Chemical Properties of Hydrogen

At room temperature hydrogen displays little activity if it is in the molecular state, but in the nascent state its activity is considerably increased.

At high temperatures the activity of molecular hydrogen increases. Hydrogen has the property of being absorbed by metals. The amount of hydrogen absorbed depends to a large extent upon the specific surface of the metal. The largest amount of hydrogen is being absorbed by palladium which not only adsorbs but also dissolves hydrogen. The solubility of hydrogen is connected with its property of permeating through red hot iron, platinum and even more readily through palladium, which it permeates readily even at 240 degrees. Hydrogen permeates through rubber but not through glass.

Hydrogen combines very readily with metalloids. It combines most readily with fluorine. Even liquid hydrogen and solid fluorine combine explosively. With chlorine the reaction takes place explosively only under the action of light of short wave length or at a high temperature.

A mixture of two volumes of hydrogen and one volume of oxygen is known as detonating gas. The reaction begins to an appreciable extent at 180 degrees and is rapidly accelerated on further heating. The reaction velocity can be greatly influenced by the catalytic action of the container material and the amount of water vapor present in the gases. Under the action of a flame, spark or high temperature, detonating gas explodes; however, dry detonating gas does not explode even at 960 degrees. Slow pressure increase even up to 150 atmospheres does not cause explosion, but the presence of a catalyst, for example, platinum black, may be the cause of an explosion. Other catalysts promote explosion only on heating.

Mixtures at other proportions are also explosion hazards. The lower limit of explosibility of a hydrogen-oxygen mixture corresponds to a content (by volume) of 5 percent H_2 and 95 percent O_2. The upper limit corresponds to 94.3 percent H_2 and 5.7 percent O_2. Mixtures of hydrogen with air also constitute explosion hazards. The lower limit of explosibility corresponds to the proportions of 5 percent H_2 and 95 percent air, the upper limit to 73.5 percent H_2 and 26.5 percent air.

Hydrogen can combine with various organic substances in the presence of catalysts -- nickel, platinum, palladium. In this manner liquid vegetable oils can be converted into solids. This process is called hydrogenation. On reactions wherein hydrogen combines with carbon monoxide are based the production of methyl alcohol (methanol) and of liquid fuel.

2. Processes Taking Place at the Electrodes in Electrolysis of Water

Pure distilled water has an electroconductivity of from 1.10^{-6} to 2.10^{-6} $ohm^{-1} \times cm^{-1}$; that is 1 cubic millimeter of such water has a resistance equal to that of a copper wire having a cross section equal to 1 millimeter square, and 200-400 thousand kilometers long. Due to such a low electrical conductivity, pure water is not convenient for use in electrolysis. But water, acidified or containing dissolved salts or hydroxides of alkali metals, is a good conductor of electrical current, and when insoluble electrodes are used, for example electrodes made of platinum, there is observed a decomposition of the water with evolution of oxygen on the anode and of hydrogen on the cathode.

On electrolysis of water, acidified, for instance with sulfuric acid, evolution of hydrogen on the cathode is the result of a primary process, that is, of direct discharge of hydrogen ions in accordance with the reaction:

$$2H^+ + 2e = H_2$$

insofar as no other positive ions are present in the solution.

Evolution of oxygen on the anode can be the result of two processes, namely: primary discharge of SO_4^{2-} ions according to the reaction:

$$SO_4^{2-} - 2e = SO_4$$

and a secondary reaction of the SO_4 radical with water, to give oxygen and sulfuric acid:

$$SO_4 + H_2O = H_2SO_4 + \frac{1}{2} O_2$$

On it can be the result of a primary discharge of hydroxyl ions with formation of water and evolution of oxygen, according to the reaction:

$$2OH^- - 2e = H_2O + \frac{1}{2} O_2$$

On electrolysis of water containing in solution an alkali, for example, caustic soda, on the other hand, evolution of hydrogen at the cathode could be, in principle, the effect either of a discharge of the Na+ ion and the reaction of the neutral sodium ion with water to give caustic soda and hydrogen, in accordance with the equations:

$$Na^+ + e = Na$$

$$Na + H_2O = NaOH + \frac{1}{2} H_2$$

or of primary discharge of hydrogen ions formed on dissociation of water.

Anodic evolution of oxygen from an alkaline electrolyte is only possible as a result of the primary process of discharge of OH^- ions, since in the alkaline solution there are absent any other ions.

Previously it was believed that in electrolysis of an alkaline electrolyte the cathodic evolution of hydrogen is a secondary process, that is, primarily the Na+ ion is discharged. However this does not correspond to actual facts, and cannot be attained if the electrolysis of water is conducted in accordance with the practice of using as a cathode not mercury but a solid metal.

Hydrogen is generated at the cathode, from an acidic as well as from an alkaline solution, as a result of a primary process. This can be readily shown, using the equation of Nernst to effect the calculations. Reverse potential of hydrogen evolution from a neutral solution is found to be equal to -0.415 volts. In order to make possible separation from the neutral solution of ions of Na+, the normal potential of which is equal to -2.71 volts, it is necessary that the more electronegative potential of Na+ ions separation approximates the value of the potential of H+ ions separation. Theoretically this can be attained if the concentration of sodium ions in the solution is increased to such an extent that the value of the potential of Na+ ions separation is equal to -0.415 volts. On using x to denote the concentration of Na+ ions in the equation of Nernst we have

$$-0.415 = -2.71 + 0.058 \lg x \qquad (1)$$

wherefrom

$$x = 3 \times 10^{39}$$

The figure thus obtained indicates a totally unreal concentration. Even on taking into account that evolution of hydrogen from the alkaline solution occurs at a more negative potential and in addition that a certain overvoltage exists, still computation shows that in such a case separation of sodium does not take place, and only discharge of hydrogen ions occurs.

Anodic evolution of oxygen from an acid solution was also considered as being a secondary process. However, this assumption also apparently does not correspond to the actual facts. In spite of the low concentration of OH^- ions in acid solution, under conditions of not too high a current density, OH^- ions are discharged first. This follows from measurements of decomposition voltages of various acids and bases. It was found that decomposition voltage of normal solutions of various acids and bases on smooth platinum electrodes has a value of about 1.7 volts.

Results of the measurements are given in Table 21.

Table 21

Decomposition voltage of normal solutions of acids and bases on smooth platinum electrodes

Substance in solution	Decomposition voltage; volts	Substance in solution	Decomposition voltage; volts
Sulfuric acid	1.67	Caustic potash	1.67
Nitric acid	1.69	Ammonium hydroxide	1.74
Phosphoric acid	1.70	Methylammonium hydroxide (0.125N)	1.75
Dichloro-acetic acid	1.66		
Malonic acid	1.69	Dimethylammonium hydroxide (0.5N)	1.68
Chloric acid	1.65		
Tartaric acid	1.62	Tetramethylammonium hydroxide (0.125N)	1.74
Caustic soda	1.69		

Close coincidence of decomposition voltages of acids and bases, and the fact that it does not depend on the nature of the acid and base, lead to belief that in all instances the same process takes place on the electrodes. Otherwise one would expect that decomposition voltage of the acid, or base, would depend upon the nature of the acid anion or base cation. The only process on the anode which can be common to the different acids and bases is the discharge of OH^- ions with separation of oxygen.

Decomposition voltage of normal solutions of hydrogen halide acids was found to be less than 1.7 volts, namely: hydrochloric acid 1.31 volts; hydrobromic acid 0.94 volts; hydriodic acid 0.52 volts.

However in this instance there is liberated on the anode not oxygen but halogen. Hence decomposition of water does not take place. If electrolysis is conducted using hydrochloric acid diluted to a concentration of 1/32 N, the decomposition potential increases to 1.69 volts and evolution of oxygen begins at the anode.

It is apparent that the potential of Cl^- ion discharge in a normal solution of hydrochloric acid is lower than that of OH^- ion discharge; because of this, electrolysis of water does not take place. In more dilute solutions of hydrochloric acid reverse correlation of discharge potentials, of ions OH^- and Cl^-, obtains. The chlorine ion is discharged at a higher potential, and decomposition voltage of the dilute acid, to give chlorine and hydrogen, should be higher than 1.69 volts; hence, as soon as the voltage reaches this value there occurs evolution of oxygen on the anode.

Thus on electrolysis of acidic, or alkaline, electrolyte with platinum electrodes at not too high current density, evolution of hydrogen on the cathode and of oxygen on the anode constitute primary processes.

Electrolysis of water takes place according to the following equations:

On the cathode:

$$2H^{+} + 2e = H_2$$

On the anode:

$$2OH^{-} - 2e = H_2O + \frac{1}{2} O_2$$

From this it is readily apparent that while two moles of water are being decomposed, on the anode there takes place simultaneously the formation of one mole of water. As a result of this, on prolonged electrolysis the electrolyte in the vicinity of the anode is depleted of acid or alkali, while near the cathode the amount of acid or alkali increases. In an alkaline solution decrease of alkali near the anode also promotes current transfer. by alkali metal cations from anode to cathode. Due to difference in concentrations there arises concentration polarization, which could be of considerable magnitude at large differences of concentration. However the diffusion process has the opposite effect -- that of equalizing the concentrations. Therefore a stable condition is reached after which the difference in concentrations does not increase.

According to Faraday's law 26.8 ampere hours liberate at 0 degree and 760 millimeters pressure, 11.2 liters of hydrogen and 5.6 liters of oxygen. One cubic meter of hydrogen and 0.5 cubic meters of oxygen require, in theory, the expenditure of 2383.8 ampere hours.

3. Theoretical Voltage of Water Decomposition

If electrolysis of water is conducted under reversible conditions, then the work expended must be numerically equal to the work performed by the reversibly operating galvanic hydrogen-oxygen cell, in which the same reaction takes place in the opposite direction.

If A_1 is the work expended on decomposition of water, and A_2 the works yielded by the galvanic cell, it follows that under reversible conditions

$$A_1 = A_2 \qquad (2)$$

According to the first law of thermodynamics

$$A_1 = nF \times E_1 \qquad (3)$$

and

$$A_2 = nF \times E_2 \qquad (4)$$

wherein

n - number of reacting or obtained chemical equivalents

F - Faraday's number

E_1 - voltage of reversible decomposition of water

E_2 - electromotive force of reversibly operating hydrogen-oxygen cell.

Consequently

$$nF \times E_1 = nF \times E_2 \qquad (5)$$

since nF in both members of the equation relates to the same reaction, which merely proceeds in opposite directions, we have

$$E_1 = E_2 \qquad (6)$$

Therefore for a reversible decomposition of water there is required a voltage equal to the electromotive force of the reversibly operating hydrogen-oxygen galvanic cell.

This is the least voltage determined solely by the decomposition work, without taking into account any losses, that is, irreversible processes, for example overvoltage at the electrodes.

From equations (3) and (4) it follows that

$$E = \frac{A}{nF} \qquad (7)$$

The value of maximum work A of the reaction

$$2H_2 + O_2 = 2H_2O$$

is given by the isotherm equation

$$A = RT \times \ln K + RT \times \ln \frac{C^2_{H2} \times C_{O_2}}{C^2_{H_2O}} \qquad (8)$$

wherein

K - Equilibrium constant of hydrogen and oxygen with water vapor

C_{H_2}, C_{O_2}, C_{H_2O} - the initial concentrations of the reacting hydrogen and oxygen and of the water formed.

On substituting in equation (7) the value of A from equation (8) we have

$$E = \frac{RT}{nF} \ln \left(K \frac{C^2_{H_2} \times C_{O_2}}{C^2_{H_2O}}\right) \qquad (9)$$

since

$$K = \frac{C^2_{1,\ H_2O}}{C^2_{1,H_2} \times C_{1,\ O_2}} \qquad (10)$$

where C_1, H_2O, C_1, H_2, C_1, O_2 - are the equilibrium concentrations of water, hydrogen and oxygen. We can write equation (9) in the following form:

$$E = \frac{RT}{nF} \ln \frac{C^2_{1,H_2O} \times C^2_{H2} \times C_{O_2}}{C^2_{1,H_2} \times C_{1,O_2} \times C^2_{H_2O}} \qquad (11)$$

Bearing in mind that the volumes at which the reaction takes place can always be selected in such a manner that $C_1, H_2O = C_{H_2O}$, that is, the concentration of the water found is equal to the equilibrium value, we have

$$E = \frac{RT}{nF} \ln \frac{C^2_{H_2} \times C_{O_2}}{C^2_{1, H_2} \times C_{1,O_2}} \qquad (12)$$

Replacing molar concentrations by partial pressures which are proportional to them, introducing the numerical values of R, F and n ; and converting to decimal logarithms, we have

$$E = \frac{8.3 \times 2.3T}{4. \times 96,500} \lg \frac{P^2_{H_2} \times P_{O_2}}{p^2_{1,H_2} \times p^2_{1,O_2}} = 0.00005\ T \times \lg \frac{P^2_{H_2} \times P_{O_2}}{P^2_{1,H_2} \times P_{1,O_2}} \qquad (13)$$

If the process takes place at atmospheric pressure, that is, if the partial pressures of hydrogen and oxygen $P_{H_2} = P_{O_2} = 1$ atmosphere, equation (13) assumes the form

$$E = 0.00005\ T \times \lg \frac{1}{p^2_{1, H_2} \times p_{1,O_2}} \qquad (14)$$

Thus determination of E can be made either on the basis of the value of maximum work of the reaction, or, as follows from equation (7), on the basis of values of partial equilibrium pressures of hydrogen and oxygen.

Partial equilibrium pressures can be computed from values of degree of dissociation of water vapor.

If the degree of dissociation of water is α, then for each mole there remains $1-\alpha$ moles of undissociated water, there are formed α moles of hydrogen and $\frac{\alpha}{2}$ moles of oxygen. In total we have $1 + \frac{\alpha}{2}$ moles.

Since the ratio of partial pressures of gases to the total pressure is the same as the ratio of their molar concentrations to the total molar concentration, we have

$$\frac{p_{1,H_2}}{P} = \frac{\alpha}{1 + \frac{\alpha}{2}} \quad \text{and} \quad \frac{p_{1,O_2}}{P} = \frac{\alpha}{2(1 + \frac{\alpha}{2})}$$

where P is the total pressure of the mixture at equilibrium.

At low temperatures the degree of dissociation of water is very small, therefore the value $\frac{\alpha}{2}$ can be disregarded, and then we have

$$p_{1,H_2} = P\alpha \qquad (15)$$

$$p_{1,O_2} = 0.5\, P\alpha \qquad (16)$$

Let us calculate the theoretical voltage of water decomposition for ordinary conditions in practice, that is at 80 degrees (T = 353 degrees) and pressure of one atmosphere.

For a temperature of 80 degrees, the degree of dissociation of water cannot be determined experimentally because of its very small value, but for these conditions it can be calculated from the values of the equilibrium constant, using an equation which in the case of our reaction at a constant pressure has the form:

$$K_p = \frac{P \times \alpha^3}{2}$$

The value of the equilibrium constant at constant pressure we can find by means of isochore equation of Van t'Hoff.

$$\ln K_p = \int \frac{Q_p}{RT} dT + I \qquad (17)$$

For this let us use the following experimental data: thermal effect of the reaction

$$2H_2 + O_2 = 2H_2O \text{ vapor}$$

at 25 degrees (T = 298 degrees) and constant pressure Q_p is equal to 115,670 calories.

Dependence of true heat capacities on the temperature:

$$C_p, H_2 = 6.50 + 0.0009\ T$$

$$C_p O_2 = 6.50 + 0.0010\ T$$

$$C_p, H_2O = 8.81 - 0.0019\ T + 0.00000222\ T^2$$

Let us find the general expression for Q_p (T) as a function of T from the equation:

$$Q_p(T) = Q_p(298^\circ) + \int_{298^\circ}^{T} \sum \nu C_p \qquad (18)$$

Since $\sum \nu$ is the algebraic sum of stoichiometric coefficients of our reaction, we have

$$\sum \nu \; C_p = 2C_{p,H_2} + C_{p,O_2} - 2C_{p,H_2O}$$

or $\sum \nu$

$$= 2(6.50 + 0.0009T) + (6.5 + 0.0010T) -$$

$$- 2\,(8.81 - 0.0019T) + 0.00000222T^2 =$$

$$= 1.88 + 0.0066T - 0.00000444T^2$$

Substituting into equation (18) values of Qp (298 degrees) and $\sum \nu$ Cp, and integrating we have

$$Qp(T) = 115{,}670 + \int_{298^\circ}^{T} 1.88 + 0.0066\,T - 0.00000444T^2 =$$

$$= 115{,}670 - 1.88 \times 298 - \frac{0.0066}{2}\,298^2 + \frac{0.00000444}{3} \times 298^3 +$$

$$+ 1.88\,T + \frac{0.0066}{2}\,T^2 - \frac{0.00000444}{3}\,T^3 =$$

$$= 114{,}856 + 1.88\,T + 0.0033\,T^2 - 0.00000\,148\,T^3$$

Substituting the value Qp(T) in equation (17) and integrating, we obtain

$$\ln K = -\frac{114{,}856}{RT} + \frac{1.88}{R}\ln T + \frac{0.033}{R}\,T - \frac{0.00000074}{R}\,T^2 + \frac{I}{R} \quad (19)$$

Substituting the values of R and converting to decimal logarithms, we have

$$\lg K = -\frac{114{,}856}{4.573\,T} + \frac{1.88}{1.986}\lg T + \frac{0.0033}{4.573}\,T - \frac{0.00000074}{4.573}\,T^2 + \frac{I}{4.573} =$$

$$= \frac{25116.1}{T} + 0.9466 \times \lg T + 0.0007216\,T -$$

$$- 0.0000001618\,T^2 + C$$

The integration constant C can be formed by substituting in equation (19) the experimentally determined value of lg K. By such use of the experimental data the mean value C = + 1.714 was found.

Using this value of C and substituting T = 353 degrees, we finally have

$$\lg K = \frac{25116.1}{353} + 0.9466 \times \lg 353 + 0.0007216 \times 353 - $$

$$- 0.0000001618 \times 353^2 + 1.714 =$$

$$= - 71.14 + 2.4117 + 0.2547 - 0.02093 + 1.714$$

$$\lg K = - 66.7805$$

Let us now determine α:

$$\lg K = \lg \frac{P\alpha^3}{2}$$

$$3 \lg \alpha = \lg K - \lg P + \lg 2$$

In view of the small value of α at 80 degrees, we can take as the total pressure of the gaseous mixture the water vapor pressure, which at 80 degrees is equal to 0.482 atmospheres.

$$3 \lg \alpha = - 66.7805 - \bar{1}.6830 + 0.3010$$

$$3 \lg \alpha = - 66.1625$$

$$\lg \alpha = - 22.0541 = \overline{23}.9459$$

$$\alpha = 8.828 \times 10^{-23}$$

wherefrom

$$P_{1,H} = 0.482 \times 8.828 \times 10^{-23}$$

$$P_{1,O_2} = 0.5 \times 0.482 \times 8.828 \times 10^{-23}$$

and finally

$$E = 0.00005 \times 353 \lg \frac{1}{(0.482 \times 8.82 \times 10^{-23})^2(0.5 \times 0.482 \times 8.82 \times 10^{-23})} =$$

$$= 0.01765\{\lg 1 - [2(\lg 0.482 + \lg 8.82 \times 10^{-23}) +$$
$$+ (\lg 0.5 + \lg 0.482 + \lg 8.82 \times 10^{-23})]\} =$$

$$= 0.01765\ \{0.00 - [2(\bar{1}.6830 + \overline{23},9459) + (\bar{1},6990 + \bar{1}.6830 +$$
$$+ 23.9459)]\} = 0.01765\ (0.00 - \overline{68}.5857) =$$

$$= 0.01765 \times 67.4143 = 1.18 \text{ volts.}$$

Calculation of theoretical potential on electrolysis at normal pressure (1 atmosphere) can be simplified if there is known the equilibrium constant for the required temperature.

In such case one may start directly from the isotherm equation:

$$A_p = RT \times \ln K_p \qquad (20)$$

For 80 degrees we have found the value $\lg K = -66.7805$. Substituting the numerical values of R, T. and $\lg K_p$, we have the maximum work of the reaction

$$A_p = -2.303 \times 1.986 \times 353(-66.7805) = 107{,}800 \text{ calories.}$$

But at 80 degrees only hydrogen and oxygen can have a pressure of one atmosphere, while water vapor has a presence of only 0.482 atmospheres. Hence it is necessary to introduce into the obtained value of maximum work a connection, that is, add the work of expansion of water vapor from the conventional pressure of 1 atmosphere that was adopted by us, to the actual pressure of 0.482 atmospheres.

For two moles of water this work is equal to

$$A_1 = 2RT \times \ln \frac{1}{0.482} = 2 \times 2.303 \times 1.986 \times 353 \times \ln \frac{1}{0.482} = 1075 \text{ calories.}$$

$$A'_p = 107,800 + 1075 = 108,875 \text{ calories}$$

wherefrom

$$E = \frac{A'_p}{nF \times 0.238} = \frac{108,875}{4 \times 96,500 \times 0.238} = 1.18 \text{ volts}$$

Maximum work A_p can be calculated also directly from equation (20), since on the basis of equation (19)

$$A_p = 114,856 - 1.88\ T \times 2.303 \lg T - 0.0033\ T^2 + \\ + 0.00000074\ T^3 - 2.303\ C \times RT$$

Taking the value C = 1.714, we have for 80 degrees

$$A_p = 107,821 \text{ calories}$$

$$A'_p = 107,821 + 1075 = 108,896 \text{ calories}$$

$$E - 1.18 \text{ volts}$$

Similar computations for an electrolyte temperature of 17 degrees give a theoretical decomposition voltage of 1.23 volts.

The theoretical voltage thus decreases with increasing temperature, and the temperature coefficient of electromotive force of hydrogen-oxygen circuit, within this temperature range is equal to

$$\frac{dE}{dt} = 0.0008 \text{ volts}$$

When the temperature coefficient of the electromotive force is known, the theoretical potential can be calculated on the basis of thermal effect values of the reaction, by using Gibbs-Helmholtz equation

$$E = \frac{Q}{2 \times 96{,}500 \times 0.239} + \frac{dE}{dT} T \qquad (21)$$

4. Balance of Voltage

Balance of Cell Voltage

In practice, of course, electrolysis cannot be effected in reverse since it is not possible to operate at vanishingly small current densities so as to avoid power losses by overcoming of a number of harmful resistances, like overvoltage of gases on electrodes, electrolyte resistance, diaphragm resistance, resistance of electrodes, of contacts and the like. Hence the cell voltage always exceeds, to a larger or smaller extent, the theoretical voltage.

The cell voltage V, that is, the difference of potentials between the electrodes, is thus equal to the arithmetical sum of the voltage decrease within the individual areas of the cell.

$$V = +\epsilon_a + \epsilon_k + \eta_a + \eta_k + e_1 + e_2 + e_3 + e_4 + e_5$$

where ϵa and ϵk are reversible potentials of anode and cathode the sum of which is equal to the theoretical decomposition voltage ηa and ηk -- respectively, overvoltage of oxygen on the anode and of hydrogen on the cathode.

e_1 - voltage loss in the electrolyte

e_2 - voltage loss in the diaphragm

e_3 - voltage loss in conductors of the first kind - in electrodes

e_4 - voltage loss in contacts

e_5 - concentration polarization

Depending upon operational conditions and design of the cell, harmful resistances can be very substantial, as a result of which, the actual cell voltage may exceed the theoretical 1.5 - 2 times. Most important are losses due to overcoming overvoltage at the electrodes and resistance of the electrolyte.

Losses e_3 and e_4, if the cell is properly designed and adequately maintained, can be very small. Just as small are the values e_2 and e_5 which ordinarily have no substantial practical significance.

Overvoltage of Hydrogen and Oxygen

As is known overvoltage of gases is not a constant quantity and depends upon many factors: current density, nature of the electrode surfaces, temperature of the electrolyte, material of the electrodes, duration of electrolysis. In the last 20 years theoretical electrochemistry has attained signal successes in the domain of the study of gas overvoltages, nonetheless it has not succeeded fully to establish the theory of dependence of overvoltage on the above listed factors. Therefore in estimating the magnitudes of hydrogen and oxygen overvoltage, it is necessary to resort to experimental data. But experimental data also are of relative value and provide but an approximate estimate of the overvoltage, because experimental conditions cannot be readily duplicated.

Values of hydrogen and oxygen overvoltage at various current densities and temperatures on different materials, in the electrolysis of a 16 percent solution of caustic soda, are shown in Tables 22 and 23.

Table 22

Hydrogen overvoltage in a 16 percent solution of caustic soda; in volts

Material	Current density amp./m^2 at 18 degrees				Current density amp./m^2 at 80 degrees				
	100	500	1000	2000	100	500	1000	2000	3500
Platinized platinum	0.04	0.06	0.08	0.095	0.01	0.03	0.045	0.055	-
Galvanic nickel, Sulfur containing	0.11	0.16	0.10	0.21	0.02	0.06	0.08	0.10	-
Nickel steel, sand blasted	0.21	0.31	0.36	0.40	0.11	0.15	0.18	0.23	-
Nickel, rolled	0.37	0.47	0.51	0.55	0.3	0.39	0.43	0.47	-
Iron, sand blasted	0.26	0.35	0.39	0.45	0.12	0.18	0.22	0.27	0.345
Iron, nickel coated	0.25	0.39	0.49	0.56	0.16	0.24	0.26	0.30	-
Iron, cobalt coated	-	-	0.42	0.47	0.20	0.30	0.36	0.42	-

Table 23

Oxygen overvoltage in a 16 percent solution of caustic soda; in volts

Material	Current density amp./m^2 at 18 degrees				Current density amp./m^2 at 80 degrees				
	100	500	1000	2000	100	500	1000	2000	3500
Galvanic nickel, Sulfur containing	0.32	0.36	0.385	0.42	0.18	0.22	0.24	0.265	-
Nickel steel, sand blasted	0.35	0.40	0.44	0.48	0.25	0.275	0.29	0.31	0.34
Nickel, rolled	0.55	0.77	0.82	0.85	0.31	0.36	0.40	0.43	-
Iron, cobalt coated	0.31	0.35	0.37	0.39	0.23	0.25	0.27	0.29	-

As can be seen from the table overvoltage of both gases, in accordance with the general rule, increases with increasing current density. Increase of temperature considerably decreases overvoltage. The overvoltage is affected not only by the material of the electrodes but also by the condition of their surface. On rough surfaces, the overvoltage is lower than on smooth and shiny surfaces. Apparently this is connected with the fact that the actual working surface of rough electrodes is considerably greater than their geometrical surface, as a result of which, on rough surfaces the current density is less than on smooth ones.

In construction, on taking into consideration the overvoltage values on different materials, metal corrosion in the electrolyte and the economic factors, one uses for the cathode soft iron, in most instances treated with sand, to roughen the surface, by means of sand-blast machines; as the anode there is used soft iron galvanically coated with a mat layer of nickel.

Voltage Loss in the Electrolyte

In modern practice of water electrolysis there are used as electrolytes exclusively, solutions of caustic soda or caustic potash, since acidic electrolytes cause strong corrosion of the equipment. The choice of one or the other of these alkalies is determined by working conditions and cost of the alkali. Usually, if electrolysis is conducted at less elevated temperatures, caustic potash is used, because under these conditions it has a higher electrical conductivity than caustic soda. At higher temperatures this advantage of the potassium salt becomes less pronounced. Since caustic potash causes strong corrosion of the equipment, especially at an elevated temperature, and its cost is higher than than of caustic soda it is more expedient to use caustic soda for electrolysis at a high temperature.

Loss of voltage in overcoming resistance of the electrolyte can be calculated according to the law of Ohm.

$$e_1 = \rho \frac{I \times l}{f} \qquad (22)$$

where

- specific resistance of electrolyte

I - current intensity

l - distance between electrodes in centimeters (path of current)

f - cross section of the electrolyte in square centimeters

Actually, however, voltage decrease in the electrolyte is always somewhat greater than that computed on the basis of Ohm's law. This deviation becomes the more pronounced with increasing current density at equal distance between the electrodes.

This is due to the fact that in electrolysis the electrolyte is filled with ascending gas bubbles which decrease the active cross section of the electrolyte. Therefore calculation of the actual voltage decrease requires the taking into account of the degree of so-called gas saturation of the electrolyte. The gas saturation of an electrolyte is expressed as the ratio (in percent) of gas bubbles volume to the total volume of the electrolyte (liquid + gas).

[See next page for Table 24]

Table 24

Specific resistance of aqueous solutions of caustic alkalies; in ohms

Temperature °C	NaOH content of Solution; in Percent										
	15	17.5	20	22.5	25	27.5	30	32.5	35	37.5	40
50	1.575	1.527	1.508	1.520	1.583	1.692	1.780	1.923	1.950	2.105	2.232
55	1.460	1.408	1.381	1.385	1.428	1.566	1.567	1.650	1.695	1.800	1.905
60	1.333	1.300	1.272	1.266	1.290	1.346	1.392	1.450	1.506	1.562	1.640
65	1.250	1.209	1.170	1.164	1.180	1.220	1.256	1.300	1.342	1.385	1.443
70	1.172	1.130	1.088	1.081	1.088	1.117	1.166	1.176	1.200	1.242	1.287
75	1.162	1.062	1.018	1.007	1.010	1.030	1.050	1.075	1.103	1.127	1.164
80	1.046	1.000	0.956	0.943	0.941	0.955	0.969	0.990	1.011	1.031	1.058

Temperature °C	KOH Content of Solution; in Percent								
	20	22.5	25	27.5	30	32.5	35	37.5	40
50	1.250	1.158	1.104	1.061	1.042	1.060	1.075	1.100	1.153
55	1.174	1.096	1.036	0.999	0.988	0.988	1.000	1.020	1.064
60	1.099	1.027	0.970	0.933	0.922	0.921	0.929	0.945	0.980
65	1.046	0.968	0.923	0.901	0.867	0.864	0.870	0.883	0.913
70	0.988	0.909	0.865	0.833	0.827	0.814	0.818	0.828	0.852
75	0.928	0.863	0.820	0.788	0.775	0.769	0.772	0.779	0.800
80	0.882	0.833	0.790	0.751	0.737	0.730	0.731	0.736	0.754

Gas saturation depends on current density, temperature of the electrolyte, size of gas bubbles, cell design, and is determined experimentally.

Figure 77 shows the relative increase of electrolyte resistance at various degrees of gas saturation filling. As can be seen from the diagram, this factor is of substantial importance. Thus at gas saturation filling of 35 percent the resistance is increased to a value equal twice that of the electrolyte free of gas bubbles.

Voltage loss in the electrolyte, as is apparent from equation (22), is proportional to its specific resistance. Consequently it is very important to use an electrolyte of least resistance.

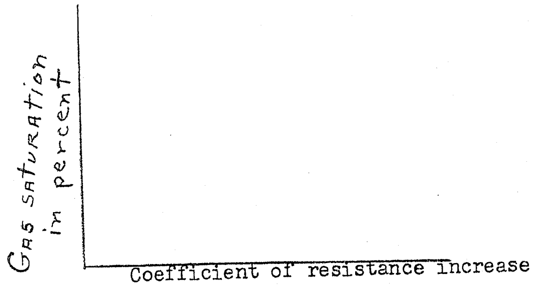

Figure 77. Effect of gas saturation on electrolyte resistance

1 - measured resistance; 2 - calculated resistance

Table 24 shows the values of specific resistance of caustic alkali solutions at various concentrations and different temperatures.

This table shows that with increasing temperature the value of minimum specific resistance is shifted toward the more concentrated solutions. Consequently, selection of concentration of the solution having least resistance, must be made in accordance with the proposed temperature of electrolysis. Usually, in electrolytic production of hydrogen and oxygen at 60-65 degrees, there are used 25-29 percent solutions of caustic potash or 16-18 percent solutions of caustic soda.

5. Power and Material Balance

Power Expenditure and Yield on Electrical Current Basis

Magnitude of electrical power is proportional to voltage and amount of electricity

$$W = V \times Q \qquad (23)$$

It follows that the theoretical expenditure of electrical power per cubic meter of hydrogen and 0.5 cubic meters of oxygen at 0 degrees and 760 millimeters of mercury pressure, is

$$W = 1.23 \frac{2 \times 96{,}500 \times 1000}{22.4 \times 3{,}600 \times 1000} = 2.95 \text{ Kilowatt-hour.}$$

wherein 1.23 is the theoretical reversible voltage of water decomposition.

The actual power expenditure is considerably greater than the theoretical, which is primarily due to the higher voltage of the cell and also to the somewhat greater expenditure of electricity in comparison with the theory. The ratio (in percent) of the theoretical amount of electricity Q, required according to Faraday's law for the production of a given amount of substance, for instance of 1 mole hydrogen and 0.5 moles of oxygen, to the amount Q' actually expended is called yield on the basis of electrical current, that is, the yield (in percent)

$$A = \frac{Q}{Q'} 100$$

The yield on the basis of electrical current of an electrochemical process characterizes the process from the standpoint of efficacious utilization of electricity and the taking into account of electricity losses in electrochemical and chemical side-reactions within the cell.

We have seen previously that the basic electrochemical process -- discharge of H+ and OH- ions, is not accompanied by any side-reactions; therefore yield on the current basis in this instance depends solely on efficiency of separation of the gases and absence of leaks of electricity.

In modern designs and installations these losses are negligible (not in excess of 1 percent) and only in cells of the old types (filter press, bipolar) losses due to electrical leaks were substantial and reached 10 percent.

Thus, in practice, power expenditure is given by the equation

$$W = \frac{VQ}{A} \qquad (24)$$

In view of the high yields, on the basis of electrical current, which render the value of A approximal equal to one, power expenditure may be considered, for every practical purpose, as being dependent only on the cell voltage. We have already stated that cell voltage exceeds the theoretical by 1.5-2 times, and the actual expenditure of power in Kilowatt-hours per one cubic meter of hydrogen and 0.5 cubic meters of oxygen at 0 degrees and 760 millimeters of mercury, fluctuates within the range of 4.5 to 6 Kilowatt-hours.

Water Expenditure

Foundation of one cubic meter of hydrogen and 0.5 cubic meters of oxygen under normal conditions, uses up, in theory, 805 grams of water. Actually, expenditure of water in the cell, is however somewhat greater because hydrogen and oxygen withdrawn from the cell carry with them water vapors.

If the temperature in the cell is t, the pressure of moist gases P atmospheres, and the pressure of water vapor above the electrolyte of a given concentration at t is equal to p atmospheres, the amount of water vapor carried away by the gases can be calculated as follows:

The volume, in liters, of 1 mole of hydrogen and 0.5 mole of oxygen, under the given conditions is,

$$v = \frac{(22.4 + 11.2)\ (273 + t)\ 760}{273\ (P - p)}$$

The weight of 1 liter of water vapor, in grams, under the same conditions is,

$$\gamma = \frac{18 \times p \times 273}{22.4 \times 760(273 + t)}$$

The amount of water vapor saturating the volume v is,

$$G = v \times \gamma = \frac{(22.4 + 11.2)\ 18 \times p}{22.4\ (P - p)}$$

or, the amount of water vapor, in grams, which is carried out of the cell by the gases, per one cubic meter of hydrogen at normal conditions is equal to:

$$G_1 = \frac{(22.4 + 11.2)\ 18 \times p \times 1000}{22.4 \times 22.4\ (P - p)} = 1207\ \frac{p}{P - p}$$

Thus the amount of water vapor removed with the gases will be greater with higher cell temperature, which determines the volume V of the gases evolved, and also the pressure of saturated water vapor over the electrolyte. The amount of water vapor removed, will be smaller with increasing pressure of the gases in the cell and with increasing concentration of the electrolyte; factors determining the boiling temperature of the electrolyte and depression of water vapor pressure.

Boiling temperature curves of solutions of caustic soda and caustic potash of various concentration are shown in figure 78.

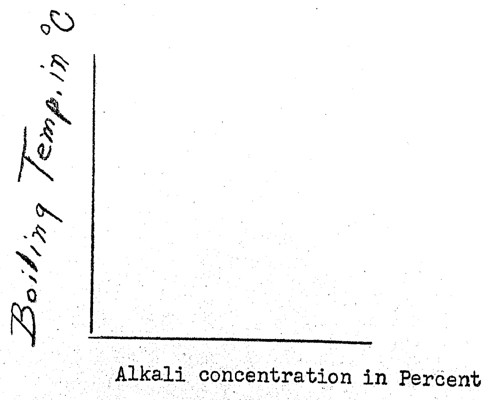

Figure 78. Dependence of boiling temperature of solutions of caustic soda and potash upon concentration.

To compensate the water expended in the decomposition and removed with the gases as water vapor it is necessary to introduce into the cell, at intervals or continuously, additional amounts of water. Water added into the cell must be previously purified to remove mechanically admixed impurities and dissolved mineral salts. This is usually effected either by distillation or by electro-osmotic purification. Water is considered suitable for use in electrolysis if its specific resistance is not less than 60 thousand ohms and the dry residue content not more than 7 milligrams per liter.

Heat Balance of the Cell

On considering the balance of voltage and power expenditure, we have seen that only 60-50 percent of the electrical energy supplied to the cell is expended for decomposition of water. The remainder of this energy, consumed in overcoming internal resistances, constitutes a loss and is given off in form of heat within the cell. The amount of heat evolved, Q, increases with increasing cell voltage and with increasing current intensity; it can be so great as to cause excessive overheating of the cell. To avoid this, recourse is available to auxiliary cooling by providing the cell with a water cooling jacket, or more commonly, with a water cooling coil. Thus excess heat is dissipated and electrolysis temperature is regulated to maintain it at the desired level. Under such conditions the heat regimen of a cell is characterized by the following balance:

$$Q = q_1 + q_2 + q_3 + q_4 + q_5 \qquad (25)$$

wherein

q_1 - heat removed by the cooling water

q_2 - heat consumed in heating the feed water to electrolysis temperature

q_3 - heat consumed in evaporation of water

q_4 - heat removed with the hydrogen and oxygen

q_5 - heat lost to the surrounding medium

At constant temperature of electrolysis, and of the surrounding medium, q_2, q_3, q_4 and q_5 are constants and consequently q_1 which determines expenditure of cooling water depends upon the amount of heat Q, generated in the cell. It would appear that Q should be equivalent to the difference between the amount of electrical energy, actually expended in the cell, and that theoretically required for the decomposition of water.

Energy expended is equal to

$$W = V \times nF \times 0.238 \text{ calories} \qquad (26)$$

where V is cellvoltage.

Energy theoretically required for decomposition of water is equal to the maximum work of the hydrogen-oxygen galvanic cell.

$$W_1 = 1.23 \times nF \times 0.238 \text{ calories} \qquad (27)$$

where 1.23 is the reversible theoretical voltage of water decomposition, or the electromotive force of the hydrogen-oxygen cell.

Hence, Q must be equal to

$$Q = W - W_1 = nF(V) - 1.23)\ 0.238 \text{ calories} \qquad (28)$$

However, this correlation is but a specific instance, which holds where maximum work performed by the system, is numerically equal to the total change of the internal energy of the system, that is, to the thermal effect of the reaction. In other words, when in the equation of dependence of maximum work and thermal effect

$$A = Q + q \qquad (29)$$

q is equal to zero.

In our case, at 25 degrees and 1 atmosphere, the thermal effect of the reaction

$$H_2O \rightleftarrows H_2 + \frac{1}{2} O_2$$

amounts to ± 68 330 calories.

Whereas maximum work is

$$A = 1.23 \times nF \times 0.238 = 1.23 \times 2 \times 96{,}000 \times 0.238 = 56{,}560 \text{ calories.}$$

Hence

$$q = 68{,}330 - 56{,}560 = 11{,}770 \text{ calories}$$

Thus, we can see that in the case of reversible work the hydrogen-oxygen cell at 17 degrees performs not only the work

$$W_1 = 1.23 \times nF \times 0.238 \text{ calories}$$

but also generates the amount of heat $q = 11{,}770$ calories per 1 mole of water.

Consequently in the reverse process -- electrolysis of water -- there will be expended not only the electrical energy W_1 but also absorbed the heat q.

Therefore the amount of heat liberated in the cell will be:

$$Q = V \times nF \times 0.238 - (1.23 \times nF \times 0.238 + q) =$$
$$= V \times nF \times 0.238 - 68{,}330 \text{ calories}$$

Expressing, for convenience of calculation, the subtrahend in units of the same dimensions as the minuend, we have

$$Q = V \times nF \times 0.238 - 1.48 \times nF \times 0.238 =$$
$$= nF \times 0.238\ (V - 1.48)$$

Substituting the amount of electricity nF by current intensity, and multiplying by 3600 (number of seconds in an hour) we have the hourly amount of liberated heat (in calories/hour)

$$Q = \frac{I \times 3600 \times 0.238}{1{,}000} (V - 1.48) = I \times 0.856(V - 1.48) \quad (30)$$

We see that the amount of heat generated depends only on current intensity and cell voltage and increases in proportion to their increase.

Thus the conclusion can be arrived at, that should it be possible to conduct decomposition of water at reverse potential

1.23 the cell would operate endothermically and in order to maintain the thermal equilibrium it would be necessary to supply external heat in the amount of 11,770 calories (q) for each mole of water decomposed.

B. Principles of Design and Operation of Cells for Water Electrolysis

1. Efficient Conditions of Electrolysis

The problem of any efficiently run production, besides providing best working conditions and obtaining a high quality product, is attaining minimum production expenses, that is, least cost of products obtained. Production costs in the present case consist essentially of expenditures for electrical power, labor wages, repairs and amortization of the equipment. It is necessary to strive for such a regimen of the technological process at which expenditure of electric power, which constitutes the primary factor which determines the cost of electrolysis, is at a minimum. The cells must have large volumetric output, they must be cheap and be readily maintained. Fulfillment of these conditions constitutes a very complex technological problem, which is far from being completely solved, if we bear in mind that utilization of power still fluctuates at only about 55 percent.

From the foregoing it follows that power expenditure must be very materially affected by overvoltage at electrodes, gas saturation of electrolyte and its resistance. Decrease of overvoltage can be achieved by increasing electrolysis temperature, by selection of suitable material for the electrodes, and by decreasing current density.

However, increase of temperature, under conditions of electrolysis at normal atmospheric pressure, is limited, as is apparent from the diagram shown in figure 78, by the boiling temperature of the electrolyte and increased corrosion of iron parts of the cell. Selection of electrode material is also limited by economic factors, and in practice the cells are constructed solely of steel and iron coated within individual areas with nickel.

The most expedient measure, therefore, is decreasing current density at the electrodes, which in practice is attained by various constructive embodiments and electrode processing methods, intended to provide increased surfaces. Thus, for example, the electrodes are subjected to sand blasting; the cathodes are coated with molten oxides of iron which on reduction form a layer of spongy iron, or, finally, the electrodes are galvanically coated with iron or nickel containing sulfur, and with metallic alloys.

Gas saturation can be decreased by increasing the distance between the electrodes and decreasing current density. But both these measures cannot be considered efficacious since the first by increasing ohmic resistance of the electrolyte correspondingly increases power expenditure, while the second decreases output of the cell. One strives to decrease gas saturation by a choice of an effective form of the electrodes and by an increase of electrolyte circulation velocity, so as to remove rapidly the gas bubbles from the path of the current. It has also been proposed to add certain ingredients to the electrolyte, for instance to add finely powdered graphite, in the presence of which small gas bubbles combine into larger ones and are more rapidly removed from the electrolyte.

Electrolysis under increased pressure also decreases gas saturation.

Decreased ohmic resistance of the electrolyte is achieved, besides the choice of a solution concentration having maximum conductivity and increased electrolysis temperature by lessening the distance between electrodes. But since shorter distance between electrodes increases gas saturation, perforated or reticulate electrodes are used in these cases so as to render them permeable to gases.

2. Electrode types

The great variety of electrode designs for use in hydrogen cells, which have been proposed and are used in electrolysis practice is due precisely to efforts aimed at attainment of minimum power expenditure with concomitant increase of the output of the cell. Let us review the most important designs which have found utilization in practice.

Simple Plate Electrodes

An electrode of most primitive design consists of a smooth iron sheet from 1.5 to 2 millimeter thick, with two iron rods welded on, which are used to suspend the electrode in the cell and to conduct the current. Such a construction being most simple is of poor efficiency from the standpoint of measures tending to decrease voltage. Gas saturation, on use of such electrodes, will be very substantial; it will be the more pronounced the greater the current density and the height of the electrode. Therefore such electrodes are of small height which must not exceed one half of their length. Current density at the electrodes must also be low (from 200 to 300 ampere per square meter).

Double Plate Electrodes

The electrode (figure 79) consists of two flat parallel sheets, provided for added strength with embossed ribs. The sheets are 2 millimeters thick, the distance between the sheets is 6 millimeters. The size of the sheets is 1000 x 1000 millimeters. An iron rod is riveted to the sheets for suspending them. Current is supplied through a copper bus bar.

Considerable height of the electrode unavoidably increases gas saturation especially in the upper part of the cell, were it not for the fact that the design of the electrode promotes circulation of the electrolyte along the working surface of the electrode. The working faces of the electrode are only its outer surfaces; the inner surfaces are inactive, and the electrolyte between the sheets remains free of gas bubbles. The density of the electrolyte at the outer surfaces of the electrode becomes lower, due to the presence of gas bubbles, than that of the electrolyte between the sheets. Hence electrolyte between the sheets flow downward, forcing the electrolyte at the outer surfaces to rise upward and carry the gas bubbles out of the path of the current.

Thus the design of the double electrode promotes decreased gas saturation. This however is still insufficient for achieving a considerable voltage reducing effect within the electrolytic bath and for that reason electrodes of this type are used with low current densities (about 400 amperes per square meter).

Figure 79. Double plane electrode.

Laminary Electrodes

In electrodes of this type an attempt is made to decrease the working surface of the electrode thereby decreasing the effective current density. Laminary electrode (figure 80) consists of vertically disposed parallel narrow iron strips 1. The strips are disposed at an equal distance from one another, which is attained by means of iron rings 2 located between them. All the strips are held together as a unit with bolts 3. The electrode is suspended on iron rods 4 which serve also to conduct the current. Some electrodes of this type consist of a very large number (up to 360) strips. An electrode 1100 millimeters long and 965 millimeters high, consisting of 360 strips, 22 millimeters wide and 0.8 millimeters thick has an effective surface of 18.32 square meters, that is exceeds nine times the surface of an electrode of identical lengths and height, but shaped in the form of a flat sheet.

Current density on such an electrode varies over its surface. It reaches highest value at the end surfaces of the strips and decreases with increasing distance from end toward the middle portion of the strip. Therefore the mean density of current on the electrode decreases not nine times in comparison with the plate electrode, but somewhat less, but is still considerably lower. Use of laminary electrodes apparently also decreases somewhat gas saturation of the electrolyte in the path of the current and by so doing also promotes voltage decrease in the cell. In view of their extensive surface area laminary electrodes permit application of a considerably higher density of current, up to 1500 amperes per one square meter of geometric projection, that is, about five times more than that of a simple plane electrode.

Figure 80. Laminary electrode. 1 - iron slats; 2 - iron rings; 3 - bolts; 4 - iron rods.

Louvered Electrodes

In all of the hitherto described electrodes the gas saturation increases with decreasing distance from the surface of the electrolyte, and the resistance of the electrode in the upper portion of the cell is considerably greater than in the lower. In the louvered electrode (figure 81) this disadvantage is eliminated. The electrode consists of two iron bars of square cross section terminated at their upper end by circular cross section rods. These bars are used as supports of the electrode and as current conductors. Welded to both sides of the bars are iron strips disposed at a certain angle with respect to the vertical axis of the bars. The strips are positioned one underneath the other in close proximity, so that they are separated from one another by narrow slanted slits. Gas bubbles on detaching themselves from the strip rise upwards and impinging upon the next-above strip, slide along its inclined surface into the inner space of the electrode within which they then rise to the surface of the electrolyte.

Figure 81. Louvered electrode.

Thus, in theory, no gas bubbles enter the space between consecutive electrodes -- anode and cathode, and are so completely removed from the path of the current. In the path of the current between strips there are present but a few bubbles, and their number is practically the same at the lower and at the upper portion of the electrode. This arrangement unquestionably greatly decreases the harmful effect of gas saturation. In addition there takes place circulation of the electrolyte, upwards inside the electrode and downwards between two consecutive electrodes, which further facilitates rapid elimination of gas from the electrolyte. Finally, the increase in comparison with a plane surface of the electrode induces decreased current density.

All this makes it possible when the number of strips is extensive to utilize with such electrodes current densities up to 2500 amperes per square meter of geometrical projection of the electrode. A shortcoming of the louvered electrode as well as of the laminary electrode is complexity of construction.

Perforated Electrodes

The desire to simplify and to render less costly manufacture of electrodes while retaining at the same time the advantages of electrodes of extensive surface and permeable to gases, has led to the construction of perforated electrodes.

Figure 82. Perforated electrode.

Such an electrode (figure 82) consists of two iron sheets welded to two iron bars which serve to suspend the electrode and to conduct the current. The iron sheets are 3 millimeters thick and are perforated with a great number of circular apertures.

Although it would appear that perforation would decrease the surface of the electrode, it is possible by adequate selection of apertures diameter and distances between them to attain an increase of the working surface, since in the punching out of the holes a new lateral surface is formed. Furthermore perforation makes possible utilization of the back side of the sheets which increases the overall working area of the electrode in comparison with a plane one. On a perforated electrode a considerable portion of the gas passes into the inner space of the electrode and there takes place intensified circulation of the electrolyte. This decreases gas saturation in the zone between adjacent electrodes and permits to place them more closely together, thereby decreasing the resistance of the electrolyte.

Removal of gases into the internal space, utilization of the reverse side, induced circulation and especially close proximity of the electrodes make it possible to use current densities up to 2500 amperes per square meter of electrode projection. In addition an advantageous feature of perforated electrodes is their greatly simplified manufacture in comparison with laminary and louvered electrodes.

In other designs the same principles are utilized and they differ only in constructional features.

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3. Separation and Removal of Gases

Separation of the Gases

By means of electrolysis completely pure gases can be produced. This requires only a careful separation of hydrogen and oxygen, thereby precluding contamination of one gas by the other as a result of mechanic mixture or of diffusion. Separation of the gases is important not only because it is necessary to produce them in a pure state, but also because a question of safety is involved namely avoidance of detonating gas formation.

The simplest method of gas separation consists in the use of wide, deeply immersed bells as is shown in figure 83. Electrodes 1 and 2 are located inside the iron bells 3 and 4 which are deeply immersed in the electrolyte. To prevent evolution of gases on the external surfaces of the bells, the electrodes are provided with insulators 5. The generated gases rise vertically, enter the bells and are removed separately through suitable gas outlet pipes.

Such a scheme though dependable and simple is not expedient for large industrial cells. Wide bells make it necessary to space the electrodes wide apart and in addition by shielding a large portion of the electrodes lengthen the path of the current. This causes great losses of voltage in overcoming resistance of the electrolyte.

Figure 83. Separation of gases by means of bells: 1 and 2 - electrodes; 3 and 4 - iron bells; 5 - insulators

For this reason in the large modern cells there is used for separation of the gases, only a diaphragm, that is a porous partition, readily permeable to ions but impermeable to small gas bubbles. The electrodes, as this is shown in figure 84, are still placed inside of bells 1 and 2; the lower part of the bells is immersed in the electrolyte but the height of the bells is considerably smaller. At the lower end of one of the bells, and in some cases of every bell, there is provided a bag-like porous diaphragm 3 which completely surrounds the electrode. In such an arrangement the electrodes can be placed considerably closer together, and still the gases practically do not mix if the diaphragm is in good working condition. It is merely necessary to make certain that the electrolyte level in the cell does not drop below the rim of the bell and the diaphragm does not protrude above the electrolyte. Otherwise the gases diffuse readily through the diaphragm.

Figure 84. Separation of gases by means of diaphragm. 1 and 2 - bells; 3 - porous diaphragm.

Diaphragms

Diaphragms used for the separation of gases must meet the following prerequisites: (1) Possess low electrical resistance (2) Be sufficiently dense to preclude passage of gas bubbles through the diaphragm (3) Be sufficiently strong mechanically (4) Be chemically resistant toward the electrolyte.

Asbestos diaphragms: The above listed conditions are most fully met by asbestos fabric, which is used almost exclusively in modern cells. In the manufacture of strong asbestos fabric there is used pure, alkali resistant long fiber asbestos. The best grade is considered to be hand processed "crude" asbestos with fibers from 15 to 25 millimeters long. From the long fibers can be made a strong yarn, out of which the asbestos fabric is woven. The fabric must be closely woven, must appear opaque when viewed against the light and possess sufficient tensile strength. In most cases single plain weave fabric from 1.5 to 2 millimeters thick is adequate. For more heavy duty there is used double twill weave fabric from 3 to 3.5 millimeters thick. Sometimes for increased mechanical strength the weft threads are reinforced with nickel wire 0.16 millimeters in diameter.

The life of an asbestos diaphragm is usually of several years' duration (3-5 or more) if the diaphragm is not subjected in the course of its use to drastic mechanical action, which may take place for example as a result of hydrogen and oxygen pressure fluctuations.

Metal diaphragms: Much less frequently porous metal diaphragms are used. In practice diaphragms of thin nickel foil containing a large number of small apertures (800-1400 apertures per centimeter square) are being utilized. Such a diaphragm is made by electroplating methods. Nickel is deposited by electroplating on a copper matrix the surface of which is covered with minute dot-like recesses. The matrix is coated with an insulating varnish which fills the recesses. When the varnish has dried it is scraped off the surface but is retained in the recesses.

The matrix is then nickel-plated. In the course of this operation the nickel is deposited upon the entire surface of the matrix except at the points retaining the varnish coating. The nickel plated surface is then slightly oxidized and on the oxidized surface the diaphragm foil is then produced, and can be readily removed therefrom. Nickel diaphragms are stronger than asbestos diaphragms but by the action of the electrolyte they also are adversely affected and require periodic overhauling which is effected by fastening patches over the damaged areas.

Metal diaphragms on breaking down may cause short circuiting of the electrodes, and are in this respect less satisfactory than those made of asbestos. For this reason it is dangerous to place the electrodes very close together.

Cooling, Washing and Regulating the Pressure of the Gases

The gases leave the cell at a temperature of 60 degrees-80 degrees, and carry with them, as was pointed out previously, considerable amounts of water vapor. Moreover together with the water vapors there are being entrained particles of the electrolyte in the form of minute droplets and of alkaline mist.

Since removal, with the gases, of large amounts of vapor would cause increased expenditure of distilled water, while removal of electrolyte -- increased expenditure of caustic, an effort is made to cool the gases immediately upon egress from the cell. On cooling the greatest part of the vapor condenses and flows back into the cell. To attain this, cooling with water is resorted to of the covers or of the bells under which the gases collect, gas outlet pipes are made sufficiently long, and finally the gas is made to bubble through a layer of cold feed water. In the latter treatment, purification of the gases takes place simultaneously from a considerable portion of the alkali contained therein and equalization of pressures within the hydrogen and the oxygen compartments of the cell.

Differences of gas pressure in the cell can arise as a result of various conditions; for example, different resistances in the pipe manifolds, formation of liquid seals in the pipes, unequal rate of gas removal, and so forth. At the same time maintenance of a constant pressure of the gases is of great importance, since excessive pressure increase of one gas within the bell may cause lowering of the electrolyte level below the rim of the bell, exposing the diaphragm, or even project the electrolyte over the rim of the cell. Exposure of the diaphragm, as pointed out previously, will cause mixing of the gases, with possible formation of an explosive mixture. On the other hand, frequent and drastic fluctuation of gas pressure by subjecting the diaphragm to excessive mechanical action will result in its rapid deterioration. Hence, regulation of the gas pressure is most important. It can be effected for each individual cell, or more commonly, for a given group of cells.

Figure 85 shows diagrammatically a hydraulic gas pressure regulator in which scrubbing of gases also takes place. The regulator consists of two vessels 1 and 2 connected at their bottom by a junction pipe and filled with water. Oxygen and hydrogen flow through connecting pipes into the vessels of the regulator and after bubbling through a layer of water, pass into the collector pipes. If in the collector pipes the pressure of one of the gases undergoes a change, this has no effect upon the pressure of the gases within the bells of the cell.

Figure 85. Hydraulic regulator of gas pressure.

1 and 2 - connected vessels.

If for example the pressure of the hydrogen increases, water will be expelled from vessel 2, through the junction pipe, into vessel 1. In the vessels there will be established, a difference in level d which will counterbalance the pressure difference between hydrogen and oxygen. But under these conditions the oxygen will bubble in vessel 1, through a layer of liquid having the height K, while hydrogen in vessel 2, through a layer h. Since $h + d = k$, it is obvious that the pressure within the bells will remain the same for both gases. If the junction pipe between the vessels is of sufficiently large diameter, the flow of water from one vessel into the other can take place so rapidly that no appreciable pressure fluctuation will occur within the bells.

4. Water Feed of the Cells

Because of the decomposition of the water, the level of the electrolyte in the cell drops continuously and may descend below the permissible limit, if the cell is not being adequately supplied with fresh feed water. In small installations the fresh water can be added intermittently at intervals of several hours, depending upon the size of the cell volume not filled by the electrolyte. Small periodic changes of alkali concentration in the electrolyte are of no importance since the resistance of the electrolyte is altered but little.

This method, however, becomes impracticable in large installations. In these, addition of water is made automatically. This is done by providing the cells with float controlled level regulators. A common water supply pipe is installed alongside the cells from which individual connections lead to each cell.

Water flows into the cell from a pressure tank. Depending upon the position of the electrolyte level, the float opens or closes the water intake pipe. For simplicity of operation, a single float actuated regulator is provided for an entire group of cells. In such a case the float is contained in a separate vessel connected with the cells by means of a system of pipes. Into this vessel flows the water from the pressure tank; the water level in the vessel is maintained by the regulator at the same height as that of the electrolyte in the cells. This simplification is inconvenient in this respect that it may cause forcing of the electrolyte into the feed system and its passage into other cells. To avoid this it is expedient to install the feed pipes above the cells and to provide inlet pipes extending downward into each cell almost to its bottom.

Feed and automatic regulation of the electrolyte level in the cells which are hermetically closed by means of a cover, can be readily attained by using a pressure regulator the design of which is shown diagrammatically in figure 86.

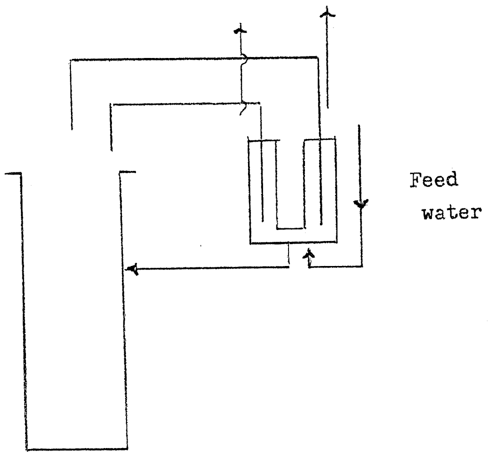

Figure 86. Diagram of regulation of the electrolyte level in the cell. 1 and 2 - gas bubblers

Feed water in the necessary amount is periodically charged, or continuously introduced, into the pressure regulator from which it passes through the pipes into the cell. The gas bubblers 1 and 2, are positioned in the regulator at a height approximately equal to that at which it is desired to maintain the electrolyte level in the cell. The level of the electrolyte in the cell will be below that of the bubblers by a height difference equal to Δh. The value of Δh depends on the density of the electrolyte and the location of the feed pipe outlet and does not depend on the water level and gas pressure in the regulator.

Indeed, let us consider the pressure in the pipes to the left and to the right of the section f, assuming that the pressure of the gases in the regulator is equal to atmospheric

$$p_{H_2} = p_{O_2} = 1 \text{ atmosphere.}$$

Pressure of the gases in the cell, with a scrubbing height h and a density of the feed water γ, is

$$p'_{H_2} = p_{O_2} = 1 \text{ atmosphere} + h\gamma \qquad (31)$$

Then the pressure at section f from the left hand side, if γ' is the density of the electrolyte, will be

$$P_f = 1 \text{ atmosphere} + h\gamma + h'_1\gamma' \qquad (32)$$

and the pressure from the right-hand side:

$$P'_f = 1 \text{ atmosphere} + h\gamma + h_1\gamma \qquad (33)$$

At the state of equilibrium when the liquid does not flow in either direction, we have

$$P_f = P'_f = h'_1\gamma' = h_1\gamma \qquad (34)$$

and

$$h'_1 = \frac{h_1\gamma}{\gamma'}$$

Since,

$$h'_1 = h_1 - \Delta h$$

it follows that,

$$\Delta h = h_1 - \frac{h_1\gamma}{\gamma'}$$

that is, the level of the electrolyte in the cell will tend to be equal with that of the bubbler with decreasing difference between density of solution in the regulator and that of the electrolyte, and also with decreasing height h_1, that is the distance of the feed pipe outlet in the cell from the level of the bubblers.

When γ and γ' are equal, the level of the electrolyte will be that of the bubblers, but cannot exceed that level since γ cannot be greater than γ'. A drop of the electrolyte level below the height h_1' cannot occur, because disruption of the state of equilibrium will be immediately compensated by inflow of water from the regulator, which will take place until the water level in the regulator drops below that of the bubblers.

B. Industrial Cells for the Electrolysis of Water

1. Industrial Cell Types and Their Classification

In the practice of electrolytic production of hydrogen and oxygen there are being utilized, cells of widely different designs, which in spite of their apparent dissimilarities can be segregated into several groups on the basis of design characteristics common to all members of each group.

Cells of all types can be divided into two basic groups: monopolar and bipolar. The common feature of all cells in each group is the system of connecting the cell electrodes to the electrical circuit.

Monopolar cells (figure 87) have a number of parallel electrodes 1. One half of these electrodes is connected in parallel to the positive terminal of electrical circuit. These electrodes constitute the anodes. The other half is connected in the same manner with the negative terminal. These electrodes serve as cathodes. In such a connection system, each electrode considered separately has but one polarity, that is, constitutes either an anode or a cathode.

Figure 87. Diagram of a monopolar cell: 1 - electrodes; 2 - box.

Current intensity in the cell is proportional to current density and the surface of all the electrodes of the same polarity, while the cell voltage is determined by the difference of potential of one pair of electrodes (cathode and anode). Therefore the characteristic electrical feature of monopolar cells is the fact that current intensity in such cells is always many hundred and even thousand times greater than the voltage.

Bipolar cells (figure 88), the same as monopolar, have a number of parallel electrodes 1, which are, however, connected to the circuit in series. Current is conveyed only to the terminal electrodes, - the anode 2 and the cathode 3. From the anode the current flows to the electrolyte, is transferred by the ions to the intermediate electrode 1, imparting to it a negative charge, passes through it and from its opposite side enters again the electrolyte, imparting to this opposite side of the electrode a positive charge. Thus the current flows through the entire cell and reaches cathode 3. The terminal electrodes 2 and 3 are thus monopolar, while all the intermediate electrodes are bipolar, that is, one side of each of them operates as a cathode and the other as an anode.

Figure 88. Diagram of bipolar cell: 1 - bipolar electrodes; 2 - anode; 3 - cathode; 4 - section.

Current intensity in a bipolar cell depends only on current density and the surface of one monopolar electrode (anode or cathode) and does not depend upon the number of bipolar electrodes. Voltage of the cell on the other hand depends on the difference of potential between consecutive electrodes and is directly proportional to the number of pairs of cathodes and anodes. If the difference of potential between anode and cathode is equal to 2 volts, then the voltage of the cell shown in figure 88 is equal to 2 x 6 = 12 volts.

In bipolar cells the characteristic electrical feature is the fact that their voltage is several times ten, or even several times one hundred, over that of monopolar cells, while current intensity is usually considerably smaller. Thus the electrical capacity of bipolar cells exceeds that of monopolar cells by a several times ten factor.

Monopolar and bipolar cells can be divided into box cells and filter-press cells. Monopolar cells are almost exclusively of the box type.

The essential portion of box cells is a container of any suitable shape, holding the electrolyte, into which are immersed the electrodes. The container can be open at the top (in which case the electrolyte is in contact with the atmosphere) or closed by a cover. Closed cells are more complex in construction and of more costly production than the open ones, but in them losses of gas are smaller, the electrolyte is protected from impurities (carbonization by carbon dioxide of the air), and it is possible to produce in them the gases under higher pressure. The container, or box, 2 of monopolar cells (figure 87) is made of iron and must meet only the prerequisites of mechanical and chemical durability. Monopolar electrodes of one of either signs may be in contact with the box, but the box should not be in contact with both the cathodes and the anodes.

The box of a bipolar cell (figure 88) must be made non-conducting for the electrical current. The electrodes must partition the space within the box into a number of sections 4, insulated from one another, and which can be connected only through narrow gas channels and channels for the introduction of feed water into the sections. Construction of such boxes is costly and complicated.

The essential parts of a filter-press bipolar cell (figure 89) are the steel frames 1, rectangular or circular in cross-section, and the bipolar electrodes 2. The electrodes are located between the frames and are separated from them by insulating and sealing gaskets 3. Frames and electrodes are tightly drawn together by means of bolts and form a single cell unit composing any given number of electrodes.

Further classification of monopolar cells can be made by type of electrodes, thus subdividing them into cells with simple plane electrodes and cells with complex electrodes. The latter group composes most monopolar box cells.

Figure 89. Diagram of filter press cell: 1 - steel frames; 2 - bipolar electrodes; 3 - sealing gaskets.

Bipolar filter-press cells can be further subdivided into cells without external circulation.

Finally cells of all types can be divided into cells operating at normal atmospheric pressure, or at a pressure approximately equal thereto, and cells operating at high pressures.

2. Monopolar Cells with Simple Electrodes

Cell with Plane Electrodes

External appearance of a cell with plane electrodes and its internal configuration are shown in figure 90. In an iron box electrodes 1 are disposed in parallel relation made from plane, smooth, sheet iron having a thickness of 2 to 3 millimeters. The anodes are coated electrolytically with a layer of nickel to protect the iron from anodic oxidation and to decrease oxygen overvoltage, which is less on nickel than on iron. The electrodes are suspended from iron rods 2 connecting them to the collecting bells 3 which in their turn are supported by lugs resting on the rim of the box. Rods 2 also serve to conduct the current and are insulated from the bells.

Figure 90. Cell with plane electrodes: 1 - electrodes; 2 - iron rods; 3 - bells; 4 - asbestos diaphragms; 5 - collecting pipes; 6 - manifold pipe lines.

The manner of suspending the electrodes and insulating them from the bells is shown more in detail in figure 91. To the bell 1 there is welded a spacer tube 2, inside of this extends suspension support 3, enclosed in insulator tube 4. Bottom and top of the suspension support are covered by insulating collars 5 and 6. The electrode is fastened by means of nuts 7 between which is held the current conveying bus bar 8.

Figure 91. Suspension of plane electrode: 1 - bell; 2 - iron spacing tube; 3 - support; 4 - isolator tube; 5 and 6 - isolation bushings; 7 - nut; 8 - bus bar.

To effect separation of gases the cathodes are surrounded by asbestos diaphragms 4 (figure 90) fastened to the bottom rim of the hydrogen collecting bells and depending therefrom in the form of open-bottom bags. Bells 3 are immersed into the electrolyte; gas pressure within them must be such as to maintain the electrolyte within the bell at 5-7 centimeters above the lower insulation collar. Hydrogen and oxygen rising vertically collect under the corresponding bells and pass through the outlets into collecting pipes 5 and from these into the manifold pipes 6. The latter are of zigzag shape to promote cooling of gases and condensation of water vapors. Due to the sloping angle of these pipes, the condensed water together with the entrained alkali flows back into the cell. The manifold gas pipes are provided with glass sections with rubber connections, located between each pair of cells by the provision of which electrical leaks are obviated. From the manifold pipes the gases pass into scrubbers where on bubbling through a layer of water they are freed of alkali.

As the electrolyte an 18-20 percent solution of caustic soda is used and much less frequently a solution of caustic potash. Open construction of the cell permits contact of electrolyte with the atmosphere as a result of which there takes place a gradual carbonization of the alkali by atmospheric carbon dioxide and a decrease of the conductivity of the electrolyte. Therefore at periodic intervals, about once every two-three years, the alkali is being replaced, at which time the cell is also cleaned and inspected.

Feeding of water into the cell is done either manually or automatically from a small pressure tank provided with a constant level regulator. The feed tank is connected through pipes with the gas scrubbers, so that in these also the water level is maintained constant, thereby ensuring a constant gas pressure within the bells.

In the event of a breakdown, or of insufficient feed of water, lowering of the electrolyte level can be readily, and sufficiently early detected because the gases begin to escape to the atmosphere, from the cell. This takes place when the electrolyte drops below collar 5 and the gases are afforded a free outlet, through pipe 2, by the leaky connections provided on purpose in this method of attacking the electrodes.

Life of the diaphragm is, on the average, 5-7 years. Electrolysis is conducted at a temperature of 60 degrees. In cells designed for heavy amperage loads, a cooling coil is provided on the bottom for temperature regulation.

Cells are built for different loads (from 166 up to 10000 amperes) in accordance with which dimensions and number of electrodes vary. Cells of 10000 amperes have 41 electrodes; are 1240 millimeters long; 2400 millimeters wide, and 1270 millimeters high. Current density is maintained low -- about 350 amperes per square meter, however the voltage of the cell even at this current density is equal to 2.25 volts, while an increase of the load up to 15000 amperes rises to 2.5 volts.

Diagram of figure 92 shows dependence of cell voltage on ampere load. Power expenditure with a voltage of 2.25 volts amounts to 5.4 Kilowatt-hours per cubic meter of hydrogen at 0 degrees and 760 millimeters of mercury. Purity of the gases: hydrogen 99.5 percent and oxygen 99.0%.

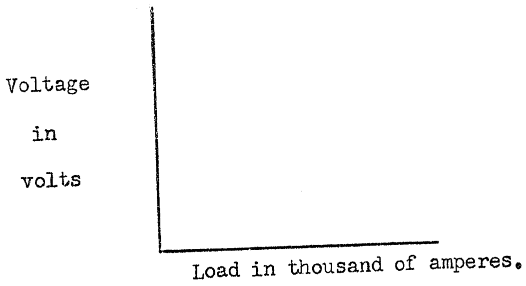

Figure 92. Dependence of voltage on load in cell with plane electrodes.

Figure 93 shows the general appearance of the installation; the zigzag shape of the manifold pipes which is characteristic of these installations can be seen.

Figure 93. Overall view of installation with plane electrode cells.

Open Cell with Double Plate Electrodes

Figure 94 shows the longitudinal and transversal vertical sections of the cell. This is also an open cell, a characteristic feature of which is the simplicity of construction.

Each of the electrodes 1, consists of two plane iron sheets, 1000 x 1000 millimeters in size and 2 millimeters thick, parallel to each other and disposed at a distance of 6 millimeters. To the electrode is riveted an iron rod 2 by means of which the electrode is suspended from the gas bell. Each bell 3 consists of a narrow iron box having a small cupola 4, through which passes the electrode rod, insulated from the cupola and fastened by a nut. Bells 3 are supported by lugs resting on the iron casing of the cell. To the edge of each bell is attached a diaphragm of asbestos fabric, surrounding the electrode. The electrodes are located at a distance from one another, amounting to 50 millimeters at their centers. In order to retain the plane form of the electrodes, in view of their relatively small thickness, the sheets are provided with several embossed ribs 6, which impart rigidity to the sheets. The anodes are nickel coated.

Current is supplied to the electrodes by means of a nickel plated copper bus bar 7 and is carried off by a similar bar from another electrode at the opposite side. The bar is riveted to the sheets of the electrode and passes through the bell 3. It is insulated from the bell and the electrolyte by an eternit bushing and cement lining which seal the point of passage of the bar through the bell and preclude leakage of gas.

Hydrogen collecting in bells 4, passes through opening 8, in the upper part of the cupola, and collects in a single overall collecting bell 9, which covers all of the cupolas of hydrogen bells 4. From the collecting bells the gas passes into the collecting manifold pipes. In the same manner by means of a collecting bell 10, is effected the removal of oxygen.

Figure 94. Diagram of cell with double plane electrodes: 1 - electrode; 2 - iron rod; 3 - gas bell; 4 - cupola of bell; 5 - cell casing; 6 - embossed ribs; 7 - copper bar; 8 - aperture in bell cupola; 9 - collecting bell for hydrogen; 10 - collecting bell for oxygen.

As the electrolyte a solution of caustic soda or potash of suitable concentration is used. The level of electrolyte is maintained above the surface of the electrode bells. Above the surface of the electrolyte are only the cupolas 4. Gas collecting bells 9 and 10 have their lower edge immersed in the electrolyte thereby forming a seal for the gases. The large area of electrolyte in contact with the atmosphere causes, after 2-2.5 years, carbonization of almost one half of the total amount of alkali in the electrolyte. Carbonized electrolyte is removed from the cells and is regenerated (causticized) by treatment with lime. Temperature of electrolyte is maintained at 60 to 70 degrees. Temperature regulation in high-load cells is attained by flowing water over the external surfaces of the cell casing. For this purpose there is installed along the upper edge of the cell wall a perforated water pipe. The water flows from the cell wall on the floor and is then discarded to the sewer.

Feed water is supplied to the cells from a common tank supplying a group of cells and provided with a constant level device. Electrolyte level is maintained by a float actuated regulator, each cell being so equipped.

Cells with double plane electrodes are built for loads of 6000 to 14000 amperes. The 14000 amperes cell has 11 cathodes and 10 anodes. The length of the cell is 1080 millimeters, its width 860 millimeters, and its height 1220 millimeters. Use of double electrodes increases electrolyte circulation, decreasing gas saturation; therefore, in spite of the plane form of the electrodes and almost double height of the electrodes, as compared with the plane electrodes described above, the voltage of the cell with double plane electrodes is somewhat lower.

Figure 95 shows the dependence of cell voltage on current density. The cells are usually operated at current densities of 400-600 amperes per square meter, which results in voltage fluctuation from 2.1 to 2.3 volts.

Closed Cell with Double Electrodes

Electrodes of this cell consist of two parallel plane iron sheets welded to two iron current conveyers. The distance between the sheets of the electrode is about 50 millimeters; that between the working surfaces of anode and cathode about 12 millimeters. The upper part of each sheet is provided with several apertures to permit circulation of the electrolyte. Anodes are nickel plated while the cathodes are sand blasted.

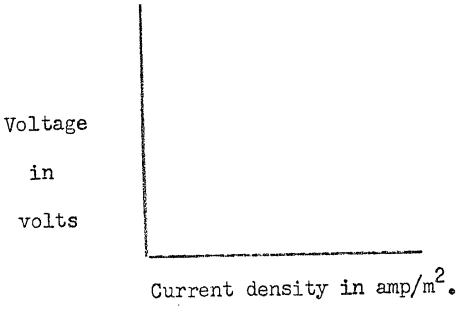

Figure 95. Dependence of voltage upon current density, in cell with double plane electrodes.

The electrodes are fastened to the cast iron or steel cover provided with partitions forming a single overall bell for hydrogen and several bells for the oxygen. Oxygen is removed through outlet pipes from each of the bells. To the oxygen bells is attached a diaphragm of asbestos cloth. In view of the short distance between electrodes (12 millimeters) to avoid adherence of the diaphragm to one of the electrodes small ebonite bolts are inserted through the cloth in several places and are maintained in position by means of ebonite nuts. These bolts are about 12 millimeters long, located between the electrodes they hold the diaphragm in fixed position half way between the electrodes. The body of the cell is made of welded iron sheets 3 millimeters thick, flanged at the top. The cell cover is bolted on to this flange; seal is provided by a rubber gasket.

Normal current density of the cell is 600 amperes per square meter, but due to the decreased distance between electrodes, amounting to 12 millimeters, and the efficient circulation of electrolyte, attained by the same principle as in the cell having double plane electrodes, the voltage is of only about 2.05 volts. Low cell voltage makes it possible to dispense with auxiliary cooling. Spontaneous dissipation of heat through the cell walls holds the temperature within the limits of 40 to 50 degrees. Caustic soda or caustic potash are used as the electrolyte. The cells are fed with distilled water, manually.

Small load cells are built for 1200 and 2400 amperes having three and five electrodes, respectively, but, of course, the possibility of constructing larger capacity cells is not excluded.

3. Monopolar Cells with Complex Electrodes

Cell with Louvered Electrodes

The primary and essential purpose of the design of cells with louvered electrodes is to achieve separation of gases without the use of a diaphragm.

Arrangement of a cell without diaphragm is shown in figure 96. Louvered electrodes 1, the construction principle of which has been described on page 209 [of original document] terminate at the top by wide slats 2. The electrodes are suspended through insulation bushings 3, from the cell cover 4, and held by nuts. The cover is divided in longitudinal direction by iron partitions 5, into a number of compartments which serve as gas bells. The electrodes fastened to the cover are located in the iron casing of the cell 6.

Figure 96. Cell with louvered electrodes: 1 - louvered electrodes; 2 - slats; 3 - isolation; 4 - cell cover; 5 - iron partitions; 6 - iron cell casing; 7 - outlet pipes; 8 and 9 - manifold gas collectors.

The electrolyte is maintained at such a level that the gas bells are immersed into it to a depth sufficient to form a hydraulic seal. The gases are removed through exit pipes 7 and collectors 8 and 9 into a common main. Gas bubbles on detaching themselves from the slats of the electrode rise vertically and encountering the slat disposed above slide along its surface into the inner space of the electrode without penetrating into the space between the electrodes. The saturation of the inner space of the electrode with gas causes intensified circulation of electrolyte which promotes the sucking-in of gas bubbles into the inner space of the electrode. The gas emulsion on rising reaches the interior of the bells: at the electrolyte surface the gases separate from the liquid which descends again into the interelectrode space.

On using louvered electrodes it is possible under certain conditions to separate the gases without resorting to a diaphragm. However it is readily apparent that completeness of gas separation and faultless operation of such a device will depend to a great extent upon the maintenance of a constant gas pressure within the bells. On fluctuation of the pressure the liquid within the bells will fall and rise, disturbing the circulation and expelling the gases from the inner space of the electrodes into the area between the electrodes. Good separation is attained only in small cells, at limited loads, that is precisely in those instances when it is easy to ensure constant pressure of the gases. In large industrial installations fluctuation of pressure always takes place, if only for the reason of different resistances of gas pipe lines, formation of liquid seals in the pipe lines, unequal gas removal, and the like; as a result of which operation without a diaphragm is found to be unsatisfactory.

Therefore in later designed cells louvered electrodes are retained but only for the purpose of decreasing gas saturation and to increase the surface areas; to obtain separation of the gases the cathodes are surrounded by a diaphragm of asbestos fabric suspended from the rim of the gas bells.

Cells with Laminar Electrodes

Electrodes used in these cells consist of a large number of vertically disposed thin and narrow non strips, fastened together by means of bolts.

A cell of this type is shown in figure 97. The iron casing 3 is closed with a cover 4, sealed either by means of a hydraulic seal or a flange closure. The cover is provided with partitions forming the bells to which are suspended asbestos diaphragms closed at the bottom. For the circulation of the electrolyte, small round openings are provided at the lower end of the diaphragm.

Figure 97. Cell with laminar electrodes: 1 - laminar electrodes (cathodes); 2 - clamping bolts; 3 - iron cell casing; 4 - cell cover; 5 - rods for suspension of cathodes (current conductors); 6 - anodes; 7 - lugs for fastening of anodes; 8 - negative current bar; 9 - gas outlet pipes; 10 - connecting channel for hydrogen.

Inside the diaphragm bag are located the laminar cathode 1, suspended from the cell cover by means of rods 5, which serve as current conductors. Anodes 6 located outside of the diaphragms are fastened by means of bolts and lugs 7 to the cell casing. Correspondingly the current conducting positive bus bar is fastened to the cell casing, while the negative one 8, to the cathodic conductor 5. With this system of electrode attachment the cover has fewer current conductors for the electrodes which simplifies assembling work. Moreover the cover has fewer sealings, and finally a more even distribution of current to the electrodes is obtained.

The cell cover has only two gas outlets 9: the right-hand outlet for oxygen, which collects between the hydrogen bells, and the left-hand outlet for the removal of hydrogen; to make this possible all the hydrogen bells are connected inside the cell by channels 10.

As the electrolyte there is used a solution of caustic soda or caustic potash. Due to the closed construction of the cell, the electrolyte is not in contact with the atmosphere and is not carbonized. Increased surface of the electrodes makes it possible to operate at high current densities. The cells are built for loads up to 18000 amperes. Average voltage of the cell at a 10000 amperes load is 2.19 volts. Purity of the gases: hydrogen 99.5-99.9 percent and oxygen 99.5 percent.

Cells can be installed in series of 250-350 cells with a current feed of voltage from 500 to 700 volts. To save floor space the cells can be installed in several tiers.

A somewhat different construction of a cell of the same type is shown in figure 98. This cell operates at very high current density, and accordingly the electrodes are positioned very closely together and provision is made for intensive electrolyte circulation. The cell casing 1 is hermetically closed by cover 2 bolted to the casing flanges. Welded to the cover is a single oxygen bell 3. To the flanged rim of the bell is fastened a rectangular iron frame 4 having welded on sections 5 of angle iron forming an inversed trough. To the angle iron ledge are fastened by small bolts diaphragm bags 6, open at the bottom, and made of asbestos fabric, which surround the anodes 7.

Anodes and cathodes are assembled of iron strips 11, which are 25 millimeters wide and are 0.25 millimeters thick in the cathode and 0.63 millimeters thick in the anode. Round protuberances are embossed on the strips, their height being 1 millimeter in the cathode and 1.59 millimeters in the anode, which maintain the strips at an equal distance from one another. The cathode consists of 600 strips and the anode of 220. After being assembled the anodes are nickel plated. The strips are welded at one end to the current conductor plates 8. The entire electrode is also held together by two bolts passing through suitable apertures in the strips. The electrodes are suspended from the cell cover by means of iron rods which are welded to the current conducting plates 8. Location of the rods which serve also to conduct the current is such that the rods supporting the anode are within the bell while those of the cathode are outside of it.

Figure 98. Cell with slat electrodes for high current density operation: 1 - cell casing; 2 - iron cell cover- 3 - common oxygen bell; 4 - iron frame; 5 - sections of angle iron; 6 - diaphragm bags; 7 - anodes; 8 - current distributing plates; 9 - gas scrubbers and coolers; 10 - empty diaphragm bag; 11 - iron electrode strips.

The anodes, as was mentioned, one located within the diaphragm bags, hence the oxygen passes inside the bell. The rising hydrogen is led by the angle iron trough into the space between the bell and the cell casing. The gases then pass into scrubbers and coolers 9. Here the gases are cooled, are freed of alkali and then pass into the manifold pipe lines. Water which condenses in the scrubbers flows off through syphon tubes extending to the bottom of the bell and is returned to the cell into the cathodic or the anodic section respectively.

Forced circulation of electrolyte is produced in the cell by the use of an empty diaphragm bag 10, which hangs parallel to the electrodes from the edge of the bell. The electrolyte separated from the oxygen, flows through the bag to the bottom of the cell, displacing from the space between the electrodes the lighter electrolyte containing gas bubbles.

The electrolyte used is a solution of caustic potash. The bell is immersed in the electrolyte to a depth sufficient to ensure formation of an adequate hydraulic seal. Distilled feed water flows into the cell through an inlet pipe welded to the cell casing. Lowering of the electrolyte level below the normal limit is detected by the noise caused by the gas escaping through the syphon tubes into the scrubbers 9. Electrolysis is conducted at 55-65 degrees.

Cell with Mesh Electrodes

Characteristic features of this cell (figure 99) are the design of the electrodes and the method of gas removal from the cell. Electrodes 1, are made of a double iron screen welded to the current conducting plate 2. At the bottom the screens are welded to a small channel iron bar, and have to increase their rigidity, several spacers 3. Dimensions of the electrodes are: height 1300 millimeters, width 1000 millimeters, thickness 50 millimeters. The iron mesh of the anodes is nickel plated. The electrodes are supported by ten current conductors from the gas collecting bells and are electrically insulated from the bells.

Figure 99. Cell with screen electrodes: 1 - screen electrodes; 2 - current distributing plate; 3 - screen spacers; 4 - lugs supporting gas collecting bells; 5 - outlet pipes for oxygen and hydrogen; 6 - collecting pipes for the gases; 7 - vertical extensions of collecting pipes; 8 - bell pockets; 9 - bell in-run strip; 10 - manifold gas pipes; 11 - rubber sections for insulation of cells from pipe lines.

Gas collecting bells are supported by lugs 4 resting on the rim of the iron cell casing. The cell casing has two welded in outlet pipes 5 for the removal of hydrogen and oxygen. Inside the cell to these outlet pipes are welded collecting pipes 6, provided with vertical extensions 7. The number of these extensions in the oxygen collecting pipe is equal to the number of the anodes, in the hydrogen collecting pipe it is equal to the number of cathodes. Each bell has a pocket 8, into which projects the extension of the gas collecting pipe. The hydrogen collecting bells support the diaphragm which is open at the bottom. The diaphragm is fastened to the bell by bolts and shaped strips 9. Oxygen collecting bells have no diaphragm and are somewhat shorter than the hydrogen bells. The bottom edge of the oxygen bell extends below the upper rim of the strip 9. This prevents the escape of a portion of the oxygen into the space between two adjacent bells.

Gases collecting within the bells pass through the pockets and outlet pipes 7 into gas collecting pipes 6 and then through an inlet pipe enter the manifold gas pipelines 10, supported by the cell casing. To avoid leakage of current, the cells are insulated from the pipeline by rubber inserts 11.

The electrodes are maintained at a distance of 65 millimeters from each other at their center, which with a 50 millimeter thickness of the electrode corresponds to a distance of 15 millimeters between cathode and anode surfaces. The cell operates at a current density of 450 amperes per square meter and at a temperature of 65 degrees; the voltage under these conditions is of 2.05-2.1 volts. The load of the cell is 5000 amperes. This load can be increased, of course, if the number of electrodes is increased.

In comparison with other cells of the open type the cell possesses the advantage that due to the original method of gas removal it is most readily assembled and dismantled and has an extensive electrode surface; but in comparison with a cell having double plane electrodes, the circulation of electrolyte is not as good. The difficulty of producing a good deposit of nickel on an iron screen results in a gradual dissolution of the iron anodes, a progressive metallization of the diaphragm and formation of a spongy iron deposit on the cathodes. Metallization of the diaphragm, resulting in obstruction of the pores by the iron deposit, increases its resistance and makes it necessary to wash periodically the diaphragm.

Cell V-3

In the USSR cells have been designed of several types for different loads. Cell V-3 with double perforated electrodes is intended for use at large hydrogen producing installations and is accordingly designed for a load of 14000 amperes.

The arrangment of the cell is shown in figure 100. The cell casing 1 is of welded sheet iron 5 millimeters thick and it is provided at the top with an angle iron flange. The cell is closed hermetically by a bolted cover, sealed by means of an asbestos-rubber cement gasket coated with asphalt. Fastened to the cell cover are 21 electrodes: 10 anodes and 11 cathodes. The anodes are located inside the gas collecting bells 15, welded to the cover, and are surrounded by an asbestos diaphragm which is attached to the bottom rim of the bells by means of strips and bolts.

Oxygen passes from the bells into collecting pipe 2, the hydrogen from the space between the bells into the parallel pipe 3. The hot and moist gases carrying droplets of electrolyte, pass for cooling and scrubbing into small columns 4, which are identical in construction for both the hydrogen and the oxygen. The gas scrubbing columns are supported directly on the cell and consist of an iron cylinder 150 millimeters in diameter and 1000 millimeters high. Inside the column is a cooling coil 5, a gas bubbler 6, and a screen 7, for breaking up the foam. From collecting pipe lines 2 and 3 the gases having a temperature of about 70 degrees enter into their respective scrubber (under the bubbler). The gases then pass through a layer of water (or more accurately a weak alkaline solution) filling the scrubber; thus they are washed free of droplets of entrained alkali and cooled to 30 degrees. The cooled gases pass through screen 7 and into the corresponding manifold pipe lines 8.

Figure 100. Cell V-3: 1 - cell casing; 2 - collecting pipe for oxygen; 3 - hydrogen pipe; 4 - column for gas scrubbing; 5 - cooling coil; 6 - gas bubbler; 7 - foam breaking screen; 8 - gas pipe manifolds; 9 - cooling coils; 10 - water pipeline; 11 - cooling water pipes; 12 - sewer discharge; 13 and 14 - cooling water valves; 15 - gas collecting bells.

To maintain the temperature within the cell at the normal level of 70 degrees the cell is equipped with two cooling coils 9, through which circulates cooling water which flows from pipe 10 through two parallel pipes first into the coils of the scrubbers and then through pipes 11 into the cooling coils of the cell; from the coils the water is discharged through a funnel into sewer pipe 12. Cooling water system is provided with valves 13 and 14 by means of which cooling of the cell can be cut out and only the scrubbers cooled.

The gas scrubbers, as described on page 214 [of original document] serve also concurrently for automatically supplying the cells with distilled feed water, for maintaining the electrolyte level at the proper height, and for equalizing hydrogen and oxygen pressures within the bells. The cell can operate with gas pressure fluctuations in the manifold collectors up to 500 millimeters of water column height. Under such conditions, inside the cell the pressure of hydrogen and oxygen remains at a constant value equal approximately to 600-650 millimeters of water.

Design of the electrodes of cell V-3 (figure 101), differs somewhat from the designs of previously discussed electrodes. The electrodes, anodes and cathodes, consist of two perforated iron sheets, 2 millimeters thick, measuring 1000 x 1000 millimeters, disposed at a distance of 30 millimeters from each other. The sheets of the electrode are welded to three iron current conductors 1. Into the top part of the current conductors are screwed copper pins 2 by means of which the electrodes are fastened to the cover and the current is led in. At the point of passage of current conductors through the cover, seals and insulation of conductors from the cover, are provided by asbestos-rubber cement washers 3 and vulcanized fiber bushings 4, fitted over the lead in pins.

Figure 101. Electrodes of cell V-3: 1 - iron current conductors; 2 - copper pins; 3 - asbestos-rubber cement gaskets; 4 - fiber bushings.

As is apparent from the description of monopolar cells, the amount of power needed in their operation does not exceed 35-40 Kilowatts. Consequently at large hydrogen producing installations there are in operation several hundred individual units, which require a large area of buildings, large expenditures for leads, installation of long pipe lines and finally complicates servicing. On equipping small installations with monopolar cells there arise difficulties with selection of direct current sources, since they require current of high intensity and relatively low voltage. Installation of mechanical converters of such characteristics is costly, and the machines themselves require much space. The use of mercury rectifiers is here not expedient because of their poor efficiency in low voltage operations.

Therefore in spite of the very simple construction, ready assemblage and maintenance of the monopolar cells, in recent years the bipolar cells are being utilized increasingly more often.

4. Bipolar Cells

Box Cell

The main difficulty in the construction of a bipolar box cell is the arrangement of the box which must not be a conductor of electricity. In the cell of figure 102, the box consists of separate frames 1 and 2 bent to a rectangular U-shape. The channels of frames 1 face inwardly those of frames 2 toward the exterior of the box. The frames are positioned in such a manner that their channels overlap but are not in contact with one another. To the terminal channel-iron frames are welded iron sheets 3 and 4 which form the end walls of the box. The space between the frames is filled with special composition concrete which holds the frames together and renders the box impermeable to water. In more recent designs between the side walls of the frames are inserted rubber gaskets in lieu of the concrete and adjacent frames are separated from each other by wooden edges. Thus a single open top box is formed, the side walls and bottom do not conduct the current because the frames which form them are insulated from one another. Into the grooves between adjacent frames 2 are inserted bipolar electrodes 5, and stretched over frames, diaphragms 6.

Figure 102. Box cell: 1 and 2 - channel bar frames; 3-4 - iron sheet forming end walls of box; 5 - bipolar electrodes; 6 - diaphragms; 7-8 ledges of angle iron; 9 - parts of electrodes consisting of offset sheets; 10 - perforated asbestos fabric; 11 - gas collecting bells.

Bipolar electrodes 5 consist of a solid iron sheet provided at the top with two angle iron ledges 7 and 8, and of two offset perforated sheets 9. Terminal monopolar electrodes have but one offset sheet each. The diaphragm frame holds an asbestos fabric. The frame is also provided at the top with two angle iron ledges. Electrodes and diaphragm frames are insulated from the channel bar frames by an asbestos cord packing. The cell is divided by the diaphragms into separate sections each of which contains one bipolar electrode.

On the ledges 7 and 8 of each adjacent frame and electrode is placed, as a seal and for electrical insulation, a piece of asbestos fabric 10, provided with apertures. On the asbestos fabric are placed gas collecting bells 11, within each of which accumulates the gas from each offset sheet of a bipolar electrode. Electrolyte is charged to the cell up to a level such that the bottom rims of the bells are immersed therein so as to form a hydraulic seal. From the bells the gases pass through connecting pipes into collecting pipes from which they pass into alkali separators which can be seen in figure 103, and then into manifold collectors.

Figure 103. External appearance of box cell.

Temperature of the electrolysis is 60-70 degrees.

With a current density of about 500-600 amperes per square meter, the voltage across one section is about 2.1-2.2 volts. To maintain, under these conditions, the temperature at 60 to 70 degrees, it is necessary to cool the cell. This is done by placing the cell in a wooden box through which flows cooling water.

The yield, on the basis of current, is of only about 88-90 percent, due to electrical leaks and losses of gases. The purity of the gases is: 99.8-99.9 percent for hydrogen and 98-98.5 percent for oxygen. Expenditure of power at a current density of 500 amperes per square meter, and using caustic potash, is 5.7 Kilowatt-hours per cubic meter of hydrogen (at 0 degrees and 760 millimeters of mercury), and at a double current density -- about 6 Kilowatt-hours.

Box cells are built for current intensities up to 1500 amperes. A cell for 800 amperes consists of 15 electrodes and 14 diaphragms with the central electrode sheet measuring 1100 x 990 millimeters and a box of the size 2000 x 1350 x 1800 millimeters. The cell voltage amounts to 27 to 30 volts.

Multiple tier Cell

Another type of bipolar box cell is the multiple tier cell. Essentially this cell consists of a combination of several monopolar cells disposed one above the other.

Figure 104 shows a double tier cell. The electrodes 1 are fastened at the bottom of each cell, while the electrodes 2 are suspended since they are fastened to the bottom of each of the cells located above them. Only the electrodes 2 are provided with gas bells 3 and diaphragms 4. Gas from the bells collects in the space above the intermediate bottom 5, while the other gas collects in the space below the intermediate bottom. The iron casing of each cell rests upon the casing of the cell below it, with an insulation packing being inserted between them.

Figure 104. Multiple tier (double) cell.

1 and 2 - electrodes; 3 - gas bells; 4 - diaphragms; 5 - intermediate bottom.

The cells can comprise as many as ten tiers, which greatly reduces floor space occupied by the installation.

Current is led in through bus bars only to the bottom cell of the column, and is conveyed from the top cell to the top cell of the adjacent column. Each column, with a rated load of 6400 amperes, covers an area of about 5.6 square meters, including the necessary service space. Height of a 10-cell column is of about 8.5 meters.

Filter-press Cell with Plane Electrodes

The first industrial embodiment of bipolar filter press cell was not extensively used because of defects which caused considerable electrical leakage and mutual contamination of the gases.

Following design improvements bipolar filter press cells have found wide utilization.

Figure 105 shows plan and side views of the filter press cell.

Figure 105. Filter press cell with plane electrodes.
1 - electrode; 2 - clamping bolts; 3 - stationary plate;
4 - mobile plate; 5 - gas separating column for oxygen;
6 - gas separating column for hydrogen; 7 - cooler;
8 - gas removal pipes; 9 - insulators.

The electrode 1, consists of a plane iron sheet, up to 2 millimeters thick, nickel plated on the anode side. At the upper part of the electrode are provided apertures for the passage of gases, and at the lower part apertures for a flow of the electrolyte and its passage into the cathode and anode compartments of the sections. The diaphragm frame is made of channel iron. Held in the frame is a diaphragm of nickel foil 0.1 millimeters thick, with numerous apertures (900-1000 per square centimeter) less than 0.1 millimeter square in size. The upper part of the diaphragm, above the electrolyte level, is not perforated to avoid mixing of the gases.

The diaphragm frame has also apertures for the passage of gases and electrolyte.

Electrodes and diaphragms are disposed in alternating order. To provide electrical insulation and a hermetic seal between them, asbestos cord saturated with asphalt is used as a packing.

A number of thus arranged electrodes and frames is tightly connected into a unit, similar to a filter press, by clamping bolts 2, with thick terminal steel plates, plate 3 fixedly connected to the base, and plate 4 which is movable on rollers along a slideway. Each diaphragm frame with the adjoining electrodes constitutes a section with a diaphragm. Apertures in electrodes and frames form, lengthwise through the entire cell, two gas channels at the top and two channels for the electrolyte at the bottom.

Gases formed in the sections together with electrolyte foam enter the corresponding channels and passing through apertures in plate 3, enter the gas separation columns 5 and 6, for oxygen and hydrogen, respectively. The gases rise into the upper part of the columns, where they are washed free of electrolyte drops, by being bubbled through a layer of distilled water, after which they pass through pipe lines into collectors. The hot electrolyte freed of gases flows down into cooler 7, in the lower part of columns 5 and 6 and after being cooled enters the lower channels of the cell and through these into the individual sections.

Thus the electrolyte circulates continuously through the cell and the gas separation columns. This circulation is induced by the difference in density between electrolyte in sections of the cell and in the cooler 7. In the sections the electrolyte has a lower density because of gas saturation and is thus displaced by the heavier column of electrolyte in cooler 7. Due to the circulation of electrolyte excess Joule-effect heat is dissipated from the cell and temperature within the cell is regulated, and also with sufficient circulation velocity the gas saturation is decreased.

Feed water is supplied through a funnel into the upper part of the gas separation columns, where it is utilized first to scrub the gases and is then combined with the electrolyte in the cell.

The gas separation columns being connected with each other by a pipe, also serve as gas pressure regulators. On considerable lowering of the electrolyte level in one of the gas separation columns because of a pronounced difference of hydrogen and oxygen pressures, the gas escapes to the atmosphere through pipe 8. The same pipe connected by means of a three-way cock with the gas pipe lines, is also used to release insufficiently pure gases into the atmosphere.

The cell is installed on insulators 9 and rests on them supported by the lower clamping bolts. Every tenth electrode rests on these bolts through two lugs and underlying insulation pads. The remaining electrodes and frames are held in position solely by compression. Terminal plates and clamping bolts are insulated from one another from the frames and the electrodes. Current is supplied only to the terminal electrodes. The number of sections as well as their diameter depends upon the output of the cell.

In large models the number of sections reaches 115. With 88 sections with electrodes 1.8 meters in diameter the length of the cell is 8 meters and its height, measured from the floor, 2.5 meters. With an average voltage of 2.5 volts, across one section, the cell voltage amounts to 220 volts. The cells operate at current densities from 650 to 700 amperes per square meter and at a temperature of 65-80 degrees.

As the electrolyte, a 28 percent solution of caustic potash is used. With the cell in a good condition, voltage across a section is of 2.35-2.4 volts. In the course of operation pores of the diaphragm become clogged and voltage increases to 2.5 or even 2.6 volts. Purity of gases: hydrogen 99.2-99.6 percent, and oxygen 98-98.7 percent.

Figure 106 shows the external appearance of the filter press cells. Usually into one bank are connected, in series, two cells, supplied with current of 1000 to 1500 amperes and a voltage of 400 to 500 volts. Output of a 106 section cell with a 1500 amperes load amounts to 65 cubic meters of hydrogen per hour.

Figure 106. General view of filter press cell installation.

Cell with Offset Electrodes

Successful operation, in practice, of filter-press cells with plane electrodes and increasing demand for pure hydrogen have prompted further improvements of bipolar filter press cells, aimed primarily at increasing their output and the current density.

Figure 107 shows diagrammatically electrolytic units with off-center electrodes of a high output cell producing up to 500 cubic meters of hydrogen per hour. Each section consists of a steel diaphragm 1, of rectangular cross section approximately 2300 x 1650 x 50 millimeters, made from iron bars of a special complex T-like cross section design, welded together. To the ledge 2, of the bar is fastened by means of steel strips and rivets, the diaphragm 3 made of heavy asbestos fabric, containing for added strength interwoven nickel-steel wires. Electrode 4 consists of the basic electrode -- a solid steel sheet 5 millimeters thick, and two offset electrodes -- perforated sheets 5 and 6 each 3 millimeters thick which are fastened to the middle sheet with tie rods. The offset electrode forming the cathode is attached at a greater distance from the middle sheet than the other offset electrode forming the anode. The different spacing of the offset electrodes corresponds to the difference in volume of hydrogen and oxygen formed on the electrodes. At the top of the frame are provided openings for removal of gases into which are welded steel pipes 7. To the ends of these pipes are welded steel rings 8, forming the collector channels for the gases. Between frames and the middle sheets of the electrodes, and also between the rings are inserted insulating sealing gaskets. On clamping the frames together by means of bolts, the sections are sealed hermetically, that is no leaks of electrolyte occur at the points of junction.

Figure 107. Section of cell with offset electrodes. 1 - steel diaphragm frames; 2 - ledges; 3 - diaphragm; 4 - electrode of solid steel sheet; 5 - offset perforated electrodes; 7 - steel pipes for gas removal; 8 - steel rings.

The assembled cell is shown in figure 108. In the middle chamber intended for the cooling of electrolyte and separation of the gases therefrom. On both sides of the middle chamber are located the electrolytic sections 1, held together by four clamping bolts 2, between the compression plates 3. Steel disk springs 4, ensure the resilience of the entire system.

Figure 108. Cell with offset electrodes in assembled condition: 1 - electrolytic sections; 2 - clamping bolts; 3 - pressure plates; 4 - steel disc springs; 5 and 6 horizontal gas collecting cylinders; 7 - pipe connecting cylinders with gas cupolas; 8 - outlet pipes; 9 - three-way cocks; 10 - pipes leading to collecting bells; 11 - pipe leading to atmosphere; 12 - insulating glass section; 13 - reservoir for compensation of electrolyte volume increase; 14-15 - porcelain insulators; 16 - filter for electrolyte purification; 17 - feeding channel; 18 - pipeline with valve; 19 - bus bar for conveying current to terminal electrodes.

In the cell are distributed horizontal gas collecting cylinders 5 and 6, for the scrubbing and cooling of the gases, connected through pipe 7 with the gas cupolas of the middle chamber. To the gas collectors are welded connecting pipes 8, with three-way cocks 9, which make it possible to pass the gases either into the assembly collectors through outlet pipe 10, or to discharge them into the atmosphere through pipe 11. The iron outlet pipes are fitted with glass insulating sections 12, to prevent current leakage. At the bottom, under the gas collecting cylinders is located reservoir 13 for compensating volume increase of electrolyte caused by gas saturation on starting operation of the cell. The cell is placed on procelain insulators 14, onto which rest the two lower clamping bolts.

These bolts support the diaphragm frames each of which rests on two porcelain insulators 15, which can slide along the bolts when the cell is being assembled. Below the middle chamber is installed filter 16, for purification of the electrolyte from extraneous admixtures such as, for example, fibers of the diaphragm and the like adventitious impurities. For introducing the cooled electrolyte from the middle chamber into the sections, use is made of feeding channel 17 with which is connected each of the sections. Cooling water is supplied, and also drained, through pipelines equipped with valves 18. Current is conveyed only to the terminal electrodes through bus bars 19.

A cell having an output up to 500 cubic meters of hydrogen per hour consists of 160 sections, and is 12 meters long, 2.6 meters wide and 5 meters high. At a current intensity of 7500 amperes the current density is 2500 amperes per square meter. On using as electrolyte a 26-27 percent solution of caustic potash and at a temperature of electrolysis of 75-80 degrees, voltage across a section amounts to 2.18-2.2 volts which gives a voltage across the entire cell of about 350 volts and an input of approximately 2000 kilowatts. Power expenditure amounts to 5.32-5.37 Kilowatt-hours per cubic meter of hydrogen.

Cell Without Electrolyte Circulation

A cell without circulation of the electrolyte while retaining all the advantages of modern filter press cells, is favorably differentiated from them by its simplicity of construction. Sections of the cell are made of ordinary channel bar iron; external circulation of electrolyte is absent; as diaphragm there is used a heavy asbestos cloth which contains no nickel wires.

Figure 109 shows the diagram of a cell without electrolyte circulation. The essential part of the cell is the diaphragm frame 1, welded from ordinary channel iron in such a manner that the upper and lower bars have their channel sides facing inwardly, while those of the lateral bars face outwardly. Inside of frame 1, there is welded-on, a second frame made of iron strips, to which is fastened the diaphragm 2. The diaphragm consists of strong, tightly woven asbestos fabric, riveted to a separate frame which is bolted to the inner frame of the channel iron unit.

Figure 109. Diagram of cell without electrolyte circulation: 1 - diaphragm frame; 2 - diaphragm; 3 - short iron pipes; 4 - middle sheet of electrode; 5 - offset perforated electrode sheets; 6 - level regulator; 7 - glass tubes; 8 - iron collectors; 9 - water pressure tank; 10 - water feed pipe line.

For removal of gases there are provided in the upper part of the frame, on both sides of the diaphragm, apertures into which are welded short iron tubes 3. Between each pair of diaphragm frames there is clamped, between rubber gaskets, a bipolar electrode, consisting of a middle iron sheet 4, and two offset perforated sheets 5. The anode surface of the electrode is nickel plated, while the cathode is subjected to a special treatment for decreasing the hydrogen overvoltage.

Frames and electrodes are clamped together, between two cast iron plates, by means of steel clamping bolts. The cast iron plates have large apertures for current lead-in. The terminal electrodes have welded-on heavy iron rings to which are fastened by means of bolts, the current conductors.

The sections are filled with electrolyte not fully but to such an extent that there remains in the section sufficient free space for the separation of the electrolyte from the gases. Commingling of the gases is avoided by making the upper ledge of the inner frame, to which is fastened the diaphragm, quite wide and immersing its lower edge in the electrolyte.

The gases leaving the sections through outlet pipes 7, which are held in rubber sleeve connections, flow into iron collectors 8, and are removed from the unit for scrubbing and cooling.

Feed water from the small pressure tank 9 is admitted through pipe line 10, extending within the hydrogen collector. The water is fed into the cathode space of each section. The water feed is effected automatically by means of level regulator 6, the float of which is connected with an electrical contact and relay. In order to maintain equal level in all the sections, the lower part of the middle sheet of the bipolar electrodes is provided with apertures. Since no external circulation of the electrolyte takes place in the unit, cooling of the cell is effected almost exclusively through the external walls, which is made possible by the large finned surface of the lateral walls.

External view of the cell is shown in figure 110, wherein the fins of the diaphragm frames can be readily seen. To increase the coefficient of heat emission from walls to the ambient atmosphere the cell is enclosed in a dismountable iron housing, out of which the warm air is being drawn off and replaced by cooler outside air flowing in from the bottom. High rate of flow of air passing between housing and frame fins considerably increases heat dissipation and makes it possible to operate at high current densities.

Figure 110. External view of cell without electrolyte circulation.

A cell having an output of 36 cubic meters of hydrogen per hour, operates at a load of 1500 amperes and has the following dimensions: length 5150 millimeters, width 1650 millimeters, height 2350 millimeters; electrode dimensions, 1650 x 1650 millimeters. Distance between the offset electrodes is about 5 millimeters.

As the electrolyte, a solution of caustic potash is used; temperature of electrolysis 80 degrees. At current density of about 600 amperes per square meter, voltage across a section is of only about 1.8 volts; at a current density of 1500 amperes per square meter the voltage across a section is 1.95 volts.

D. Electrolysis of water under pressure

1. General data and theoretical fundamentals

On electrolysis of water in a hermetically sealed vessel, pressure of evolved gases will rise up to the moment when the volume of newly formed gases is equal to the volume of water being decomposed. Computation shows that this equality of volumes is attained at a pressure of about 2000 atmospheres.

Thus by electrolysis in a suitable apparatus, it is possible in theory, to obtain hydrogen and oxygen under very high pressure. Such a method of operation is of great practical interest.

The practical significance of electrolysis under pressure is still further enhanced due to the fact that voltage across the cell is not increased in comparison with electrolysis under normal pressure, and under certain conditions is even somewhat decreased.

Figure 111 shows graphs indicating the dependence of cell voltage on the pressure.

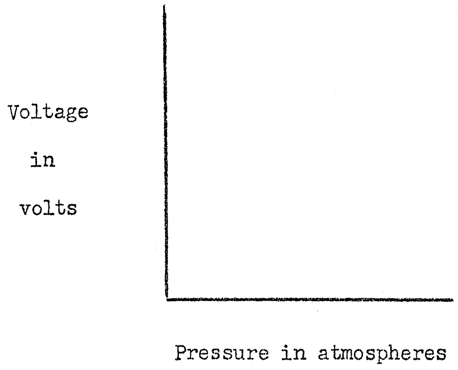

Figure 111. Dependence of cell voltage on pressure.

It can be seen from this graph that the most pronounced voltage decrease takes place at high current densities and within the area of pressure increase amounting approximately up to 30-40 atmospheres. With current intensity of 1500 amperes and pressure increase up to 40 atmospheres, there is observed a voltage decrease of 0.33 volts; and on further rise of pressure, from 40 to 200 atmosphere an additional voltage drop of 0.07 volts takes place.

Thus it can be contended that in electrolysis under pressure power expenditure, per cubic meter of hydrogen, not only does not increase by the work expended in compression, but even some saving of power is attained in comparison with electrolysis at a normal pressure.

This assumption, however, is not always substantiated. Experimental data are available which show that with increased pressure, there occurs concurrently with a voltage decrease also a lowering of yield on the basis of the current. (See for instance Table 25).

Table 25

Decrease in yields on the basis of the current with increasing pressure

Pressure; atmospheres	Voltage across the terminals; in volts	Yield on the basis of current in Percent
1	1.84	100
100	2.243	95.5
120	2.292	94.7
140	2.343	94.4

Dependence of Theoretical Decomposition Potential on the Pressure

On considering the process of electrolysis under pressure it appears natural to expect an increase of the voltage, since the process of compression must require expenditure of energy. Hence absence of voltage increase, and even more so a decrease of voltage, appear strange and difficult to understand.

This inconsistency is dispelled, however, if one recalls that the voltage across the cell consists of the value of reversible potential and potential losses due to irreversible phenomena, such as: overvoltage at electrodes, ohmic resistance of electrolyte, and so forth. Upon the various voltage components the pressure factor may have a different effect, either increasing or decreasing them.

Effect of pressure upon the reversible potential is elucidated on the basis of the laws of thermodynamics.

According to the formula of Nernst reversible potential of hydrogen electrode is

$$E' = -\frac{0.0002T}{2} \lg \frac{p_{H_2}}{p^2_{H+}} \qquad (35)$$

that of the oxygen electrode:

$$E'' = \frac{0.0002T}{4} \lg \frac{p_{O_2}}{p^2_{O^{2-}}} \qquad (36)$$

wherein p_{H_2} and p_{o_2} are the pressures of gaseous hydrogen and oxygen, respectively.

Thus the electro-motive force of the hydrogen-oxygen cell is,

$$E = E'' - E' = \frac{0.0002T}{4} \left(\lg \frac{p_{O_2}}{p^2_{O\,2-}} + 2 \lg \frac{p_{H_2}}{p^2_{H+}}\right) \qquad (37)$$

Subtracting therefrom the electromotive force, for another, lower gas pressure $p^0_{H_2}$ and $p^0_{O_2}$, we have the alteration of electromotive force on passing from pressure p to p^0:

$$E - E^0 = \frac{0.0002T}{4}\left(\lg \frac{p_{O_2}}{p^0_{O_2}} + 2 \lg \frac{p_{H_2}}{p^0_{H_2}}\right) = \frac{0.0002T}{4} \lg \frac{p_{O_2} \times p^2_{H_2}}{p^0_{O_2} \times p^{0\,2}_{H_2}} \qquad (38)$$

If hydrogen and oxygen are under identical pressure, that is, if:

$$p_{H_2} = p_{O_2} = p$$

and

$$p^0_{H_2} = p^0_{O_2} = p^0$$

then

$$E - E^0 = \frac{3}{4} \times 0.0002T \times \lg \frac{p}{p^0}$$

At 18 degrees change of electromotive force of the hydrogen-oxygen couple will be equal to:

$$E - E^0 = 0.0435 \lg \frac{p}{p^0}$$

It is apparent therefrom that on change of pressure, amounting to a tenfold one, that is from 1 atmosphere to 10 atmospheres or from 10 atmospheres to 100 atmospheres, reversible potential increases by 0.0435 volts.

Consequently the observed decrease of the voltage across the cell must take place as a result of decreased loss of energy consumed by irreversible processes.

As the basic factor there is being pointed out decreased electrolyte resistance as a result of lowered gas saturation, since the gases being under pressure occupy a smaller volume. Furthermore it is also pointed out that considerable effect is produced by depolarization of electrodes by dissolved gases, the solubility of which increases with increasing pressure; this is connected with the observed decrease of yields on increasing pressure.

2. Practical Application of Water Electrolysis under Pressure

Attainment of electrolytic hydrogen and oxygen production under high pressure (50-200 atmospheres) on an industrial scale is hampered by construction and economic difficulties which up to now have not been overcome. The difficulties consist mainly in this, that to build cells which operate at high pressure, it is necessary in order to ensure their strength, either to use large quantities of metal or to construct small volume cells, and consequently to utilize a great number of them. In the former instance, expenditures required for a long installation are not compensated for by the saving of electrical power thus attained; in the second instance it is difficult to service a large number of small units and to control their operation.

As can be seen from figure 111, greatest saving of power is obtained on electrolysis at a pressure up to 40 atmospheres. Consequently there are no economic inducements to strive for a further increase of pressure, especially since power expenditure to effect compression, is in accordance with gas laws about the same, regardless whether the gas is compressed from 1 to 10 atmospheres or from 10 to 100 atmospheres, or from 20 to 200 atmospheres.

From this standpoint it is economically advantageous to produce by electrolysis gases at relatively low pressures (10-20 atmospheres) and to use compressors for bringing them to a higher pressure.

Up to the present time almost all of the proposed designs of high pressure cells have remained unutilized.

Figure 112 shows the overall view of the cell (A) and the diagram of an installation (B) devised in the USSR for the production of hydrogen and oxygen at pressure up to 8-10 atmosphere, for use in cutting and welding of metals.

Figure 112. Installation for production of hydrogen and oxygen under pressure: A - overall view of cell; B - diagram of installation; 1 - gas separation columns; 2 - gas scrubbers; 3 - gas pressure regulators; 4 - drying columns; 5-6- receivers; 7 - electrolyte filter; 8 - cell; 9 - feed water tank.

The cell consists of 100 bipolar sections (about 650 millimeters in diameter) clamped together by four clamping bolts between cast steel pressure plates. The cell is supplied with current of 200 amperes at a voltage of 230-240 volts, from a mercury rectifier. Output of the cell is of about 8.5 cubic meters of hydrogen per hour. Above the cell are located the gas channels, while the feed channel is under the cell. The gases together with the electrolyte pass from the cell in the form of foam, along the iron pipe line into separatory columns 1, where separation of gases from electrolyte takes place. The separatory columns are connected at the bottom with one another and thus serve also to achieve an exact equalization of the pressure of gases. From separatory columns the gases pass into scrubbers 2 where they bubble through a layer of water, thereby being simultaneously scrubbed and cooled. From the scrubbers the gases flow into float actuated pressure regulators 3, the purpose of which is to equalize, roughly, pressure of the gases when these are being withdrawn in unequal amounts by the consumer.

The gases then pass through drying columns 4, packed with calcium chloride, and enter the receivers 5 and 6 wherefrom they are forwarded to the consumer.

The electrolyte after cooling in the separatory columns, drops through filter 7 back into cell 8. Distilled feed water is supplied from tank 9, from which it is fed first into the lower part of scrubber 2, and from there together with the electrolyte it flows into the cell.

In addition to the fixed installation for water electrolysis under pressure there has been developed in the USSR for the same purpose (metal welding and cutting), the design of a mobile installation, erected on the platform of an automotive vehicle. The cell is supplied with current from a standard generator driven by the automobile engine. A diagram of the installation is shown in figure 113.

Figure 113. Diagram of mobile unit for water electrolysis under pressure.

The installation is intended as a service unit in construction works involving the laying of any kind steel pipe lines, for example of oil or gas pipe lines and so forth.

C. Electrodes and Diaphragms for Chlorine Cells

1. Anodes and cathodes

Requirements which Must be Met by the Anodic Materials

The anodes of a chlorine cell operate under conditions of direct contact with such chemically active substances as moist chlorine, oxygen in the nascent state, and hydrochloric and hypochlorous acids. Hence the basic prerequisite of the anode material is chemical stability. In addition the anode material must promote discharge of Cl^- ions, that is the chlorine overvoltage on it must be at a minimum, the anode material must be a good conductor of electricity, possess mechanical durability and must be readily workable.

For making anodes there have been used platinum, carbon, and magnetite. At present artificial graphite is being used exclusively. Each of these materials possesses specific advantages and faults. Platinum meets best the prerequisites. Its basic disadvantage is the high cost. To decrease expenditures on platinum, the anodes were made of thin platinum foil or wire mesh and were used at high current densities (up to 3000 amperes per square meter). Conveying current to the thin and fragile electrodes was most complicated and was effected by means of a great number of soldered-on, thin, platinum wires. To increase the strength of the platinum it was alloyed with 10 percent of iridium. Thin platinum electrodes under conditions of high current density produced increased cell voltage.

Magnetite electrodes are made of molten mixed oxide of iron Fez O4. As the raw material, iron ore or pyrite cinders are used. Magnetite electrodes possess high chemical stability but low electrical conductivity. Specific resistance of magnetite varies from 0.036 to 1.32 ohms per centimeter. In addition magnetite produces high chlorine overvoltage, is very brittle, and cannot be worked mechanically. For chlorine cells the magnetite anodes were cast in the shape of round, hollow rods, open at one end. To increase electrical conductivity, the internal walls of the electrode were coated electrolytically with a layer of copper.

Carbon electrodes found a wider utilization and in some cells were used over a great length of time. However, due to low stability and being readily oxidized by oxygen, they caused contamination of chlorine with large amounts of carbon dioxide. At the same time there was formed in the cell much carbon sludge which plugged the diaphragm. Electrical conductivity of carbon electrodes is low. Their specific resistance fluctuates from 0.0042 to 0.012 ohms.

These disadvantages are inherent to a considerably lesser degree to electrodes made of artificial graphite, which is at present the only material used for making chlorine cell anodes.

Method of Production and Properties of Graphite Electrodes

Raw materials for the production of graphite electrodes are various carboniferous products: anthracite, retort and petroleum coke, graphite, coal tar and pitch. The carbonferous material is first broken up in roller crushers, into fragments from 30 to 50 millimeter size, and is then calcinated in gas or electrically heated shaft furnaces. The purpose of calcination is to remove hydrocarbons and moisture, to increase the density and electrical conductivity of the raw material. The calcinated product is then ground in ball mills to a particle size of less than 1 millimeter. On completion of grinding the predominant portion of the material must consist of particles 0.5-0.1 millimeter in size. The ground material is screened to separate it into fractions according to degree of comminution, and is then forwarded sometimes after being passed through a magnetic separator, to storage bins. From the storage bins it is withdrawn for compounding and mixing. Compounding of the carbonaceous materials is done on a weight basis.

To the dry carbonaceious materials is added as a binder, coal tar or pitch and the whole mass is thoroughly mixed at 80-105 degrees in kneading mixers. Compounding and selection of the granulometric composition of the carbonaceous materials, as well as the mixing, are very responsible operations which determine to a considerable degree the quality of the electrodes. The well-mixed, dough-like plastic mass is fed into hydraulic presses wherein the electrodes are pressed at 300-400 atmospheres.

Pressing is done in closed molds or the mass is extruded through dies. The moist, so-called "green electrodes" leaving the press are stored until cooled and are then fired.

Firing is effected in gas or electrical resistance furnaces. Depending upon the scale of manufacture there are used either single-chamber, intermittently-operated gas furnaces, or continuous-operation, multiple-chamber or duct furnaces. In the firing the tarry products, added to the carbonaceous materials as a binder, undergo coking and this coke cements the particles of carbonaceous powders. Since in the course of firing of the electrodes, volatile products are liberated, the temperature in the furnace must be raised very slowly. If this is not done, a large proportion of defective products will be produced, due to the fact that the gaseous products' not being allowed sufficient time to escape from ~~the~~ within the electrodes, causes bending and rupture of the electrode structure. The technique of firing depends upon the nature of the binder material used.

Usually the firing process is divided into four periods. During the first period -- of preheating and distillation, for the duration of 3-4 days, the temperature is raised very slowly to 350 degrees; the main portion of volatiles is liberated during this time. In the second period, over a length of time amounting to 20-30 hours, the temperature is raised rapidly up to 850 degrees and the electrodes undergo coking. In the third period of 25-50 hour duration the temperature is increased to 1300 degrees--1450 degrees. The electrodes are calcinated throughout and are held at this temperature from 25 to 30 hours. During the fourth period the furnace is gradually allowed to cool which lasts 4 to 6 days. Thus the entire firing process requires from 10 to 15 days.

The fired electrodes consist of dense, strong carbon material, emitting a metallic sound on impact, and quite difficult to process by mechanical means. Following cleaning and surface shipping they are ready for use.

For the production of graphite electrodes, these carbon electrodes are subjected to a second firing operation at a temperature of about 2300-2400 degrees. During this second firing the amorphous mass (or more precisely, the fine graphite crystals) of the carbon electrode undergoes crystallization to artificial graphite (having larger crystals). Following graphitizing the electrode displays a readily apparent crystalline structure. In it individual graphite crystals are bonded, by action of molecular forces, along cleavage surfaces of the crystals.

Graphite electrodes do not consist of a continuous monolithic mass, but are perforated throughout by minute pores. Porosity of electrodes is expressed by the ratio (in percent) of the volume of the pores to that of the total electrode. Porosity constitutes an important characteristic of the electrodes.

The quality criterion of carbon and graphite electrodes is their stability toward conditions of electrolysis.

Definite prerequisites have not yet been established in this respect. Usually the stability of electrodes being tested is compared with that displayed under the same conditions by the best specimens.

Some researchers have established that stability of carbon electrodes increases with increasing temperature of firing at above 1200 degrees. Stability of graphite electrodes is substantially affected by the physico-chemical properties of the initial raw material and the granulometric composition of the batch.

Table 41

Characteristics of carbon and graphite electrodes

Electrodes	Specific electrical resistance ohm/em	Apparent density	Beginning of combustion °C	Heat Conductivity cal/cm°C	Ash Content %	Tensile strength kg/em^2	Mechanical Workability
Graphite	0.0008-0.0012	1.6-1.8	560-640	3.6	Less than 1	56-72	Good
Carbon	0.0032	1.5-1.7	450	0.95	Not more than 6	72-109	Poor

Porosity of electrodes is also an important factor determining their stability; with increasing porosity their stability decreases. Stability of carbon electrodes under conditions of electrolysis of sodium and potassium chlorides is two to three times less than those of graphite electrodes; their porosity is greater and electrical conductivity lower. Carbon electrodes are considerably less well adapted for working by mechanical means. Comparative characteristics of carbon and graphite electrodes are given in Table 41.

Breakdown of Graphite Electrodes and Means of Combating It

The essential cause inducing distruction of graphite electrodes is the discharge of OH^- ions. Oxygen evolved in this process oxidized the carbon of the electrodes to give carbon dioxide according to the equation:

$$C + 2O = CO_2$$

On using carbon or graphite anode, the chlorine produced always contains a certain amount of carbon dioxide. The carbon dioxide content increases with increasing temperature with decreasing yields on the basis of the current and with decreasing stability of the anodes. On partial burning out of the carbon, the bond between remaining particles of the anode is weakened and small carbon particles begin to separate from the electrode.

This process of crumbling or disintegration of the electrode is the more intensive the less homogeneous the electrode and the more coarsely granular its structure. Carbon electrodes in which separate graphite grains are bonded less strongly than they are in graphite electrodes and the electrode mass itself consists of larger particles, undergo on disintegration much more extensive crumbling than the graphite electrodes.

Data characterizing breakdown by combustion and crumbling of graphite and carbon electrodes are given in Table 42.

Table 42
Breakdown characteristics of different electrodes

Electrodes	Weight losses on electrolysis in gm per one ampere hour	Losses by combustion gm	percent	Losses by crumbling gm	percent
Graphite	0.0554	0.0414	74.6	0.0142	26.4
Carbon	0.1762	0.0715	40.6	0.1045	59.4

The stability of graphite electrode is greatly affected by temperature of electrolysis; at higher temperature breakdown increases. This is explained by the fact that with increasing temperature the rate of the oxidation reaction increases, oxygen overvoltage decreases and the percentage of current used up for oxygen formation is correspondingly increased. An analogous effect is produced by polarization of the anode and current density. At a high anodic potential of the order of 1.8-1.9 volts breakdown of the graphite is increased. At high current densities, when anodic potential reaches the indicated limits, breakdown will accordingly also be increased in connection with the greater amount of oxygen evolved. However, very low current densities also cause increased anode breakdown.

The cause of this becomes apparent on considering the polarization curves of oxygen and chlorine on graphite, shown in figure 117.

In this figure, 1 is the polarization curve of chlorine evolution from a solution of sodium chloride under the conditions of a technical electrolysis, while 2 is the polarization curve of oxygen evolution from a neutral sodium sulfate solution. From the shape of the curves it can be seen that under conditions of very low current densities, the amount of evolved oxygen (relative to that of chlorine) is greater than at higher current densities, since on conjoint discharge upon an inert electrode of two or of several ions, each of them is discharged at that current density, which would correspond to the given electrode potential on discharge of the ion from solution in absence of other ions. We have previously mentioned the detrimental effect of porosity on the stability of electrodes. Pores of an electrode on its polarization are readily permeated with electrolyte and the electrolysis process takes place not only upon the electrode surface but also inside of the pores.

Measurement of electrode potential in depth of electrode, that is within its pores shows that the potential decreases rapidly with increasing distance from the electrode surface, and can reach even a lower value than that of the equilibrium potential of chlorine, but at the same time it always remains above the equilibrium potential of oxygen.

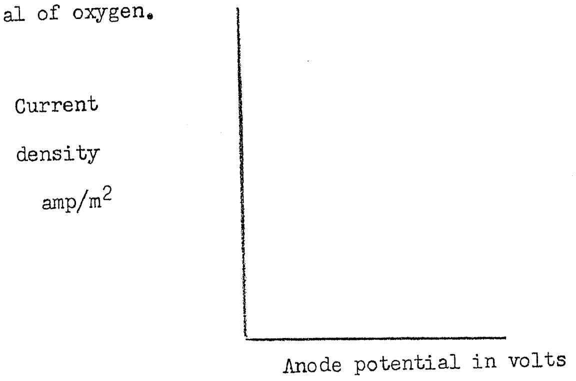

Figure 117. Potentials of chlorine and oxygen evolution on graphite: 1 - chlorine curve; 2 - oxygen curve.

Thus, the electrolysis process within the pores occurs at very low current densities, which correspond to low values of electrode potential.

Considering the polarization curves (figure 117) we have seen that under such conditions a considerable part of the current is used up for oxygen liberation, and the relative amount of oxygen evolved within the pores is larger than on the electrode surface where the anode potential is higher. The greater the porosity of an electrode, the larger is the part of current used for electrolysis within the pores and at the same time a substantial area of the electrode undergoes oxidation.

Consequently highly porous electrodes undergo rapid breakdown.

It follows from what has been stated, that it is necessary to eliminate the electrolysis process occurring within the pores. In practice this is attained by means of electrode impregnation, that is, by saturating the electrodes with various substances which seal up the pores. Among the numerous impregnation methods, the one most commonly used is impregnation with linseed oil followed by chlorination. The electrodes are first thoroughly dried to remove moisture from the pores and are then placed in an iron reservoir filled with linseed oil. Saturation is effected at 100-110 degrees over a period of 24 hours. Electrodes absorb the oil in amounts of about 13-16 percent of their weight. Upon completion of the saturation, the oil is drained from the reservoir, the electrodes are removed and wiped dry. They are then placed in a wooden tank, are covered with cold water, and by introducing 1 chlorine the electrodes are chlorinated for a 24 hour period. After this steam is introduced into the tank together with the chlorine, whereby the water is heated to 100 degrees, and the hot chlorination is continued for an additional 24 hours.

The thus-treated electrodes before being used must be stored in a dry, well-ventilated building for 6-8 months. This period of storage increases the stability of the electrodes.

The method of treating electrodes with linseed oil and subsequent chlorination does not have the same degree of effectiveness insofar as increased stability of different kinds of graphite electrodes is concerned. Best results are obtained with Acheson graphite. The life of impregnated electrodes in comparison with untreated electrodes, is increased almost twice. It must be pointed out, however, that cell voltage, using impregnated electrodes, is always somewhat higher.

Table 43

Operation characteristics of impregnated and of unimpregnated graphite electrodes

Electrode	Average cell voltage during first four months; volts.	Average carbon dioxide content of chlorine; %		Deterioration of electrode by volume; %	
		First 4 months	Subsequent 4 months	First 4 months	Subsequent 4 months
Unimpregnated	3.52	0.4	0.26	31.5	70
Impregnated	3.67	0.1	0.1	24	45

In Table 43 are shown data relative to the performances of impregnated and unimpregnated graphite electrodes under industrial conditions over a 8 months period at current density of about 800 amperes per square meter, and at a temperature of 60 to 70 degrees.

Material and Design of Cathodes

In electrolysis with a solid cathode, the cathode functions in an atmosphere of hydrogen and is in contact with alkali containing normally from 2.5 to 3.5 equivalents of caustic soda or caustic alkali, and from 2.5 to 3.25 equivalents of the corresponding chloride salt. The presence in the cathodic alkali of insignificant amounts of hypochlorite and chlorate salts, does not alter the essential nature of the medium.

Chemical stability requirements of the cathode in the medium involved is fully met under ordinary circumstances, by iron, from which the chlorine cell cathodes are thus exclusively made; on soft iron hydrogen overvoltage is lower than for many other metals, such as for instance nickel, brass, copper, lead etc. Consequently in this respect also it is found to be fully suitable.

Cathodes, in cells operating on the counter current principle with a filtering diaphragm are made either of iron sheets, 1.5-2 millimeters thick, perforated to permit flow-off of the alkali, or from heavy iron screening. Shapes of perforation vary. Figure 118, A, B, C, show slit, circular and herring-bone perforations. Perforation is usually made in such a manner that the area of the openings constitute from 24 to 28 percent of the entire surface of the cathode. In this ratio the perforation in a cathode from 1.5 to 2 millimeters thick not only does not decrease the effective area but actually increases it due to the fact that the lateral surfaces of the openings have a larger area than the area of the perforations.

Figure 118. Shapes of cathode perforations.

A - slit; B - circular; C - "herringbone";
D - slits with increased surface

In some cells the principal cathode sheet is covered with a fine iron screen. This iron screen facilitates evolution of hydrogen and serves as a framework for the soft diaphragms. Moreover the screen increases the surface of the cathode. For the same purpose of increasing the surface use is being made of the perforations shown in figure 118 D. Here the opening is made ~~but~~ by cutting out three sides of the area and bending out the slat thus formed. In this instance the entire surface of the metal is retained, and in addition the new surface formed by the perforation is supplied.

In other less frequently utilized cells, the cathodes are plane iron sheets or rod having a T-like cross section.

Life of the cathodes if they are not subjected to the action of acidic anolyte is in excess of two and one half years. The life of the supplementary light iron screens is of about 6 months.

2. Diaphragms

Types of diaphragms

Segregation of cathodic and anodic products in the methods utilizing a solid cathode is attained either by stratification or by means of porous partitions -- diaphragms, which are located between anode and cathode.

In principle, work of diaphragms can be divided into two groups: immersed or non-filtering diaphragms and the filtering diaphragms.

The function of diaphragms of the first group consists in this, that being located in the stationary electrolyte, between anode and cathode, they divide the cell into anodic and cathodic compartments and inhibit mixing of alkaline catholite with acidic anolyte by mechanical mixing of the liquid by gases being liberated and by thermal convection. They also preclude alkali diffusion.

The immersed diaphragms must meet the following requirements: (1) Stability toward chemical action of alkali and of acidic anolyte as well as mechanical strength. (2) Great diffusional resistance, and (3) the property of readily permitting passage of ions, that is, low electrical resistance.

Diaphragms of the second group -- the filtering diaphragms -- operate under different conditions, namely at a continuous, slow flow of electrolyte from anode to cathode. Filtering diaphragms must also inhibit mechanical mixing of catholyte and anolyte and physical diffusion; they must be permeable to ions, and in addition they must be permeable to the electrolyte. Therefore these diaphragms must first of all meet the following conditions: (1) Possess the property to filter, at a given rate, the electrolyte. (2) Not to be destroyed by the chemical action of alkali and of the acidic anolyte and to retain their mechanical strength. (3) Possess low electrical resistance.

Insofar as diffusional resistance is concerned, it is not of great importance in this instance because diffusion is hampered by, flow of electrolyte in the opposite direction.

The material used in the production of immersed diaphragms, in the practice of electrolysis of sodium and potassium chlorides, is almost exclusively cement; while asbestos is used for the production of filtering diaphragms.

Physical Properties of the Diaphragms

Porosity: Filtration of electrolyte through the diaphragm, as well as ion permeability and diffusion are possible only if the diaphragm has pores. The greater the number of pores; the larger the pores; the less winding are the pores; the greater is the filtering capacity of the diaphragm.

In practice, on testing the diaphragm, the testing is limited to determining the volumetric porosity, that is the ration (in percent) of the pores' volume to the total volume of the diaphragm:

$$\sigma = \frac{\text{Volume of the pores}}{\text{Volume of diaphragm}} \; 100$$

Volumetric porosity does not fully characterize the diaphragm, and specifically does not give the amount of liquid that filters through the diaphragm. Diaphragms of the same volumetric porosity but of different types and methods of preparation may have different permeability.

The amount of liquid Q permeating through the diaphragm over the length of time t, will be in proportion to the hydrostatic pressure of the liquid, H; to the area of the diaphragm S, and will be inversely proportional to the thickness of the diaphragm N, and the liquid viscosity η :

$$Q = K \frac{SHt}{N \eta}$$

Wherein K- is the coefficient of proportionality, which is called the absolute coefficient of diaphragm permeability; the physical meaning of K is elucidated on assuming S, H, t and η equal to the unity. Then,

$$K = Q$$

Thus the absolute coefficient of permeability is the number of milliliters of liquid flowing through the diaphragm, where the diaphragm area S = 1 decimeter square, the time t = 1 hour, the hydrostatic pressure H = 1 centimeter, the diaphragm thickness N = 1 centimeter, and the viscosity η = 1 centipoise.

The absolute coefficient of permeability is a quantity specific for a diaphragm of each type and kind and depends upon the cross section, number of pores, and their convolutions, that is, length.

Electrical resistance: The electrical resistance of the diaphragm with the same composition of the electrolyte characterizes the permeability of the diaphragm to ions, and depends upon the same factors as the coefficient of permeability. In the general case, electrical resistance can be calculated according to the equation:

$$W = \rho \frac{N \times \beta^2}{S \sigma}$$

where: ρ - specific resistance of electrolyte within the pores of the diaphragm.

β - coefficient characterizing the length of the pores in relation to the thickness of diaphragm

σ - volumetric porosity

Diffusion: Diffusion of alkali through the diaphragm from the cathode into the anode space is proportional to the difference of concentration of alkali in the cathode and the anode compartments, to the diffusion coefficient and the time. The amount of alkali diffused through is:

$$P = \frac{S \times \sigma (C' - C) D \times t}{N \times \beta^2} \text{ grams}$$

where: (C' - C) difference of concentration of alkali at the beginning and at the end of the diffusion process.

D - Diffusion coefficient of alkali at the given concentration and temperature

t - time in 24 hours period

Cement Diaphragms and their Preparation

The essential problem in the making of cement diaphragms is the formation of numerous small pores in the body of cement mass. This is attained by the expedient of adding to the cement powder finely comminuted crystals of sodium chloride; or by mixing the cement with a salt solution whereby formation of salt crystals is induced at the moment of setting of the cement. After the cement has set, the salt crystals are dissolved in water and voids are thus formed in the cement mass, which render it porous. On varying the ratio of cement and salt, and also the degree of salt comminution diaphragms of different volumetric porosities can be produced.

Dependence of diaphragm porosity on the amount of added salt and salt solution are shown in Table 44.

The effect of salt comminution, as can be seen from Table 44, manifests itself not only in the volumetric porosity, but also in the size of the pores and the resistance of the diaphragm. To impart mechanical strength to cement diaphragms of large size (about 0.23 square meters) they are made relatively thick (from 15 to 20 millimeters). Cement is not entirely resistant to the action of anolyte and catholyte and the diaphragm undergoes gradual deterioration. Nevertheless the life of cement diaphragms in chlorine cells is of relatively long duration -- from 1 to 2 years.

In the course of operation, the pores become clogged by various precipitates, as a result of which the electrical resistance of the diaphragm increases and toward the end of operation may reach an appreciable value, which causes voltage losses up to 1 volt.

Table 44

Effect of added Salt on properties of the diaphragm

Solid salt grams	Asbestos grams	Saturated salt solution; milliliters	Hydrochloric acid; milliliters	Volumetric porosity %	Ratio of specific diaphragm resistance to specific resistance of electrolyte
10 (fine)	-	40	-	41.5	23.00
30 "	-	55	-	59	12.00
40 "	5	70	-	62	10.00
35 (coarse)	-	40	-	46	8.65
60 "	-	50	-	54	7.50
75 "	-	55	-	70	6.20
60 "	10	120	-	81	3.25
	-	49	14.6	53	5.30

Cement diaphragms are made in the following manner. First the cement mass is prepared according to formulas given in Table 45.

Table 45

Composition of the cement mass

Components	Formula 1	Formula 2
	Contents %	
Portland cement	45	60
Saturated salt solution	27	32
Sodium chloride (ground)	28	-
Hydrochloric acid (30-39%)	-	8

The brine is changed to the mixer and the cement is added gradually with agitation. After thorough mixing, the hydrochloric acid is added, and mixing is continued for several minutes. The mass so obtained is poured into shallow forms and before it has set, a large mesh, fine wire screen is placed into it so that it is in the center of the diaphragm. After the mass has hardened, the screen forms the framework of the diaphragm, increasing its mechanical strength. After 24 hours, when the mass has hardened, the diaphragms are removed from the forms, are piled up in bundles, are clamped by means of wedges to prevent warping, and are left in contact with air for 12-15 days to complete the hardening process. On settling of the cement, a mass of small salt crystals separates throughout its body. To speed up this crystallization, hydrochloric acid may be added as indicated in the second formula.

The fully hardened diaphragms are soaked in water for 6-12 days to dissolve the salt crystals and render the diaphragms porous. It is preferable to soak the diaphragm in hot water, to promote the salt dissolution and to decrease formation of calcium carbonate in the pores by the action of carbon dioxide dissolved in the water on the components of the cement.

Asbestos Diaphragms

Cement diaphragms have low permeability and are unsuitable as filtering diaphragms. In the production of the latter asbestos is used exclusively, in the form of a special diaphragm cardboard or cloth.

The filtering capacity of an asbestos cardboard diaphragm must be such that at normal current densities the alkali concentration in the cathodic compartment is of 100 to 110 grams per liter of NaOH. Such a filtering capacity, or permeability is acquired by the diaphragm not at once, but after 1.5 to 10 days of operation, during which time it is being formed. A new diaphragm, at first has a permeability three to five times greater than normal. On passage of the current the permeability decreases somewhat immediately, and thereafter it slowly reaches its normal value.

Figure 119 shows the course of formation of a diaphragm. In the electrolysis process, subsequent to formation, permeability may be changed by the load on the cell. Decrease of current intensity results in some increase of permeability; while increases of current intensity increases permeability up to a certain limit. Most harmful to the proper functioning of a filtering diaphragm are frequent interruptions of cement or strong fluctuation of the load. Under such conditions the time of operation at normal permeability is considerably decreased.

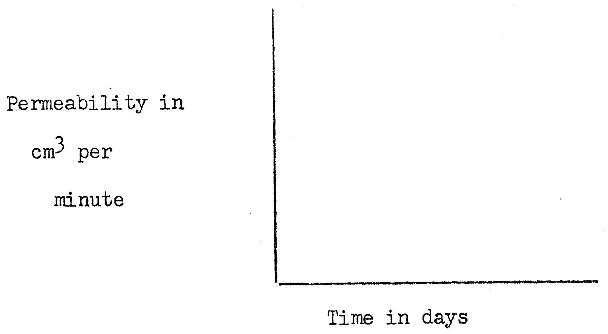

Figure 119. Alteration of permeability of an asbestos diaphragm in the process of formation.

While wet, the diaphragms have a low mechanical strength and require careful handling. For a normal operation of filtering diaphragms which are the most vulnerable element of a chlorine cell an electrolyte is required which is free of mechanical admixtures and of calcium and magnesium salts as well as a continuous and insofar as possible uniform current load.

Good asbestos diaphragm paper has a thickness of 0.65-0.7 millimeters, an absolute permeability coefficient of 0.016-0.028, and a β coefficient of about 1.45.

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