Electrolytic Production of Hydrogen Gas

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BEFORE getting into the actual discussion of the subject "Electrolytic Production of Hydrogen Gas," I would like to mention very briefly some of the other methods used in the production of hydrogen gas.

Since hydrogen does not exist in great quantities in the atmosphere, nor in its elementary state, it must therefore be secured from compounds of which it is a major part. The chief methods of production of hydrogen are as follows:

FIRST, By the action of steam on iron, commonly known as the iron-contact method.

SECOND, By thermal decomposition of hydro-carbons and by the interaction of steam with hydro-carbons.

THIRD, By the inter-action of steam and water gas in the presence of a catalyst.

FOURTH, By the liquefaction of water gas.

FIFTH, By the action of acids and alkalis on metals or alloys.

SIXTH, By the decomposition of amonia in the presence of a catalyst.

AND LASTLY, By the electrolysis of water.

This latter method, which is the subject of this paper, is also known as the electrolytic method. It is one of the simplest, most widespread, and cheapest methods, especially when electric energy is available at low rates. Some of the other advantages of this method over other methods are as follows:

FIRST, High purity gas is easily obtained. This is very important to most consumers.

SECOND, The only impurity in the hydrogen from the oxy-hydrogen cell in measurable quantities is oxygen gas, which can be readily removed by combustion, if desired.

THIRD, The cost of hydrogen thus produced is low compared to some of the other methods, especially for small capacity installations, and where the oxygen gas can be economically disposed of.

FOURTH, The electrolytic method of production is quite flexible, being adjustable to both small and large installations, as the units may readily be increased in size without discarding equipment.

FIFTH, The original cost of installing a plant is comparatively low, being roughly 50c per cubic foot of daily capacity in the larger size plant.

SIXTH, The machinery is quite simple, easily maintained, and aside from electrical energy uses only water and small quantities of electrolyte as raw materials.

In the electrolytic method, the gases are made in a cell. There are two general types of cells in use, namely, the unipolar or tank type cell, and the bipolar or filter press type cell.

The unipolar cell consists of a tank, which holds the electrolyte, into which are placed parallel plates, which are the electrodes. These electrodes are alternative, positive, and negative. Provision is made for collecting the gas formed at each electrode. The electrodes are separated by a porous diaphragm, either of asbestos or of nickel screen or perforated plate. Each cell unit may consist of one cathode and one anode or of several cathodes and several anodes. The tank may be separated from the electrode structure or may be attached to the electrode and diaphragm structure, or the electrodes may even serve as the sides of the cell tank. Several electrode and diaphragm units may be immersed in the same electrolytic tank.

The unipolar or tank type cell can be further subdivided into two general classes, namely the OPEN TANK TYPE and the CLOSED TANK TYPE, depending on whether or not the electrolyte is exposed to the air.

The Burdett cell is a good example of the unipolar open tank type cell, in which a separate unit of electrodes and diaphragms with gas collecting compartments is immersed in a tank of electrolyte. In fact, in the Burdett cell, the whole electrode unit together with the gas collecting compartments, is not only immersed in the electrolyte, but actually submerged down in the electrolyte, and has this advantage: That the gas is generated and collected under the electrolytic solution and hence any leaks are immediately noticeable.

The electrodes are suspended in a casting of multiple compartments with an asbestos diaphragm between adjacent electrodes which divide the cell into seven gas compartments, three for oxygen and four for hydrogen. The asbestos diaphragms have a free end at the base of the cell, thus allowing for shrinkage, a feature of superiority claimed for this diaphragm over the rigidly fixed type. The open end at the base insures uniform density of electrolyte and corresponding uniformity in current distribution owing to the circulation of liquor which is set up due to the difference in density of the electrolyte in the several gas compartments.

Gases collect in the upper portions of the casting and pass through off-take pipes into their respective manifolds.

These cells are made for different ratings and capacities. The normal rating of the cell is 1200 amperes and the voltage required at this amperage is 2.15 volts per cell. The gas yield per cell under these circumstances would be 19.08 cubic feet of hydrogen per clock hour. This means a kilowatt hour efficiency of 7.31 cubic feet of hydrogen.

The Knowles cell is another good example of the unipolar open tank type cell. It is likewise composed of one or more units of electrodes and associated diaphragms, and gas collecting compartments set in a tank of electrolyte. It differs from the Burdett cell, however, in that the gas collecting compartments are above the electrolyte solution.

It differs also in that the entire cell is of sheet steel construction, and that the off-take pipes are in the form of small manifolds immediately above the cell compartments, which in turn empty into their respective manifolds. A special feature of gas washing and automatic water feeding to the cells is also incorporated in the entire installation.

These cells are made for different ratings and capacities. The normal rating of the cell is 1000 amperes and the voltage required at this amperage is 2.15 volts per cell. The gas yield per cell under these circumstances would be 15.90 cubic feet of hydrogen per clock hour. This means a kilowatt hour efficiency of 7.31 cubic feet of hydrogen.

These open tank type cells have the advantage of greater flexibility, since the units can be easily taken apart for repairs and easily reassembled, as the electrode unit may be removed without disturbing the tank of solution. They have the disadvantage, however, of occuping greater floor space, and of requiring more electrolyte; and have a higher first cost. Also, the electrolyte is exposed to the air and the caustic forms carbonates on contact with the carbon dioxide in the air. However, this difficulty may be overcome by floating paraffin on top of the solution, which prevents its contact with the air. The open tank cells are also usually more rugged and will stand overloads and impure make-up water better than the closed type.

The Levin Electrolabs cell is a good example of the closed type unipolar cell. It is constructed of sheet metal and completely welded, and contains three compartments. Oxygen is generated in the two outer compartments, hydrogen in the center compartment. Two sheet metal frames carrying two asbestos diaphragms serve as the separating media between the compartments. The electrodes are quite independent of the casing, as they are separated from and securely fixed within the casing by blocks of asbestos. The electrodes are plated; the cathode with cobalt and the anode with nickel.

Each compartment has a separate water feed which also serves as a blow-off device to vent the gas from each compartment under abnormal conditions. The sight feed indicator is placed between the cell and the offtake pipe, insulating the cell from other units in the group, and also serving as a pressure regulator inside the compartments of the cell.

These cells are made for different ratings and capacities. The normal rating of the cell is 600 amperes and the voltage required at this amperage is 2.0 volts per cell. The gas yield per cell under these circumstances would be 9.54 cubic feet of hydrogen per clock hour. This means a kilowatt hour efficiency of 7.95 cubic feet of hydrogen.

This cell has the advantage over the open type cell of lower first cost and smaller floor space requirements. However, since these cells are built very compact, they have more tendency to develop trouble, such as shorts and holes in diaphragms caused by electrode warping, etc., than the open type cells.

The I.O.C. type 4-1000 cell is an excellent example of the closed type unipolar cell in which the electrodes act as the cell tank sides.

The unit is a thin cast iron box of rectangular form to which are bolted two cast iron plates serving as electrodes. The cavity between the electrodes is divided by a diaphragm of asbestos cloth bolted directly by a metal frame. This diaphragm forms the two chambers of the cell.

In the upper part of the rectangular box frame are reservoirs for the electrolyte, from which it is fed to the two sides of the diaphragm. In the upper part of the cell frame are also two gas chambers, in the form of bell jars, which permit the separation of the gases from moisture and electrolyte spray, and serve as gas traps and gas offtakes, as well as an automatic pressure controlling device.

At the bottom of the frame are communicating passageways which permit circulation of electrolyte on the two sides of the diaphragm. In the base of the cell is a drain plug for draining the electrolyte.

The cast iron electrodes are insulated from the frame and from one another. A heavy packing rim of insulating material is used and the bolts which hold the electrodes to the frame are insulated by mica bushings. The electrodes are reinforced by outside ribs, and on the inside carry a great number of pyramid-shaped projections. These increase the electrode area in contact with the electrolyte and facilitate release of the gases at the generating surface.

The anode is heavily nickel-plated while the cathode is left plain.

These cells are made for different ratings and capacities. The normal rating of the cell is 800 amperes and the voltage required at this amperage is 2.2 volts per cell. The gas yield per cell under these circumstances would be 12.72 cubic feet of hydrogen per clock hour. This means a kilowatt hour efficiency of 7.23 cubic feet of hydrogen.

These cells have the advantage of great compactness and low first cost and less bus bar requirements, since the anodes and cathodes of adjacent cells are within a few inches of each other. These cells have the disadvantage of limited electrode area and since the electrodes must be of a rigid material, such as cast iron; nickel and cobalt plating of the anodes and cathodes, when desired, is difficult and costly. These cells are difficult to seal against caustic leaks and insulate against electric shorts.

The filter press-type cell has long been used in laboratories and only recently has it been used to any great extent commercially. The filter press or bipolar cell consists of a group of electrodes in series, separated by diaphragms and sealed and insulated at the edges of the electrodes; thus one side of an electrode acts as the cathode and the other side as the anode. This type cell requires no bus bars between electrodes of separate cell units and hence a great saving in material is effected and less voltage drop is encountered. This type cell, however, has the disadvantages of electrolyte sealing and electrical insulation troubles. Also, if a unit of this type cell develops a short or a leaky diaphragm, the whole bank of cells must be shut down when the repair is made. This type cell, of which the Bamag and Shriver electrolyzers are outstanding examples, requires a minimum of floor space, electrolyte, materials, and first cost. The modern filter press type cells are being constructed more durable and with electrolyte filters and hence, little difficulty with leaks and no necessity of changing electrolyte and removing deposits, is claimed.

WATER is our basic raw material. Pure water is, however, a very poor conductor of electricity due to its very low degree of ionization, and hence, it is necessary to add an electrolyte which has a very high degree of ionization and, hence, a high conductivity to the pure water in the cells. This electrolyte must be one which will cause hydrogen to be liberated on electrolysis.

Sodium chloride is used extensively for hydrogen-chlorine cells, and with this electrolyte, hydrogen and caustic soda are formed at the cathode, while chlorine gas is formed at the anode.

Even though Sodium Chloride has a high degree of ionization, obviously this salt could not be used in oxygen-hydrogen cells.

Sulphuric acid, caustic soda, and caustic potash are electrolytes which are used in oxygen-hydrogen cells. Since sulphuric acid attacks metals, especially iron, it requires lead or other acid resisting electrodes and was early abandoned as an electrolyte for commercial units. The Schoop cell of 1900 is an outstanding example of a cell using acid electrolyte. It used a solution of 32° Baume sulphuric acid with lead electrodes.

Caustic soda, or Sodium Hydroxide, is used more extensively today than Potassium Hydroxide, mainly because of the latter's higher cost, and in spite of the latter's lower decomposition voltage, as will be shown later.

But, when either caustic soda or potash is used as an electrolyte, the positive sodium or potassium ions are attracted to the cathode or negative electrode where they are neutralized and form sodium or potassium atoms, which immediately react with water present to form caustic soda or potash and liberate hydrogen gas. The negative hydroxyl ions are attracted to the anode or positive electrode where they are neutralized and react with *each other* to form water and oxygen gas. Hydrogen is thus formed at the cathode and oxygen at the anode.

The solution tends to become more and more caustic at the cathode and more and more neutral at the anode; hence the solution must circulate in order to maintain a uniform density and minimum resistance. The electrolyte is not used up, however, and water must be added.

For 100 cubic feet of hydrogen gas produced 4.7 pounds of water are converted to gas; however, the gas carries off water vapors which increase this figure, depending on the temperature of the gas leaving the unit. For a temperature of 160° F. 7.8 pounds of water per 100 cubic feet of gas are used.

According to Faraday's law, 96,500 coulombs or ampere seconds liberate one equivalent weight of a substance in electrolysis. Therefore, 1.0078 grams of hydrogen and 8 grams of oxygen are liberated by 96,500 coulombs, or 1 coulomb liberates 10.5 micrograms (.0105 milligrams) of hydrogen. Therefore, 1 ampere hour liberates .0159 cubic feet of hydrogen and .00795 cubic feet of oxygen measured at 68° F. or 20° C. and 1 atmosphere or 760 mm. of mercury.

From thermodynamic calculations, the decomposition voltage of water would be 1.23 volts, assuming a reversible cell. It is found, however, that the minimum voltage which will decompose a solution of caustic potash or soda is in the neighborhood of 1.7 volts. This excess voltage is known as over-voltage, which is dependent upon several factors, namely,

(1) The kind, purity, and density of the electrolyte.
(2) The material of the electrodes and polarization.
(3) The current density in the electrolyte and electrodes.
(4) The distance between the electrodes.
(5) The material and type of diaphragm.

As shown above and based on the electronic theory, and Faraday's law, it must be remembered that the electrolyte is decomposed not as water but as an electrolyte, the reaction involving the water being a secondary one in which heat is liberated. The decomposition voltage of sulphuric acid is 1.67 volts, that of caustic soda is 1.69 volts, and that of caustic potash is 1.67 volts. The over-voltage due to the electrodes is divided into over-voltage at the cathode, which is known as hydrogen over-voltage, and over-voltage at the anode, which is known as oxygen over-voltage. These over-voltages are due to the resistance of the electrode material to the formation of gas atoms and due to polarization. The hydrogen over-voltage of polished platinum is 90 millivolts (.09 v., of platinized platinum 5 millivolts (.005 v.), of iron 80 millivolts (.08 v.), of cobalt 5 millivolts (.005 v.), and of polished nickel 210 millivolts (.21 v.). The oxygen over-voltage of polished platinum is 440 millivolts (.44 v.), of platinized platinum 240 millivolts (.24 v.), of polished nickel 120 millivolts (.12 v.), of sponge nickel 50 millivolts (.05 v.), and of cobalt 130 millivolts (.13 v.). Thus an anode of nickel-plated iron and a cathode of cobalt-plated iron have an over-voltage of 55 millivolts (.055 v.). If the cathode is iron and the anode is nickel-plated iron, the total over-voltage is 130 millivolts (.13 v.). These represent the best two combinations of electrodes for caustic potash or soda solutions. The nickel-plated anode and iron cathode combination is cheaper than the nickel-plated anode and cobalt-plated cathode combination and is often used instead for this reason, although the over-voltage is slightly more. The current through the electrodes and electrolyte causes a voltage drop due to the ohmic resistance of electrode material and the resistance of the solution to the migration of the ions. This voltage drop is almost directly proportional to the current for a given temperature. However, the resistance of the electrolyte decreases with an increase of temperature. The resistance of the electrolyte is, of course, proportional to the distance between electrodes and is increased by a diaphragm, since it retards or interferes with the migration of ions. Any impurity in the electrolyte increases its resistance. Caustic soda has a maximum conductance at about 19° Be. and caustic potash has a maximum conductance at about 28° Be.

Cells are designed to operate at currents of about 35 to 60 amperes per square foot of useful electrode area. At these current densities, the cell should require a voltage of not over 2.2 volts per cell, which would give an efficiency of 7.23 cubic feet of hydrogen per KWH. At 2.0 volts the cell would have an efficiency of 7.95 cubic feet of hydrogen per KWH. As the amperage of a cell is increased its production and voltage increase, but its efficiency decreases. The over-voltage causes heat to be liberated in the cells and hence aids to maintain a high efficient operating temperature, especially for compact cell units.

The points of main concern in the operation of electrolytic cells are the prevention of electrolyte leaks and losses, the maintaining of as low a cell voltage as possible, and the maintaining of as high a gas purity as possible.

The electrolyte may be lost from leaks in the tank, usually at gaskets, by being carried over in the gas to the gas lines and to the flashbacks where it may plug the lines, cause electric shorts, or be lost in the flashback water, or by being contaminated by impurities in make-up water by CO_2 from the air and hence require discarding. When the cell tank leaks, obviously a new gasket or other repairs are necessary. Many devices and designs have been made to remove the electrolyte from the gasses leaving the cells and return it to the cells. Some of these devices require the gas to be washed free from electrolyte by the pure make-up water which returns it to the cell. Others provide for the cooling of the gases as they leave the cells with the resultant condensation of water vapors which are used to wash the electrolyte back into the cells. This method also saves on make-up water. Some of the devices employ both these methods.

The electrolyte can be kept relatively pure or uncontaminated of obnoxious materials by using distilled water having a minimum or less than 5 parts per million of permanent hardness, especially iron sulphates and carbonates, and no chlorides. The amount of carbonates formed will, of course, depend upon the type of cell and whether or not paraffin is used on open cells.

The cell voltage may be kept at a minimum by using as pure an electrolyte as possible, at the density at which it has maximum conductivity, and by seeing that the anodes are kept nickel-plated and the cathodes either free from scale or cobalt-plated. The electrolyte conductivity will be greatest at a high electrolyte temperature and hence the temperature should be maintained as high as possible but not to exceed 165° F., since excess evaporation of water and attack on cell parts by the electrolyte will take place at higher temperatures.

The gas purities are the hardest items to control in cell operation. They are, however, of the greatest importance since hydrogen purities below about 92.5% and oxygen purities below about 91.5% constitute explosive mixtures. Impure gases are caused by any combination of faults, the main ones being:

(1) Holes in the diaphragms or leaks between compartments, which are large enough to permit the gases to inter-mix.

(2) Differences in pressures of the oxygen and hydrogen gases, which cause a flow of gas through the diaphragm; or, any small leaks which may exist.

(3) Shorting of an electrode to a diaphragm due to deposited impurities from the electrolyte in the case of asbestos; or, because of nickel used in the diaphragm, and thus act as an electrode.

(4) Acting of the diaphragm as a bipolar electrode, *if* it be conducting due to application of over twice the decomposition voltage to the cell.

(5) Reversed polarity of the cell due to reversed polarity of generator; or if generator voltage is less than back e.m.f. of cells; due to short circuiting of a cell upon itself.

(6) Too low a level of electrolyte, exposing porous diaphragm which would permit passage of gas because of loss of sealing effect due to liquid.

If the liquid level of the cell is maintained at the proper level, the diaphragms and gas seals are kept maintained at the proper level, the diaphragms and gas seals are kept free of leaks, pure electrolyte is maintained, gas holder pressures are balanced so that the cell gas pressures are equal, generator reverse current relays and undervoltage releases are used, plate warping is avoided by not overloading or overheating, good gas purities may be expected. If, however, the gas purities drop, the responsible cells must be located and removed from the electric circuit or vented to the outside air, until they are removed from the circuit. In the case of filter press type cells, the whole bank would perhaps require removal from service, since usually one cell cannot be vented or effectively removed from the electric circuit. The cells responsible for bad purities should be repaired as soon as possible, either to return to service or to act as standby equipment.

Since hydrogen diffuses more readily than oxygen and since it is produced in twice the quantities as oxygen, the oxygen purity will be lower than the hydrogen purity in all cases except when the cell oxygen gas pressure is greatest or when the anode shorts to the diaphragm.

If higher gas purities than are normally produced by the cells are required, the purities may be increased to any desired value by passing the gas through a purifier, which burns out the foreign gas by means of an electrically heated filament. In the case of oxygen, the life of any filament, except perhaps platinum, would be relatively short and hence the hydrogen is usually burned out in the presence of platinum chloride, deposited on an asbestos core, which acts as a catalytic agent.

This method of purification is wasteful of gas, especially where low purities are generated, since much of the gas is reconverted to water. However, it is the most practical. The better procedure is to use and maintain cells which will generate gas of the desired purity, there being cells on the market which will generate hydrogen of 99.8% and oxygen of 99.6% minimum purities.

For all around cell operation where the desire for greater flexibility, better average gas purity, fewer forced outages, and better continuity of service overweighs the increased first cost and larger required floor space, the open tank cell will prove its merits.

Review of Hydrogenation

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IN the strict sense of the word the term hydrogenation should apply to those reactions in which hydrogen unites with an unsaturated compound to give a saturated one. Probably the best known industrial application of this procedure is the hardening of vegetable or other oils which are glycerides of oleic or other unsaturated carboxylic acids. As the name implies, the physical change which occur in many instances is the transformation of a liquid to a solid material, as for example, the changing of olein into stearin.

However, hydrogenation at present includes not only those reactions as mentioned above but also others in which reduction is predominate, as the conversion of gly-