly stains the gold, which contributes to the appearance of the finished piece. Rouge is sold as a powder, paste, laced on polishing cloths, or solid bar (with a wax or grease binder) . Other polishing compounds are also often called " rouge ", even when they do not contain iron oxide. Jewelers remove the residual rouge on jewelry by use of ultrasonic cleaning.

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3 . 3 . Chemical

Iron (III) oxide is used in the production of pure iron in a blast furnace. Iron (III) oxide is also used in an extremely exothermic reaction called a thermite reaction .

$2\ Al + Fe_2\ O_3 \rightarrow 2\ Fe + Al_2\ O_3$

3 . 4 . Pigment

Iron (III) oxide is also used as a pigment, under names **Pigment Brown 6**, **Pigment Brown 7** , and **Pigment Red 101** . Some of them, e.g. Pigment Red 101 and Pigment Brown 6, are Food and Drug Administration (FDA) -approved for use in cosmetics.

3 . 5 . Biomedical

Nano particles of iron (III) oxide are bio compatible, non - toxic, are chemically active on their surface, and some are magnetic . They find wide use in biomedical applications. Can be used as contrast agents in magnetic resonance imaging, in labeling of cancerous tissues, magnetically controlled transport of pharmaceuticals, localized thermotherapy (where the tissue is labeled by iron oxide nano particles , then heated by application of AC field to particles), and preparation of ferro fluids .

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Hematite

Contents

1 . Introduction :

Hematite, also spelled as **hæmatite**, is the mineral form of Iron (III) oxide (Fe_2O_3) , one of several iron oxides. Hematite crystallizes in the rhombohedral system, and it has the same crystal structure as ilmenite and corundum. Hematite and ilmenite form a complete solid solution at temperatures above 950°C.

Hematite is a mineral, colored black to steel or silver-gray, brown to reddish brown, or red. It is mined as the main ore of iron. Varieties include *kidney ore*, *martite* (pseudomorphs after magnetite) , *iron rose* and *specularite* (specular hematite) . While the forms of hematite vary, they all have a rust - red streak. Hematite is harder than pure iron, but much more brittle. Maghemite is a hematite- and magnetite - related oxide mineral.

Huge deposits of hematite are found in banded iron formations. Grey hematite is typically found in places where there has been standing water or mineral hot springs, such as those in Yellowstone National Park in the United States. The mineral can precipitate out of water and collect in layers at the bottom of a lake, spring, or other standing water. Hematite can also occur without water, however, usually as the result of volcanic activity.

Clay - sized hematite crystals can also occur as a secondary mineral formed by weathering processes in soil, and along with other iron oxides or oxyhydroxides such as goethite, is responsible for the

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red color of many tropical, ancient, or otherwise highly weathered soils.

Good specimens of hematite come from England , Mexico, Brazil , Australia , United States and Canada.

Chemical Formula	iron (III) oxide , Fe_2O_3 , α - $Fe_2 O_3$
Color	Metallic gray to earthy red tones
Crystal habit	Tabular to thick crystals
Crystal system	Hexagonal (rhombohedral)
Mohs Scale hardness	5.5 - 6.5
Luster	Metallic to splendent
Streak	Bright red to dark red
Specific gravity	4.9 - 5.3
Refractive index	Opaque

2 . Etymology and history

The name hematite is derived from the Greek word for blood αἷμα *aima* because hematite can be red, as in rouge, a powdered form of hematite . The color of hematite lends it well in use as a pigment.

Ochre is a clay that is colored by varying amounts of hematite, varying between 20 % and 70 % . Red ochre contains unhydrated hematite , whereas yellow ochre contains hydrated hematite ($Fe_2O_3 \bullet H_2O$) . The principal use of ochre is for tinting with a permanent color .

The red chalk winning of this mineral was one of the earliest in history of mankind. The powdery mineral was first used 164,000 years ago by the Pinnacle - Point man obviously for social differentiation . Hematite residues are also found in old graveyards from 80,000 years ago. Near Rydno in Poland and Lovas in Hungary,

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palaeolitic red chalk mines have been found that are from 5000 BC, belonging to the Linear Pottery culture at the Upper Rhine.

Rich deposits of hematite have been found on the island of Elba that have been mined till the time of the Etruscans.

2 . 1 . Ancient Egyptian booby trap :

In 2001, Egyptian government archaeologist Zahi Hawass was the first to enter a previously undisturbed tomb, believed to be that of an ancient regional mayor, in the Bahariya Oasis below the town of Bawiti. Upon entering the burial chamber, Hawass discovered a booby trap consisting of 8 inches of finely powdered hematite dust covering the floor and sarcophagus . When disturbed by a tomb robber, the sharp, metallic dust was intended to become airborne and irritate the skin, eyes and mucous membranes, eventually causing lethal siderosis if exposed for long enough. The archaeological team was forced to retreat and don full body suits and respirators in order to confirm the identity of the mummy. Hawass cites the ancient Egyptians' experience with powdered hematite as a paint pigment as proof that they were aware of its irritating properties .

2 . 2 . Jewelry

Hematite's popularity in jewelry was at its highest in Europe during the Victorian era, and has since seen a strong resurgence in North America, especially in the western United States. Due to its delicate nature, the mineral is found only in precious jewelry. Extreme care should be taken in handling hematite items due to the material's susceptibility to irreversible damage.

It is also used in art such as intaglios where it is used for making hollow portraits.

3 . Magnetism

Hematite is an anti ferromagnetic material below the Morin transition at 250 K, and a canted anti ferromagnetic or weakly

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ferromagnetic above the Morin transition and below its Néel temperature at 948K, above which it is paramagnetic.

The magnetic structure of a-hematite was the subject of considerable discussion and debate in the 1950s because it appeared to be ferromagnetic with a Curie temperature of around 1000 K, but with an extremely tiny moment (0.002 μ_B) . Adding to the surprise was a transition with a decrease in temperature at around 260 K to a phase with no net magnetic moment. It was shown that the system is essentially anti ferromagnetic but that the low symmetry of the cation sites allows spin–orbit coupling to cause canting of the moments when they are in the plane perpendicular to the c axis. The disappearance of the moment with a decrease in temperature at 260 K is caused by a change in the anisotropy which causes the moments to align along the c axis. In this configuration, spin canting does not reduce the energy .

Hematite is part of a complex solid solution oxyhydroxide system having various degrees of water, hydroxyl group, and vacancy substitutions that affect the mineral's magnetic and crystal chemical properties . Two other end-members are referred to as proto hematite and hydro hematite.

3 . 1 . Iron from mine tailings

Hematite is present in the waste tailings of iron mines. A recently developed process, magnetation , uses huge magnets to glean waste hematite from old mine tailings in Minnesota's vast Mesabi Range iron district .

4 . Hematite on Mars

Image mosaic from the Mars Exploration Rover Microscopic Imager shows Hematite spherules partly embedded in rock at the Opportunity landing site .

The spectral signature of hematite was seen on the planet Mars by the infrared spectrometer on the NASA Mars Global Surveyor ("MGS") and 2001 Mars Odyssey spacecraft in orbit around Mars.[11]

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The mineral was seen in abundance at two sites [12] on the planet, the Terra Meridiani site, near the Martian equator at 0° longitude, and the second site Aram Chaos near the Valles Marineris. Several other sites also showed hematite, e.g., Aureum Chaos . Because terrestrial hematite is typically a mineral formed in aqueous environments, or by aqueous alteration, this detection was scientifically interesting enough that the second of the two Mars Exploration Rovers was targeted to a site in the Terra Meridiani region designated Meridiani Planum. In-situ investigations by the Opportunity rover showed a significant amount of hematite, much of it in the form of small spherules that were informally tagged by the science team "blueberries". Analysis indicates that these spherules are apparently concretions formed from a water solution.

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Iron (II , III) Oxide

Contents

1 . Introduction :

Iron (II , III) oxide is the chemical compound with formula Fe_3O_4. It is one of a number of iron oxides. It is found in nature as the mineral magnetite. It contains both Fe^{2+} and Fe^{3+} ions and is sometimes formulated as $FeO . Fe_2O_3$. It is encountered in the laboratory as a black powder. It exhibits permanent magnetism and is ferri magnetic , but is sometimes incorrectly described as ferro magnetic . Its most extensive use is as a black pigment which is synthesized rather than being extracted from the naturally occurring mineral as the particle size and shape can be varied by the method of production .

Other Names	ferrous ferric oxide, ferroso ferric oxide, iron (II , III) oxide, magnetite , black iron oxide, lodestone, rust
Molecular Formula	$Fe_3 O_4$ $Fe O . Fe_2 O_3$
Molar Mass	232 g / mol
Appearance	Black powder
Density	5.17 g / cm^3

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Melting Point	1597 °C
Refractive index (n_D)	2.42

2 . Preparation

Pigment quality Fe_3O_4 , so called synthetic magnetite, can be prepared using processes that utilise industrial wastes, scrap iron or solutions containing iron salts (e.g. those produced as by -products in industrial processes such as the acid treatment (pickling of steel) :

- Oxidation of Fe metal in the Laux process where nitro benzene is reacted with iron metal using $FeCl_2$ as a catalyst to produce aniline :

$$C_6H_5\,NO_2 + 9\,Fe + 2H_2O \rightarrow C_6H_5\,NH_2 + Fe_3\,O_4$$

- Oxidation of Fe^{II} compounds, e.g. the precipitation of iron (II) salts as hydroxides followed by oxidation by aeration where careful control of the pH determines the oxide produced .

Reduction of Fe_2O_3 with hydrogen :

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$$

Reduction of Fe_2O_3 with CO :

$$3Fe_2\,O_3 + CO \rightarrow 2Fe_3\,O_4 + CO_2$$

Production of nano-particles can be performed chemically by taking for example mixtures of Fe^{II} and Fe^{III} salts and mixing them with alkali to precipitate colloidal $Fe_3\,O_4$. The reaction conditions are critical to the process and determine the particle size .

3 . Reactions

Reduction of magnetite ore by CO in a blast furnace is used to produce iron as part of steel production process :

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$$

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Controlled oxidation of Fe_3O_4 is used to produce brown pigment quality γ - Fe_2O_3 (maghemite) :

$$2Fe_3O_4 + \frac{1}{2} O_2 \rightarrow 3\ (\gamma - Fe_2O_3)$$

More vigorous calcining , (roasting in air) , gives red pigment quality α - Fe_2O_3 (hematite) :

$$2Fe_3O_4 + \frac{1}{2} O_2 \rightarrow 3\ (\alpha - Fe_2O_3)$$

4 . Structure

Fe_3O_4 has a cubic inverse spinel structure which consists of a cubic close packed array of oxide ions where all of the Fe^{2+} ions occupy half of the octahedral sites and the Fe^{3+} are split evenly across the remaining octahedral sites and the tetrahedral sites.

Both FeO and γ - Fe_2O_3 have a similar cubic close packed array of oxide ions and this accounts for the ready interchangeability between the three compounds on oxidation and reduction as these reactions entail a relatively small change to the overall structure . Fe_3O_4 samples can be non-stoichiometric .

The ferri magnetism of Fe_3O_4 arises because the electron spins of the Fe^{II} and Fe^{III} ions in the octahedral sites are coupled and the spins of the Fe^{III} ions in the tetrahedral sites are coupled but anti-parallel to the former. The net effect is that the magnetic contributions of both sets are not balanced and there is a permanent magnetism .

5 . Properties

Fe_3O_4 is ferri magnetic with a Curie temperature of 858 K. There is a phase transition at 120K, the so - called **Verwey transition** where there is a discontinuity in the structure, conductivity and magnetic properties . This effect has been extensively investi -gated and whilst various explanations have been proposed, it does not appear to be fully understood .

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Fe_3O_4 is an electrical conductor with a conductivity is significantly higher (X 10^6) than $Fe_2 O_3$, and this is ascribed to electron exchange between the Fe ^{II} and Fe ^{III} centres .

6 . Uses

Fe_3O_4 is used as a black pigment and is known as **C . I pigment black 11** .

Fe_3O_4 is used as a catalyst in the Haber process and in the water gas shift reaction . The latter uses an HTS (high temperature shift catalyst) of iron oxide stabilised by chromium oxide . This iron-chrome catalyst is reduced at reactor start up to generate Fe_3O_4 from α - $Fe_2 O_3$ and $Cr_2 O_3$ to $Cr O_3$.

Nano particles of $Fe_3 O_4$ are used as contrast agents in MRI scanning .

Bluing is a passivation process that produces a layer of Fe_3O_4 on the surface of steel to protect it from rust .

7 ./ Biological Occurrence

Magnetite has been found as nano-crystals in magnetotactic bacteria (42 - 45 µ m) and in homing pigeon beak tissue .

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Magnetite

Contents

1 . Introduction ;

Magnetite is a ferri magnetic mineral with chemical formula **Fe_3O_4**, one of several iron oxides and a member of the spinal group. The chemical IUPAC name is iron (II , III) oxide and the common chemical name **ferrous - ferric oxide**. The formula for magnetite may also be written as $FeO \cdot Fe_2O_3$, which is one part wüstite (Fe O) and one part hematite (Fe_2O_3) . This refers to the different oxidation states of the iron in one structure, not a solid solution. The Curie temperature of magnetite is 858 K.

Magnetite is the most magnetic of all the naturally occurring minerals on Earth. Naturally magnetized pieces of magnetite, called lodestone, will attract small pieces of iron, and this was how ancient man first discovered the property of magnetism. Lodestone was used as an early form of magnetic compass. Magnetite typically carries the dominant magnetic signature in rocks, and so it has been a critical tool in paleo magnetism , a science important in discovering and understanding plate tectonics and as historic data for magneto hydro dynamics and other scientific fields. The relationships between magnetite and other iron - rich oxide minerals such as ilmenite , hematite, and ulvospinel have been much studied, as the complicated reactions between these minerals and oxygen influence how and when magnetite preserves records of the Earth's magnetic field.

Magnetite has been very important in understanding the conditions under which rocks form and evolve. Magnetite reacts with oxygen to produce hematite, and the mineral pair forms a buffer that

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can control oxygen fugacity. Commonly igneous rocks contain grains of two solid solutions, one between magnetite and ulvospinel and the other between ilmenite and hematite. Compositions of the mineral pairs are used to calculate how oxidizing was the magma (i.e., the oxygen fugacity of the magma): a range of oxidizing conditions are found in magmas and the oxidation state helps to determine how the magmas might evolve by fractional crystallization.

Small grains of magnetite occur in almost all igneous rocks and metamorphic rocks. Magnetite also occurs in many sedimentary rocks, including banded iron formations. In many igneous rocks, magnetite-rich and ilmenite - rich grains occur that precipitated together from magma. Magnetite also is produced from peridotites and dunites by serpentinization .

Magnetite is a valuable source of iron ore . It dissolves slowly in hydrochloric acid.

Chemical Formula	Iron (II , III) oxide , $Fe_3 O_4$
Color	Black , grayish
Crystal habit	Octahedral , fine granular to massive
Crystal system	Isometric
Mohs Scale hardness	5.5 – 6.5
Luster	Metallic
Streak	Black
Specific gravity	5.17 – 5.18
Refractive index	Opaque

2 . Distribution of deposits

Magnetite is sometimes found in large quantities in beach sand. Such black sands (mineral sands or iron sands) are found in various

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places such as California and the west coast of New Zealand. The magnetite is carried to the beach via rivers from erosion and is concentrated via wave action and currents.

Huge deposits have been found in banded iron formations. These sedimentary rocks have been used to infer changes in the oxygen content of the atmosphere of the Earth.

Large deposits of magnetite are also found in Chile , Sweden , Midwest , Australia , United States , Norway , German y, Italy , Switzerland , South Africa, India , Mexico , Oregon .

Recently, in June 2005 discovered a vast deposit of magnetite - bearing sand dunes in Peru . The dune field covers 250 square kilometers , with the highest dune at over 2,000 meters above the desert floor. The sand contains 10 % magnetite .

3 . Biological occurrences

Crystals of magnetite have been found in some bacteria (e.g., Magneto spirillum magneto tacticum) and in the brains of bees, of termites, fish, some birds (e.g., the pigeon) and humans . These crystals are thought to be involved in magneto reception , the ability to sense the polarity or the inclination of the Earth's magnetic field, and to be involved in navigation. Also, chitons have teeth made of magnetite on their radula making them unique among animals. This means they have an exceptionally abrasive tongue with which to scrape food from rocks .

4 . Preparation as a ferro fluid

Magnetite can be prepared in the laboratory as a ferrofluid in the Massart method by mixing iron (II) chloride and iron (III) chloride in the presence of sodium hydroxide .

Magnetite also can be prepared by chemical co - precipitation, which consist in a mixture of a solution 0.1 M of $Fe Cl_3 . 6H_2O$ and $FeCl_2 . 4H_2O$ with mechanic agitation of about 2000 rpm. The molar ratio of $Fe Cl_3 : Fe Cl_2$ can be 2 : 1 ; heating this solution at 70 °C,

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and immediately the rpm is elevated to 7500 rpm and adding quickly a solution of NH_4 OH (10 % in v.), immediately a dark precipitate will be formed, which consist of nano particles of magnetite.

5 . Application as a sorbent

Magnetite powder efficiently removes As (III) and As (V) from water, and the efficiency of the removal increases ~200 times when the magnetite particle size decreases from 300 to 12 nm . Arsenic (As) - contaminated drinking water is a major problem around the world, which can be solved using magnetite as a sorbent.

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Iron (III) phosphate

A sample of $(FePO_4)_2 \cdot 5H_2O$

Iron(III) phosphate, also **ferric ortho phosphate**, or **ferric phosphate**, $FePO_4$, is a phosphate of iron. It is one of the few molluscicides approved for use in the practice of organic farming.

Unlike the older metaldehyde , it is non - toxic to pets and wildlife.

It is also used rarely as an iron nutritional supplement and to reduce the risk of both haemorrhages and nosebleeds. This preparation is called *Ferrum phosphoricum*.

The substance is not allowed to be included in food inside the European Union. The substance was with drawn from the list of allowed substances in the directive 2002/46/EC in 2007.

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Iron Sulfide

1 – Introduction :

Iron sulfide or **Iron sulphide** may refer to a chemical compound of iron and sulfur with a wide range of stoechio metric formulae and different crystalline structures.

2 - Natural minerals :

By increasing order of stability:

- Iron(II) sulfide, FeS, the less stable amorphous form;
- Troilite, FeS, the end member of pyrrhotite;
- Greigite, Fe_3S_4, analog to magnetite, Fe_3O_4;
- Pyrrhotite, $Fe_{1-x}S$ (where x = 0 to 0.2), or Fe_7S_8;
- Mackinawite, $Fe_{1+x}S$ (where x = 0 to 0.1);
- Marcasite, or iron(II) disulfide, FeS_2 (orthorhombic);
- Pyrite, or iron(II) disulfide, FeS_2 (cubic), the more stable end member.

3 - Artificial product :

- Iron (III) sulfide, Fe_2S_3, a quite unstable artificial product synthesized at –20 °C and not identified in nature.

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Iron (II) sulfide

Contents

1 – Introduction :

Iron (II) sulfide or **ferrous sulfide** (Br.E. **sulphide**) is a chemical compound with the formula Fe S . In practice, iron sulfides are often non - stoichio metric . Powdered iron sulfide is pyrophoric (i.e. will ignite spontaneously in air).

Other names :Iron sulfide , ferrous sulfide , black iron sulfide	
Molecular Formula	Fe S
Molar Mass	88 g / mol
Appearance	black solid , some times in lumps or powder
Density	4.84 g / cm^3

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Melting point	1194 °C
Solubility in water	negligible (insoluble)
Solubility	reacts in acid
Hazards	
EU Index	Not listed
Main hazards	can be pyrophoric
Auto ignition temperature	variable

2 - Forms of iron sulfide :

"Iron sulfide" exists in several distinct forms, which differ in the ratio of sulfur to iron and properties :

- Pyrrhotite, $Fe_{1-x}S$, a mineral, which displays ferrimagnetism and crystallizes in monoclinic system. Iron metal shows ferromagnetism; iron sulfides do not.
- Troilite, FeS, a stoichio metric compound that adopts hexagonal symmetry.
- Mackinawite , $Fe_{1+x}S$ the least stable form of iron sulfide; mackinawite has a layered structure.
- Pyrite and marcasite, which are diamagnetic minerals, have the formula FeS_2.
- Greigite (Fe_3S_4) a ferromagnetic species akin to magnetite (Fe_3O_4).

3 - Chemical reactions :

Iron sulfide reacts with hydrochloric acid , releasing the pungent and very toxic hydrogen sulfide

$$\mathrm{Fe\,S} + 2\,\mathrm{H\,Cl} \rightarrow \mathrm{Fe\,Cl_2} + \mathrm{H_2S}$$

Fe S can be obtained by the heating of iron and sulfur :

$$\mathrm{Fe} + \mathrm{S} \rightarrow \mathrm{Fe\,S}$$

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4 - Biology and biochemistry :

Sludge from a pond ; the black color is due to metal sulfides

As organic matter decays under low - oxygen or hypoxic conditions such as in swamps or dead zones of lakes and oceans, sulfate - reducing bacteria will use the sulfates present in the water to oxidize the organic matter, producing hydrogen sulfide as waste. Some of the hydrogen sulfide will react with metal ions in the water to produce metal sulfides, which are not water soluble. These metal sulfides, such as iron (II) sulfide, are often black or brown, leading to the color of sludge.

Pyrrotite is a waste product of the *Desulfovibrio* bacteria, a sulfate reducing bacteria.

When eggs are cooked for a long time, the yolk's surface may turn green. This is due to iron (II) sulfide which forms as iron from the yolk meets hydrogen sulfide released from the egg white by the heat . This reaction occurs more rapidly in older eggs as the whites are more alkaline .

The presence of ferrous sulfide as a visible black precipitate in the growth medium peptone iron agar can be used to distinguish between microorganisms that produce the cysteine metabolizing enzyme cysteine desulfhydrase and those that do not. Peptone iron agar contains the amino acid cysteine and a chemical indicator, ferric citrate. The degradation of cysteine releases hydrogen sulfide gas that reacts with the ferric citrate to produce ferrous sulfide.

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Iron (II) Sulfate

Contents

1 . Introduction :

Iron (II) sulfate (Iron (II) sulphate) or **ferrous sulfate** (ferrous sulphate) is the chemical compound with the formula ($Fe\,SO_4$) , known since ancient times as **copperas**. It is most commonly encountered as the blue-green hepta hydrate.

Other Names	Ferrous sulphate , Green vitriol , Iron vitriol , Copperas , Melanterite
Molecular Formula	$Fe\,SO_4$
Molar Mass	152 g /mol (anhydrous) 170 g / mol (mono hydrate) 278 g / mol (hepta hydrate)
Appearance	Blue / green or white crystals
Density	2.84 g / cm^3 (anhydrous) 1.898 g / cm^3 (hepta hydrate)
Melting Point	400 °C (decomp)
Solubility in Water	25.6 g / 100mL (anhydrous)
EU classification	Harmful (**Xn**) Irritant (**Xi**)

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2 . Hydrates

Iron (II) sulfate can be found in various states of hydration , and several of these forms exist in nature.

- $Fe SO_4 \cdot H_2O$ (mineral: szomolnokite)
- $Fe SO_4 \cdot 4H_2O$ (mineral : rozenite , white)
- $Fe SO_4 \cdot 5H_2O$ (mineral : siderotil)
- $Fe SO_4 \cdot 6H_2O$ (mineral : ferrohexahydrite)
- $Fe SO_4 \cdot 7H_2O$ (mineral : melanterite , blue)

At 90°C, the hepta hydrate, also called green vitriol or copperas, loses water to form the colorless mono hydrate, In its anhydrous, crystalline state , its standard enthalpy of formation is $\Delta_f H°_{solid}$ = - 928.4 $kJ.mol^{-1}$ and its standard molar entropy is $S°_{solid}$ = 107.5 $J.K^{-1}.mol^{-1}$. All mentioned mineral forms are connected with oxidation zones of Fe-bearing ore beds (pyrite, marcasite, chalcopyrite etc) . and related environments (like coal fire sites) . Many undergo rapid dehydratation and sometimes oxidation.

3 . Production and reactions

In the finishing of steel prior to plating or coating , the steel sheet or rod is passed through pickling baths of sulfuric acid . This treatment produces large quantities of iron (II) sulfate as a by - product .

$$Fe + H_2 SO_4 \rightarrow Fe SO_4 + H_2$$

Another source of large amounts results from the production of titanium dioxide from ilmenite via the sulfate process. Ferrous sulfate is also prepared commercially by oxidation of pyrite:

$$2 Fe S_2 + 7 O_2 + 2 H_2O \rightarrow 2 Fe SO_4 + 2 H_2 SO_4$$

3 . 1 . Reactions

On heating, iron (II) sulfate first loses its water of crystallization and the original green crystals are converted into a dirty - yellow anhydrous solid . When further heated, the anhydrous material

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releases sulfur dioxide and white fumes of sulfur trioxide, leaving a reddish - brown iron (III) oxide. Decomposition of iron (II) sulfate begins at about 480 °C.

$$2\ Fe\ SO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

Like all iron (II) salts , iron (II) sulfate is reducing agent. For example, it reduces nitric acid to nitrogen oxide and chlorine to chloride:

$$6\ Fe^{2+} + 6\ H^{+} + 2\ HNO_3 \rightarrow 6\ Fe^{3+} + 4\ H_2O + 2\ NO$$
$$2\ Fe^{2+} + Cl_2 \rightarrow 2\ Fe^{3+} + 2\ Cl^{-}$$

4 . Uses

Industrially, ferrous sulfate is mainly used as a precursor to other iron compounds. It is a reducing agent , mostly for the reduction of chromate in cement.

4 . 1 . Nutritional supplement

Together with other iron compounds, ferrous sulfate is used to fortify foods and to treat iron - deficiency anemia. Copperas was given indiscriminately by untrained persons to slaves in the 18th and 19th centuries for various ailments .

Constipation is frequent and uncomfortable side effects associated with the administration of oral iron supplements. Stool softeners often are prescribed to prevent constipation.

4 . 2 . Colorant

Ferrous sulfate was used in the manufacture of inks , most notably iron gall ink , which was used from the middle ages until the end of the eighteenth century . It also finds use in wool dyeing as a mordant.

Two different methods for the direct application of indigo dye were developed in England in the eighteenth century and remained in use well into the nineteenth century . One of these, known as *china*

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blue, involved iron (II) sulfate. After printing an insoluble form of indigo onto the fabric, the indigo was reduced to *leuco* - indigo in a sequence of baths of ferrous sulfate (with reoxidation to indigo in air between immersions). The china blue process could make sharp designs, but it could not produce the dark hues of other methods .

Ferrous sulfate can also be used to stain concrete and some limes tones and sands tones a yellowish rust color .

Wood workers use ferrous sulfate solutions to color maple wood a silvery hue .

4 . 3 . Other uses

In horticulture it is used for treating iron chlorosis . It is also used as a lawn conditioner and moss killer.

In the second half of the 19th century, ferrous sulfate was also used as a photographic developer for Collodion process images.

Ferrous sulfate is sometimes added to the cooling water flowing through the brass tubes of a turbine condenser . It forms a corrosion - resistant, protective coating on the inside of the tube.

It has been applied for the purification of water by flocculation and for phosphate removal in municipal and industrial sewage treatment plants to prevent eutrophication of surface water bodies .

It is used as a traditional method of treating wood panel on houses, either alone dissolved in water or as a component of water-based paint .

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Iron (III) Sulfate

1 . Introduction :

Iron (III) sulfate, is the compound of iron and sulfate . The compound is different from the more common iron (II) sulfate in that the ratio of sulfate ions to iron ions is larger.

Usually yellow, it is a rhombic crystalline salt and soluble in water at room temperature. It is used in dyeing as a mordant, and as a coagulant for industrial wastes. It is also used in pigments, and in pickling baths for aluminum and steel . Medically it is used as an astringent and styptic .

Ferric sulfate is produced on a large scale by reacting sulfuric acid with a hot solution of ferrous sulfate, using an oxidizing agent (such as nitric acid or hydrogen peroxiden) .

In sewage plants it is used to assist in settling minute particles of untreated sewage in tank water .

Other Names	Ferric sulfate , Sulfuric acid iron (3+) salt (3 : 2)
Molecular Formula	$Fe_2 (SO_4)_3$
Molar Mass	400 g /mol (anhydrous) 490 g / mol (penta hydrate)
Appearance	white crystals
Density	3.097 g / cm^3 (anhydrous) 1.898 g / cm^3 (penta hydrate)
Melting Point	480 °C (anhydrous) 175 °C (nonahydrate)
Solubility in Water	Soluble
LD_{50}	500 mg / kg (oral , rat)

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2 . Natural occurrences :

Mikasaite , a mixed iron - aluminum sulfate of chemical formula $(Fe^{3+}, Al^{3+})_2 (SO_4)_3$ is the name of mineralogical form of iron (III) sulfate. This anhydrous form occurs very rarely and is connected with coal fires. The hydrates are more common, with coquimbite (nona hydrate) as probably the most often met among them. Para coquimbite is the other, rarely met natural nona hydrate. Kornelite (hepta hydrate) and quenstedtite (deca hydrate) are rarely found. Lausenite (hexa - or penta hydrate) is a doubtful species. All the mentioned natural hydrates are unstable compounds connected with Fe-bearing primary minerals (mainly pyrite and marcasite) oxidation in ore beds. In the solutions of the ore beds oxidation zones the iron (III) sulfate is also an important oxidative agent.

3 . Mars exploration

Ferric sulfate and jarosite have been detected by the two martian rovers Spirit and Opportunity. These substances are indicative of strongly oxidizing conditions prevailing at the surface of Mars. In May 2009, the Spirit rover became stuck when it drove on a soft spot of ferric sulfate hidden under a veneer of normal-looking soil. [6] For the rover mobility, iron sulfate is an harmful stuff with very little cohesion, so that it is very tough for the rover wheels to get a grip on it. The rover had sunk so deep that part of its belly could be resting on top of the dust, which makes it very hard for its wheels to gain traction. If JPL team fails to recover the mobility of Spirit, it could signify the end of the journey for the rover.