**Hydrogen and its applications in the steel industry**



Hydrogen and its application in the production of steel industry

Hydrogen is a chemical element， ranked first in the periodic table， with the element symbol "H". The element hydrogen has an atomic number of 1 and an atomic weight of 1.008. It is the smallest atom in the universe and the simplest element in nature. Its molecule consists of two hydrogen atoms. It is the lightest gas， with a density of about 1/14th that of air. It has three isotopes， namely (i) protium， (ii) deuterium， and (iii) tritium. Pure hydrogen gas is odorless， colorless， and tasteless.

Hydrogen has the lowest atomic weight of all substances and therefore has a very low density as a gas and as a liquid. The vapor density of hydrogen is 0.08376 kg/m3 at 20 degrees Celsius and 1 atmosphere pressure. Gaseous hydrogen has a specific gravity of 0.0696， making it about 7% as dense as air. At normal boiling point and 1 atm， the density of liquid hydrogen is 70.8 kg/m3. The specific gravity of liquid hydrogen is 0.0708， therefore， its density is about 7% of that of water.

Hydrogen is a liquid below its boiling point of -253 degrees Celsius and a solid below its melting point of -259 degrees Celsius at atmospheric pressure. It is non-toxic， but can be used as a simple asphyxiant by replacing oxygen in the air. When hydrogen is stored as a high pressure gas at 250 kg/m3 and at atmospheric temperature， it has an expansion ratio of 1:240 with respect to atmospheric pressure.

Hydrogen has smaller molecules than all other gases， and it can diffuse through many materials that are considered airtight or impermeable to other gases. This property makes hydrogen more difficult to control than other gases. Because liquid hydrogen has an extremely low boiling point， leaks of liquid hydrogen can evaporate very quickly. Hydrogen leaks are dangerous because they pose a fire hazard where they mix with air. Hydrogen leaks pose a potential fire hazard.

Hydrogen is chemically stable at room temperature， which is mainly determined by the strong covalent bonds between the hydrogen atoms of which it is composed. The hydrogen molecule is a stable molecule with a high bond energy (104 kcal/mol)， but it reacts with many different kinds of elements， forming compounds with them.

Hydrogen is reducing in nature. It reacts easily with oxygen in most mixing ratios (combustion) and forms water. This also makes it possible to use hydrogen as an energy medium.

Hydrogen has a poor energy density (because of its low density)， although it has the highest energy to weight ratio of any fuel (because it is light). At 1 atmosphere and 15 degrees Celsius， the energy density (low heating value， LHV) of hydrogen is 2400 kcal/m3 and that of liquids is 2030 Mccal/m3.

As a flammable gas， hydrogen will mix with oxygen whenever air is allowed to enter the hydrogen container or hydrogen leaks from any container into the air. The ignition source takes the form of a spark， flame or high heat. The flash point of hydrogen is below -253 degrees Celsius.

Hydrogen is explosive in a wide range of concentrations in air (4% to 75%) and in a wide range of concentrations at standard atmospheric temperature (15% to 59%). Hydrogen can also explode in mixtures of chlorine (from 5% to 95%). The flammability limit increases with increasing temperature. Therefore， even small amounts of hydrogen leaks can burn or explode. Leaking hydrogen gas can concentrate in a closed environment， thus increasing the risk of combustion and explosion. The combustion of hydrogen is described by the equation H2 + O2 = 2H2O + 136 kcal.

Hydrogen gas has a relatively high auto-ignition temperature of 585 degrees Celsius. This makes it difficult to ignite a hydrogen/air mixture with heat alone in the absence of other ignition sources. A pure hydrogen-oxygen flame emits ultraviolet light， which is not visible to the naked eye. Therefore， detecting a burning hydrogen leak is dangerous and requires a flame detector. Hydrogen has a very high research octane rating (+130) and therefore does not burst even when burned in very lean conditions.

Although hydrogen is stable， it does form compounds with most elements. When involved in a reaction， hydrogen can have a partial positive charge when reacting with more electronegative elements such as halogens or oxygen， but it can have a partial negative charge when reacting with more electronegative elements such as alkali metals. When hydrogen is combined with fluorine， oxygen， or nitrogen， it can participate in a moderately strong non-covalent (intermolecular) bond called hydrogen bonding， which is essential for the stability of many biomolecules. Compounds that have hydrogen bonds with metals and metalloids are called hydrides. The oxidation of hydrogen removes its electrons， producing hydrogen ions with a single positive charge. Usually， hydrogen ions in aqueous solutions are referred to as hydrogen ions. This species is essential in acid-base chemistry.

Hydrogen production

Although hydrogen is the preferred reductant fuel from an environmental and reduction kinetic point of view， it is currently expensive. However， there is a general expectation to develop a hydrogen economy that will lead to cheap hydrogen. A great deal of effort and many resources are being devoted to this goal. Hydrogen is currently produced using either reforming of methane or electrolysis of water， both of which are energy intensive processes. Currently， the dominant technology for direct production is steam reforming of hydrocarbons.

Large quantities of hydrogen are typically produced by steam reforming of methane or natural gas. The production of hydrogen from natural gas is currently the cheapest source of hydrogen. The process involves heating the natural gas to between 700 degrees Celsius and 1100 degrees Celsius in the presence of steam and a nickel catalyst. The resulting endothermic reaction breaks down the methane molecules and forms carbon monoxide and hydrogen gas. The carbon monoxide gas can then be passed with the steam through iron oxide or other oxides to undergo a water-gas transfer reaction to obtain more hydrogen.

In this process， high temperature (700 degrees Celsius to 1100 degrees Celsius) steam reacts endothermically with methane to produce syngas. The reaction is described by the equation CH4 + H2O = CO + 3H2. In the second stage， additional hydrogen is produced through a low-temperature， exothermic， water-gas transfer reaction that takes place at about 360 degrees Celsius. Essentially， oxygen atoms are stripped from the additional water (vapor) to oxidize carbon monoxide to carbon dioxide. This oxidation also provides the energy to sustain the reaction. The additional heat required to drive the process is typically provided by burning a fraction of the methane.

However， there is a large body of research work devoted to the use of solar energy to produce hydrogen， for example through the use of solar cells to provide the electrons needed to electrolyze water， or through photocatalytic water separation， in which the action of sunlight on a semiconductor immersed in water is used to produce hydrogen directly.

Hydrogen as a reducing agent for iron ore

In the production of iron， hydrogen combined with carbon monoxide is being used to reduce iron ore by injecting hydrogen-rich gases such as natural gas and coke oven gas， or materials such as waste plastics， into the blast furnace， or in the production of direct iron reduction from natural gas. The basic chemical reaction for the reduction of iron ore with hydrogen to produce pure iron and water is as follows.

Fe2O3 + 3H2 = 2Fe + 3H2O

Fe3O4 + H2 = 3FeO + H2O

FeO + H2 = Fe + H2O

The hydrogen consumption per ton of iron is about 500 N cum.

The reduction equilibrium of iron ore with carbon monoxide and hydrogen is well known. Above 850 degrees Celsius， hydrogen is even more reducing than carbon monoxide. Hydrogen is atomically small， highly diffusible and considered to be a faster reducing agent， thus offering the prospect of a fast reduction process with no greenhouse gas emissions. The equilibrium diagram of the reduction with carbon monoxide and hydrogen is given in Figure 1.

The equilibrium diagram in Figure 1 shows that carbon monoxide is more effective for the reduction of iron at low temperatures， while hydrogen is more effective for the reduction of iron oxide at high temperatures.

Figure 1 Equilibrium diagram for reduction with carbon monoxide and hydrogen gas

Figure 2(a) shows the extent to which the equilibrium limit can be approached in the case of particles. The gas utilization is a function of temperature and depends on the degree of reduction. The thermodynamic limit is not reached. For mineral powders in a fluidized bed reactor， the reaction kinetics are more complex. Figure 2(b) shows the reduction characteristics of a typical hematite powder when reduced in a laboratory furnace by a mixture of 50% hydrogen and 50% nitrogen between 450 and 800 degrees C.

Figure 2 Gas utilization of hydrogen as a function of temperature and reduction degree

The gas utilization depends on the temperature and the degree of reduction. Initially， the gas utilization is high， but it decreases after 50 to 60% reduction， especially at temperatures around 700 degrees Celsius. The reason for this is the rate minimization effect， which is attributed to the morphological changes in the solid phase， which usually occur between 600 and 750 degrees Celsius. One reason is the retarding effect of water vapor on the reaction FeO + H2 = Fe + H2O.

Another limiting factor for fluidized beds is adhesion， i.e.， de-fluidization through adhesion between ore particles. It leads to the breakdown of the fluidized bed and also depends on the type of ore fines and the degree of reduction. Hydrogen reduction in fluidized beds can only be achieved if it is carried out in stages， the choice of these stages depending on the degree of reduction of each fines. Similar diagrams have been created for several hematite and magnetite ores.

Hydrogen reduction process

There are several hydrogen reduction processes for iron ores， as described below.

A shaft furnace is used to reduce pallets of iron ore with reformed natural gas， which is a mixture of hydrogen and carbon monoxide. The two most relevant direct reduction processes are Midrex and Energiron (HYL-III).

The Midrex process typically applies a hydrogen/carbon monoxide ratio between 1 and 1.5， but is capable of reducing iron ore with any combination of hydrogen and carbon monoxide. The improved reaction kinetics using hydrogen is expected to be offset by the lower charge temperature due to the endothermic reduction of iron oxide. Currently， there are no Midrex plants using 100% hydrogen， simply for economic reasons.

The Energiron direct reduction process is designed to convert iron pellets/bulk ore to metallic iron through a chemical reaction based on hydrogen and carbon monoxide. The key aspect of the process is the independent control of metallization and product carbon. the Energiron direct reduction process is based on a zero reformer (ZR) scheme.

An alternative to thermal reduction of carbon is reduction using a hydrogen plasma， which consists of hydrogen in vibrational excited molecular， atomic and ionic states， all of which can reduce iron oxide， even at low temperatures. In addition to the thermodynamic and kinetic advantages of hydrogen plasma， the by-product of the reaction is water， which does not cause any environmental problems. Hydrogen in the plasma state offers thermodynamic and kinetic advantages for reduction because of the presence of atoms， ions， and vibrationally excited hydrogen species. The energy carried by these species can be released at the reduction interface， leading to local heating. Therefore， the reduction of hydrogen plasma does not require volumetric heating as in the case of molecular hydrogen. The equilibrium diagram in Figure 1 shows that carbon monoxide is more effective for the reduction of iron at low temperatures， while hydrogen is more effective for the reduction of iron oxide at high temperatures.

    The reduction of iron oxide by hydrogen plasma can occur in different physical states of iron oxide. Depending on the physical state of the iron oxide at the reaction interface， the hydrogen plasma reduction of iron oxide can be divided into two categories， namely (i) heterogeneous processes， in which the reduction reaction occurs at the interface between hydrogen and molten or solid iron oxide， and (ii) homogeneous processes， in which the iron oxide is vaporized so that the reaction occurs in the gas phase. Homogeneous processes can also be referred to as dissociative reduction. The vast majority of processes are heterogeneous， but the characteristics of homogeneous processes are instructive.

The American Iron and Steel Institute is developing a flash ironmaking process in which hydrogen is used as a reducing agent. The energy requirement of the process is 2.6 gigacalories per ton of hot metal. The process flow diagram is shown in Figure 3. In a flash ironmaking furnace， the operating temperature is 1325 degrees C and the residence time is from 2 to 10 seconds. The residence time is a function of the temperature-induced reaction rate， the feed size and the amount of excess gas/distance from the equilibrium line.