Chapter 2:
GENERATING HYDROGEN

CHEMICAL REACTIONS PRODUCING HYDROGEN

ABOUT *one billion cubic meters* (35,000,000,000 cubic feet) of hydrogen is produced in the United States yearly. This does not include amounts used in ammonia, methanol, synthesis gas, and petroleum refining.

The most common method of producing hydrogen is to remove it from hydrocarbons such as methane, gasoline, fuel oil, and crude oil. A hydrocarbon molecule, in the presence of a nickel catalyst and 700 to 1,000°C (1,290 to 1,800°F) steam, is split into carbon oxides and hydrogen gasses. The oxygen in the water combines with the carbon in the fuel to release the hydrogen. **(1)**

For propane (C_3H_9):

$$C_3H_9 + 3H_2O \text{ -----> } 3CO + 7.5H_2.$$

The product gasses can be processed further at 350°C (660°F).

$$3CO + 3H_2O \text{ -----> } 3CO_2 + 3H_2.$$

An iron oxide catalyst is generally used for this process.
Pure carbon in the form of coal or coke can be reacted with water.

$$C + 2H_2O \text{ -----> } CO_2 + 2H_2.$$

The carbon dioxide can be absorbed by a solution of monethylamine and water, leaving the hydrogen behind.

In the U.S. and many parts of the world coal is more plentiful than natural gas so that the cost of producing hydrogen by this method is the lowest cost alternative. Hydrogen can be produced at the energy equivalent of $0.04 per liter ($0.17 per gallon) of gasoline. This excludes distribution, retail costs, and tax credits which could still leave hydrogen competitive with gasoline. Billings Energy Corporation plans to adapt a housing subdivision to burning hydrogen from a small decentralized coal gasification plant.

Less common methods of hydrogen production include using high temperatures to dissociate (split) the ammonia molecule.

$$2NH_3 \text{ -----> } N_2 + 3H_2.$$

This yields only small amounts of hydrogen but is convenient for lab use. A similar process is used to "reform" liquid hydrocarbon fuels on-board a vehicle to supply hydrogen to the engine. This process is described in a later chapter.

Electrolysis gives hydrogen of high purity, in excess of 99.9%, but is relatively expensive.

$$2H_2O \text{ -----> } 2H_2 + O_2.$$

With continual research, the costs of water splitting are gradually declining. Electrolysis, however, is the most convenient way for the individual do-it-yourselfer to produce hydrogen in significant quantities.

Small amounts of hydrogen for laboratory use can be produced by reacting metals with acids. Acids are compounds which contain hydrogen. The reaction proceeds as follows.

Metal + Acid -----> Metal compound + Hydrogen gas.

The metal displaces the hydrogen in the acid. The reaction of zinc with sulfuric acid will produce hydrogen and zinc sulfate (a combination of zinc, sulfur, and oxygen). Zinc also reacts with hydrochloric acid to produce zinc chloride and hydrogen.

$$Zn + 2HCl \text{ -----> } ZnCl_2 + H_2.$$

Iron reacts, in a similar manner, with sulfuric acid.

$$Fe + H_2SO_4 \text{ -----> } FeSO_4 + H_2.$$

Sulfuric acid or hydrochloric acid can be mixed with water to any levil of dilution. Pour the acid *slowly* into the water. **Do not pour the water into the acid.** Dilute acids act vigorously with zinc to produce hydrogen. Pure acid and zinc react more slowly than dilute acid. Small amounts of copper sulfate can be added to the solution to increase the reaction rate.

Hydrogen can be purified by passing it through a sodium hydroxide solution. Water vapor can be removed by passing the gas through silica gel or concentrated sulfuric acid.

Exhibit 1 shows how hydrogen is collected "over water" in bottles. This prevents the hydrogen from flowing back into the reaction bottle. An apparatus like this, or a commercially available one-way valve *(check valve),* is used anywhere it is desirable for the gas to flow in only one direction.

The following metals will replace hydrogen in dilute sulfuric, hydrochloric, or many other common acids.

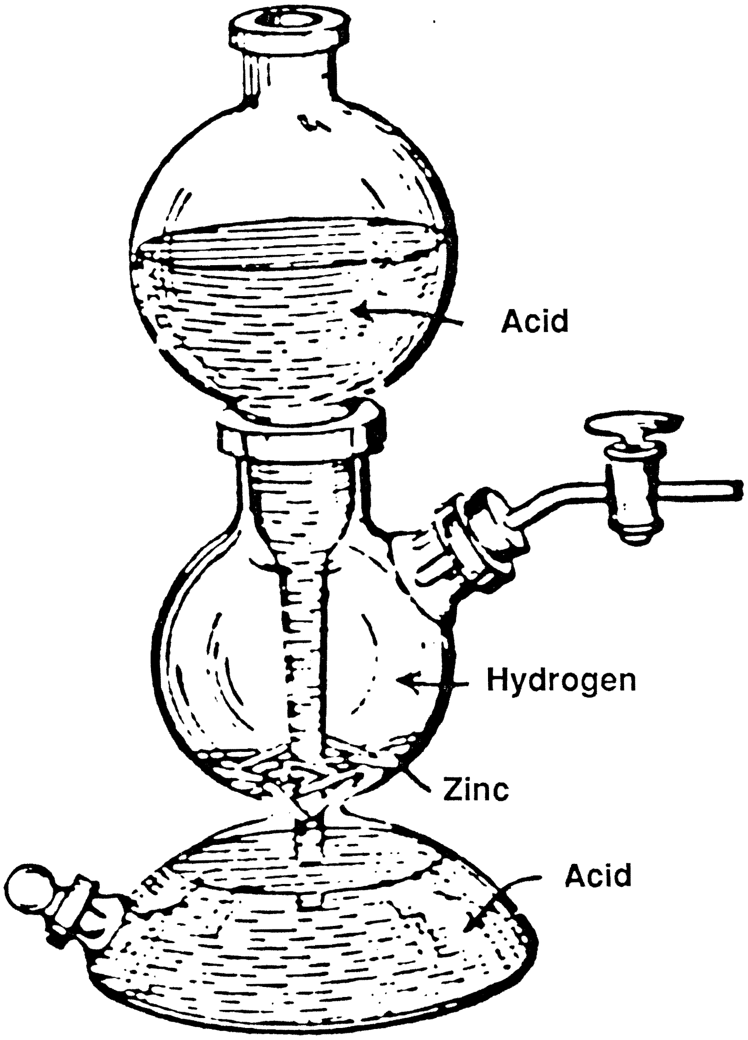
- Potassium (K)
- Sodium (Na)
- Calcium (Ca)
- Magnesium (Mg)
- Aluminum (Al)
- Zinc (Zn)
- Iron (Fe)
- Lead (Pb)

Sodium reacts with water according to the reaction:

$$2Na + 2H_2O \text{ -----> } 2NaOH + H_2.$$

Sodium and calcium metals react violently with water to produce heat and to release one

EXHIBIT 1
Kipp Generator for Making Hydrogen



hydrogen atom from the water and combine with the other atom to form a *hydroxide.* With sodium the reaction is:

$$2Na + 2H_2O \text{ -----> } H_2 + 2NaOH.$$

Sodium + Water -----> Hydrogen gas + Sodium Hydroxide.

We write H_2 instead of H because hydrogen atoms, like oxygen atoms, usually travel in pairs forming hydrogen (H_2) and oxygen (O_2) molecules.

Potassium reacts even more vigorously with water. The reaction may produce enough heat to ignite the hydrogen. Hydrogen and potassium hydroxide are formed.

Each of the elements in the above list reacts with only *half* the water. The other half is liberated. Sodium hydroxide and potassium hydroxide readily dissolve in water forming a clear solution. Calcium hydroxide remains undissolved in a milky suspension in the water.

Sodium hydroxide, water and aluminum may be further reacted to form more hydrogen. 55 square centimeters (cm^2) of aluminum reacted to produce one liter of hydrogen per minute. One square foot (ft^2) of aluminum produces 0.6 cubic feet (ft^3) of hydrogen per minute. A 1 cm (0.25 in) thick plate lasts about 24 hours. It requires about 12.5% more surface area for zinc than for aluminum.

Alkali solutions of aluminum or silicone also react with water.

$$2Al + 2NaOH + 6H_2O \text{ -----> } 2NaAl(OH)_4 + 3H_2.$$

$$Si + 4NaOH \text{ -----> } Na_4SiO4 + 2H_2.$$

Calcium hydride can produce a large volume of hydrogen, but is expensive.

$$CaH_2 + 2H_2O \text{ -----> } Ca(OH)_2 + 2H_2.$$

1 kilogram (1 kg) of CaH_2 produces 1 cubic meter (1 m^3) of hydrogen. 1 lb. yields about 16 ft^3. Sodium borohydrate produces still larger amounts of hydrogen but is even more expensive.

$$NaBH_4 + 4H_2O \text{ -----> } NaB(OH)_4 + 4H_2.$$

Exhibit 2 shows a laboratory device that delivers a continuous supply of hydrogen from the reactants. The weight of the acid in the container pressurizes the hydrogen in the middle container. As hydrogen is drawn off, the pressure is reduced in the container and the acid level in the lower chamber rises and comes into contact with them metal. More gas is generated, thereby increasing the gas pressure and forcing the acid level down. This action governs the rate of hydrogen production and prevents hydrogen production when not needed.

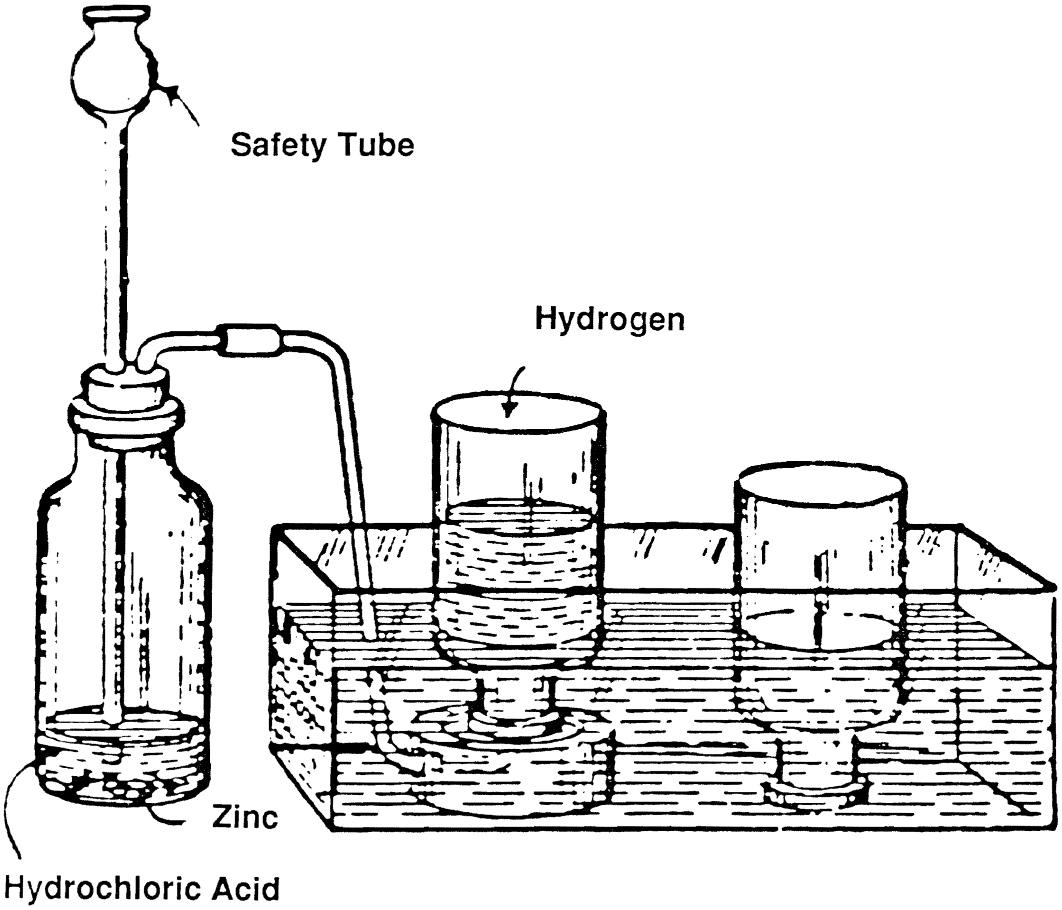
ELECTROLYSIS

Water Splitting

Electrolysis is a process of producing hydrogen and oxygen from electricity and water. Two hydrogen atoms and one oxygen atom are electrically attracted in a molecule of water: H_2O. When an electric current passes through water the chemical bond breaks

EXHIBIT 2

Collecting Hydrogen "Over Water"



down. The result is: two positively charged hydrogen atoms (positive ions) and one negatively charged oxygen ion (a negative ion).

If two oppositely charged electrodes are inserted into the water and a current is passed between them, the negative oxygen ions migrate to the positive electrode (the anode) while the positively charged hydrogen ions are attracted to the negative electrode (the cathode).

Direct current applied to water results in the following reaction:

$$2H_2O \text{ -----> } 2H_2 + O_2.$$

Half as much oxygen as hydrogen is produced. Electrons are transfered from the anode to the cathode.

The electrical resistance of pure water is high: 100 ohm/cm (254 ohm/in). This resistance may be lowered chemically by adding either 700 to 1,000^{o}C (1,290 to 1,800^{o}F), a salt (like sodium chloride), an acid (such as sulfuric acid) or a base (such as potassium hydroxide). Salts tend to corrode electrode metals. Platinum and phosporic acid can be used together but this is expensive. Potassium hydroxide (KOH) with nickle-iron (stainless steel) electrodes provides the best compromise between performance and cost.

The reaction for an alkaline electrolyte (KOH) at the anode is as follows.

$$4OH- \text{ -----> } O_2 + 2H_2O + 4 \text{ electrons.}$$

The reaction at the cathode is:

$$2H_2O + 4 \text{ electrodes -----> } H_2 + 2OH-.$$

The anode reaction is an *oxydation reaction* - free electrons are produced. The reaction at the cathode is a *reduction reaction* - free electrons are absorbed. The flow of ions is depicted in **Exhibit 3.**

The reaction for an acid electrolyte such as sulfuric acid (H_2SO_4) at the anode is given below.

$$2H_2O \text{ -----> } O_2 + 4H^+ + 4 \text{ electrons.}$$

The reaction at the cathode is:

$$4H^+ + 4 \text{ electrons -----> } 2H_2.$$

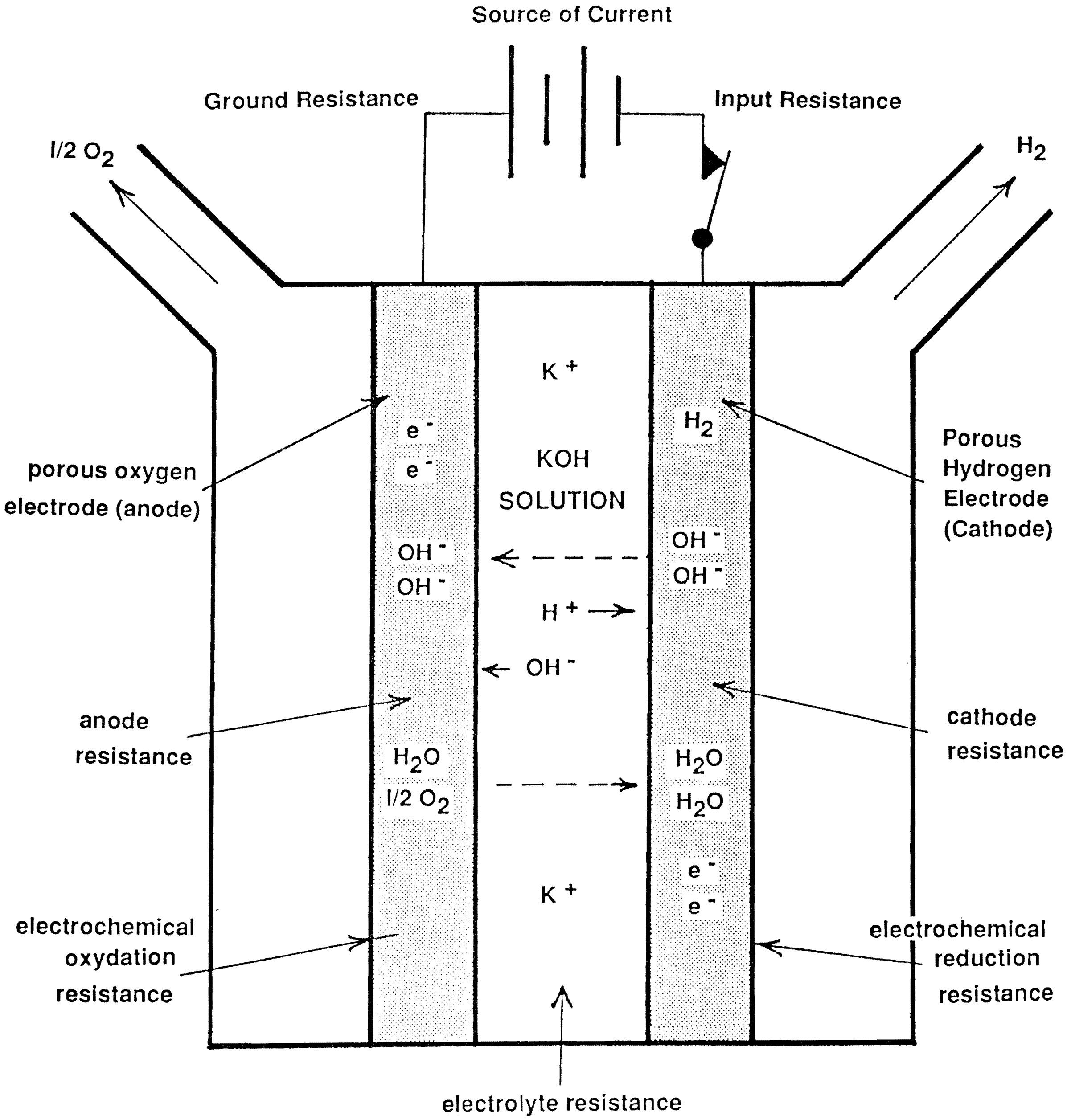
Alkaline electrolytes are less corrosive to electrode material than acids. According to G.A. Crawford, alkaline electrolyte material "... *has the most significant near-term commercial potential for recovery of hydrogen from water on a large industrial scale.*" (2) It is also more convenient to use on a smaller scale.

The two most common alkaline electrolytes used are sodium hydroxide (NaOH) and potassium hydroxide (KOH). NaOH is less conductive, but cheaper than, KOH. Since KOH combines with CO_2 in air to produce potassium carbonate, periodic replacement is needed in cells open to the atmosphere. However, air tight cells cut down on this loss.

High purity distilled water is needed because electrolytes produce chlorides and sulfates in the presence of tap water impurities. These chemicals slowly corrode the electrode material. Even under the best conditions, with distilled water, electrode materials need to be corrosion resistant. Among the readily available metals, iron cathodes and

EXHIBIT 3

Hydrogen-Oxygen Electrolyser



stainless steel anodes are recommended. **(3)**

Electrolysis is a general phenomenon that may apply to other substances. Salt, a compound of sodium and chlorine, in the molten state may be electrically split by a suitably designed electrolyser to gather solid sodium at the cathode and chlorine gas at the anode. A zinc chloride solution under electrolysis yields solid zinc at the cathode and chlorine gas at the anode.

Separators

If both hydrogen and oxygen gasses are combined during the electrolysis process, there will be a substantial risk of explosion. Mixtures of between 4 and 75% hydrogen in air and 4 and 94% of hydrogen in pure oxygen are explosive. If the hydrogen content is less than 4% or greater than 75% in air the mixture will not explode but combustion will take place.

Electrolysers are designed with separators (also called membranes or diaphragms) between the anode and cathode to keep the hydrogen and oxygen from combining and also to allow ions to be transfered in the liquid electrolyte. For this reason, the space between electrodes should be minimized. The separator must be permeable to liquids but but not permit gasses to pass. Materials such as asbestos fiber work well as separator material because the capillary pressure is greater then the cell pressure. Artificial fiber cloth, rubber cloth, or metallic mesh may also be used. **(4)**

In the simple low pressure electrolyser design that follows, a solid barrier is used to separate the gasses. A space is left at the bottom of each gas column for the ions to migrate from one electrode to another. The space is below where the gasses evolve so that the rising hydrogen and oxygen bubbles will be kept separate from each other.See **Exhibit 6.**

Measures of Efficiency

The *thermal efficiency* of electrolysis compares the energy of the combustion of hydrogen and oxygen with the energy needed to evolve the two gasses from water.

$$\text{Thermal efficiency} = H / (q + [w/e]) = H / Q = \text{Energy input / Energy output.}$$

Where:

H = energy input required to split water = 79.4 Wh/gram mole H_2 at 25°C (77°F) and 1 atm (0.1 MPa, 14.7 psi).
q = heat energy input.
e = efficiency of converting heat to electrical energy.
Q = total thermal energy required by the process.

Water electrolysis is typically 30 to 35% thermally efficient. **(5)**

The *voltage efficiency* of water electrolysis compares the theoretical minimum voltage needed to split water with the actual voltage needed in the cell.

$$\text{Voltage efficiency} = 1.24\ \text{V/cell voltage} = \text{Minimum V needed/Actual V needed.}$$

This means that the voltage efficiency of a cell varies *inversly* with the cell voltage needed. At 1.9 V (for commercial electrolysers) cell efficiency is 65%. At 1.7 V some advanced cells with expensive platinum electrodes have a voltage efficiency of 73%.

The *cell voltage* of any particular electrolyser is the sum of several variables.

$$\text{Cell voltage} = E + iR + n.$$

Where:

E = required theoretical dissolution voltage of water = 1.24 V/electron.
iR = electrolyte resistance to current flow in the electrolyser (in ohms). This is minimized by reducing separator thickness and electrode spacing.
i = current passing through the cell.
R = area resistance (in ohms) determined by the conductivity of the electrolyte and the permeability of the membrane to fluid ions.

Energy Requirements

At 25°C (77°F) the voltage needed to split water is 1.24 V. It decreases with rising cell temperature by 0.82 millivolts (0.82 mV) per 1°C (1.8°F) and increases by 44.4 mV per 1°C if the pressure is increased ten times.

Conventional electrolysers operate at 75 to 80°C (167 to 176°F) with current densities of around 2 kiloamps per square meter (0.19 kA/ft^2). Voltage requirements for electrolysers fall within a 1.9 to 2 volt range. The required energy input is 4.8 kWh per cubic meter (0.14 kWh/ft^3) of hydrogen produced. This includes the total energy requirements for pumps and other equipment.

Although the energy input to the electrolysis process may be varied over a wide range, the reaction always requires about 2 volts. **Exhibit 4** shows no upper limit for current input but voltage requirements taper off at 2 volt. The larger the current flow the lower the voltage becomes in relation to it. Electrolyser efficiency is thus increased. However, the current density on the electrodes also increases with increasing current. This increases the resistance in the electrodes. Electrode thickness must, therefore, be minimized at 0.00001 cm (0.000004 in) or less.

The smallest amount of energy needed to electrolyse one mole of water is 65.3 Wh at 25°C (77°F). When the hydrogen and oxygen are recombined into water during combustion 79.3 Wh of energy is released. 14 Wh more energy is released in burning hydrogen and oxygen than is required to split water. This excess must be absorbed from the surrounding media in the form of heat during electrolysis.**(6)**

Voltage vs Temperature

If all the energy to split water came from electric current and no heat flowed into the reaction, 1.481 volts would be needed. As temperature is increased, this voltage at 25°C (77°F) would just begin to produce waste heat. Over 1.481 volts, increasingly large amounts of heat is generated. This critical limit of 1.481 V is referred to as the *thermoneutral voltage.*

Exhibit 5 shows the relationship between electrolyte temperature and the required voltage. **(7)** At 25°C (77°F) for voltages of 1.23 to 1.47 V, the electrolysis reaction *absorbs* heat. At over 1.47 V at 25°C the reaction *gives off* heat. The horizontal scale shows the desired operating temperature of the cell. In general, for voltages between the thermoneutral (upper limit) voltage and the reversible (lower limit) voltage the electrolysis reaction absorbs heat. The electrolysis cell operates most efficiently in this range. No electrolysis occurs below the reversible voltage.

With increasing operating temperatures both the electrochemical reduction resistance and the electrolyte resistance diminish. This reduces the lower limit below which hydrogen is not produced. Lower voltages and higher temperatures mean improved efficiency.

Cost of Electrolysis

The production costs of 293 kWh (one million BTU) of hydrogen are typically 500

EXHIBIT 4
Electrolyser Polarization

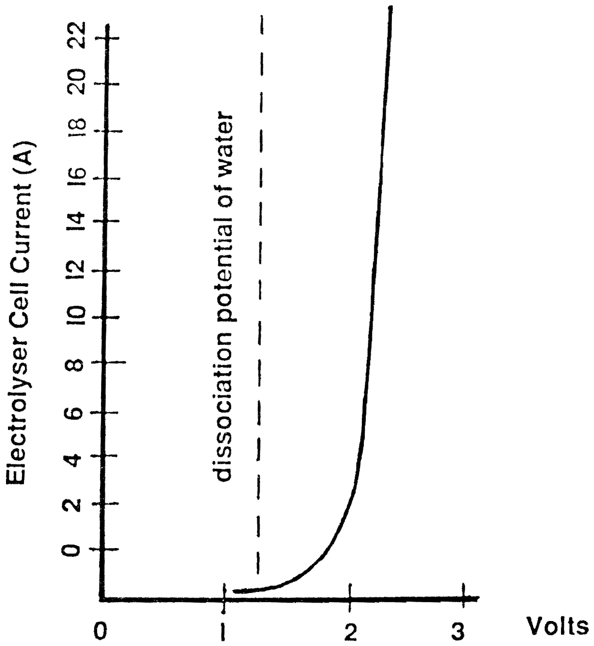
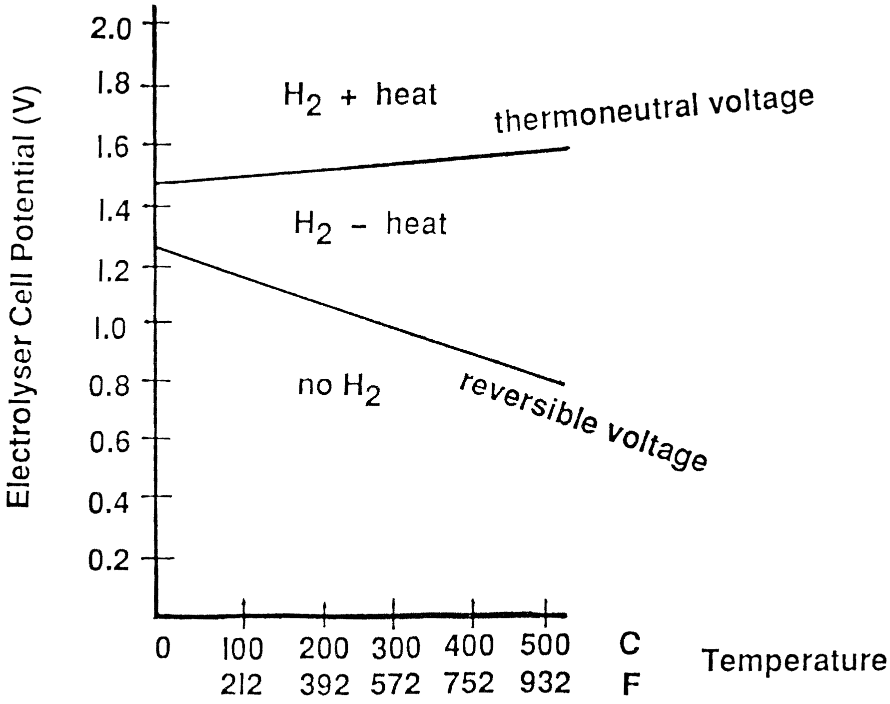


EXHIBIT 5
Temperature vs Voltage



to 775 times the cost of the electrical input. For example, if electricity costs $0.010 per kilowatt hour the cost of the hydrogen from a commercial electrolyser might be between $5.00 and $7.75 per million BTU of hydrogen fuel. **(8)**

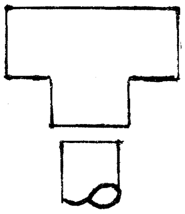
DESIGN FOR AN ELECTROLYSER

This section presents plans for building a homemade electrolyser. While not as efficient as commercial units, its cost is reasonable enough for the average do-it-yourselfer. The following components should be obtainable at local hardware stores and electrical shops for around $200.

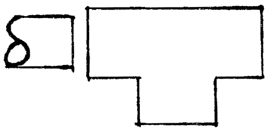
The electrolyte is 20 to 30% KOH in distilled or demineralized water. Electrode material: nickle plated steel, in the form of a solid sheet, sintered porous sheet, wire or gauze. Electric input: 2 volts per cell, 40 to 50 amps.

Materials and Parts List

- 14 terminal screws with nuts.
- Approximately 3.7 m (12 ft) of nickle wire,#12 gauge.For anode and cathode leads.
- Approximately 3.7 m (12 ft) of electrical wire, #12 gauge.
- 6 nickle or nonmagnetic stainless steel sheets 30 X 30cm (12 X 12 in). For anodes and cathodes. Cut 12.5 X 1.5 cm (2 X 6 in) squares for each electrode. Roll up 6 lengthwise, like a cigarette. See **Exhibit 7.**
- Approximately 3 m (10 ft) of PVC plastic tubing 2.5 (1 in) in diameter. For hydrogen columns and gas collection manifolds. Cut six 12.7 cm (5 in) sections for hydrogen columns.
- 7 PVC T-connections to fit the above tubing. Drill a small hole in each sufficient to accomodate one terminal screw. See **Exhibits 6** and **8.**
- One PVC L-connection to fit the tubing above.
- Approximately 1.8 m (6 ft) PVC tubing 1.3 to 1.9 cm (0.5 to 0.75 in) diameter for oxygen and water.
- 14 PVC T-connections that fit tubing, above. Glue ten 1.3 cm (0.5 in) long tube sections to ten T-connections like this.



Glue two 1.3 (0.5 in) tube sections to two T-connections, like this.



- Two PVC L-connections to fit the tubing above.
- 1.5 m (55 ft) of 7.6 cm (3 in) inside diameter PVC tubing. For electrolyte columns. Cut into six 15.2 cm lengths. Drill three holes in one container one above the other. The holes are 1.3 cm (0.5 in), 3.8 cm (1.5 in) and 7.5 cm (3 in) from the bottom as shown in **Exhibit 9** by the parts marked "B". Drill one hole in one container at the 3.8 cm (1.5 in) level marked "C" in **Exhibit 9.** Drill another hole in another container at the 3.8 cm (0.5 in) level, marked "D" in **Exhibit 9.** Drill one hole in each of six containers at the 7.6 cm (3 in) level, marked "E" in **Exhibit 9.**
- 18 PVC end caps to fit the above tubing. For the base and top of each electrolyte container. Drill 3 holes in each of six end caps. Marked "A", "B", and "C" in

Exhibit 8. "A" fits the hydrogen chamber. "B" fits the oxygen tubing shown. Drill an "A", "B" and "C" type hole in the center of each of three different end caps.

- Epoxy glue.
- Flexible sealing compound.
- Two boards 91 X 16 X 2.5 cm thick (36 X 6 X 1 in). One board 94 X 17 X 2.5 cm thick (37 X 7 X 1 in). Two boards used as base plates. Glue together as shown in **Exhibit 9.** One board is used as a frame by drilling nine holes to slip over the electrolyte columns and are spaced as shown in **Exhibit 9.**
- Two end supports marked "F" in **Exhibit 9.**
- 5 valves to accomodate the diameters of the oxygen and hydrogen tubes and for the decompression and tank valves. See **Exhibit 7.**
- 5 relief valves designed for 0 to 4.1 atm (0.41 MPa, 60 psi).
- 2 check valves (one-way valves).
- Low amp switch.
- One 15.2 cm (6 in) dowell rod 1 to 2 cm (0.25 to 0.50 in) in diameter.
- Adjustable wing nut and clamp assembly to adjust the height of the safety switch as shown in **Exhibit 9.**
- One 61 X 153 cm (24 X 60 in) aluminum or stainless steel sheet cut and folded to form the vent hood. Seal joints. If sheet this large cannot be found use smaller sections joined together.
- 8 wood screws to fasten hood to base plate as shown in **Exhibit 9.**
- 1 voltmeter and 1 amp meter.
- 1 plastic foam float to fit inside one electrolyte container. Assemble with dowell and stabilizing weight as shown in **Exhibit 9.**
- 1 small vent blower.

Cell Assembly

- Glue the undrilled end cap (the base) to the container.
- Wrap the cathode lead around the terminal screw and insert screw into hole in the T-connection. Apply sealing compound. Secure with nut.
- Repeat with anode but use the hole "B" in end cap.
- Insert cathode into hydrogen column. Glue hydrogen column to edge of hole in end cap as shown in **Exhibit 6.**
- Fit, do not glue, T-connection, hydrogen column and end cap together as shown in **Exhibit 6.** This makes it possible to replace the cathode later, if necessary. Repeat for oxygen and water T-connections.
- Insert hydrogen column through the anode loop.
- Repeat the above process for the five other cells.

Cut and fit tubing and connectors to fit as shown in **Exhibit 9.** Glue all vertical columns to connectors. Other sections may be left unglued for easier assembly and disassembly. Be sure to seal all joints left unglued to prevent hydrogen gas leaks.

WARNING: **Leaking hydrogen could cause an explosion. Vent the oxygen at least 18 meters (50 ft) from the hydrogen. Keep all flames and sparks away from the electrolyser when it is in operation. Insulate all electrical connections.**

The float-activated safety switch is shown in **Exhibit 9.** It works as follows. As hydrogen is generated and accumulates in the storage tank, pressure builds, forcing the water level down. The displaced fluid causes the level in the overflow tank to rise. As the float rises, the shaft engages the safety switch turning the electrolyser off before the pressure reaches the danger point. A compressor, if used, may automatically turn off at this point. When the pressure drops, the fluid level also drops and the electrolyser is turned back on. The compressor should be automatically turned off. Wire as shown in **Exhibit 7** and **9.**

EXHIBIT 6
Cell Crossection

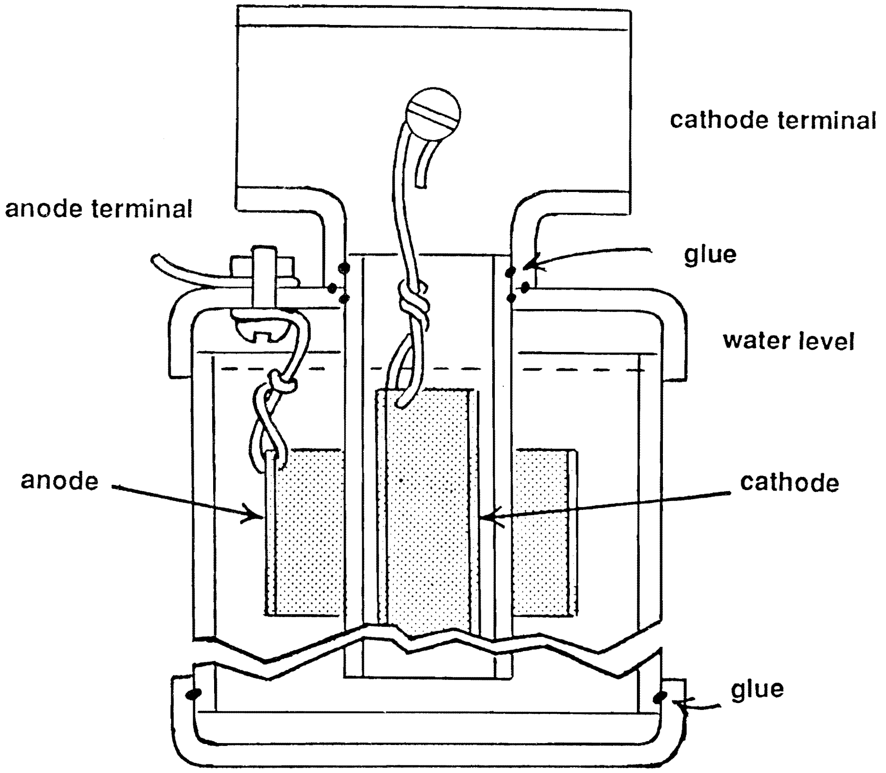


EXHIBIT 7
System Schematic

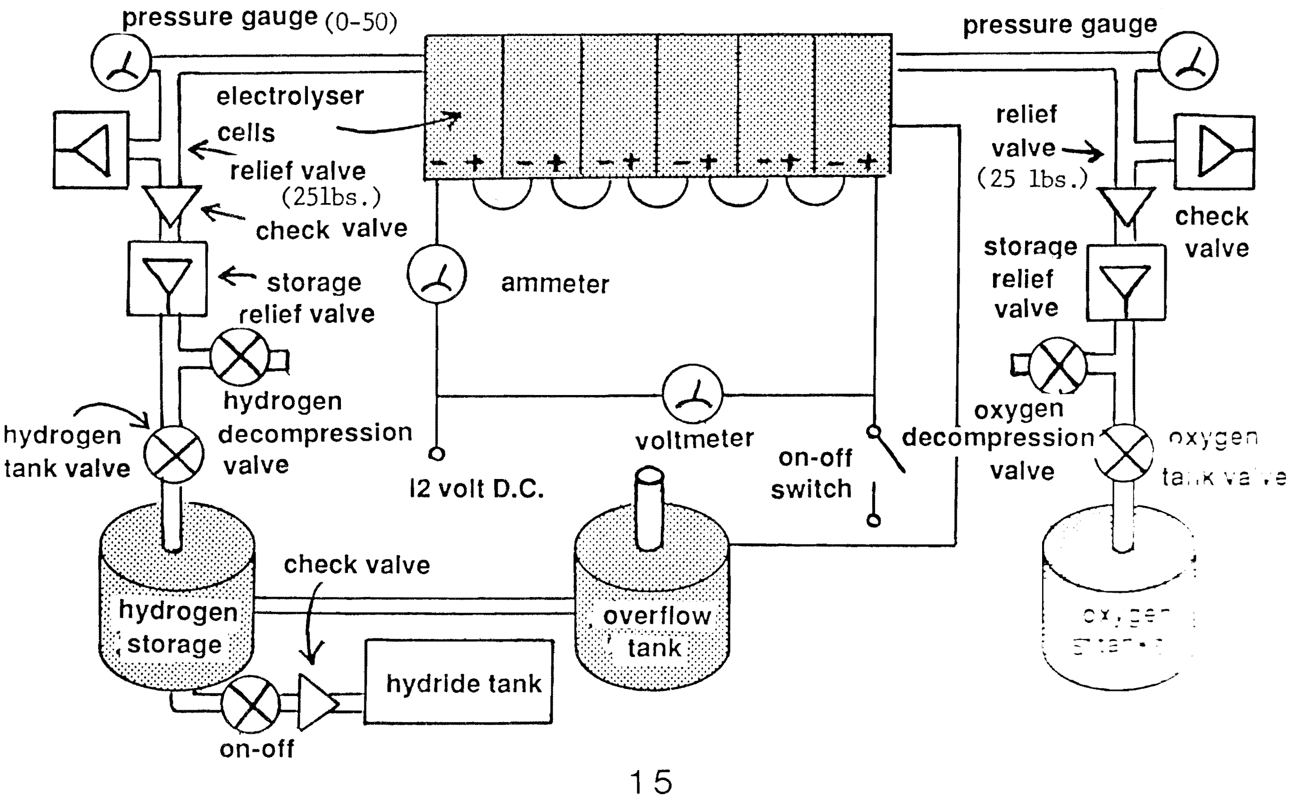


EXHIBIT 8
Exploded Diagram of Electrolysis Cell

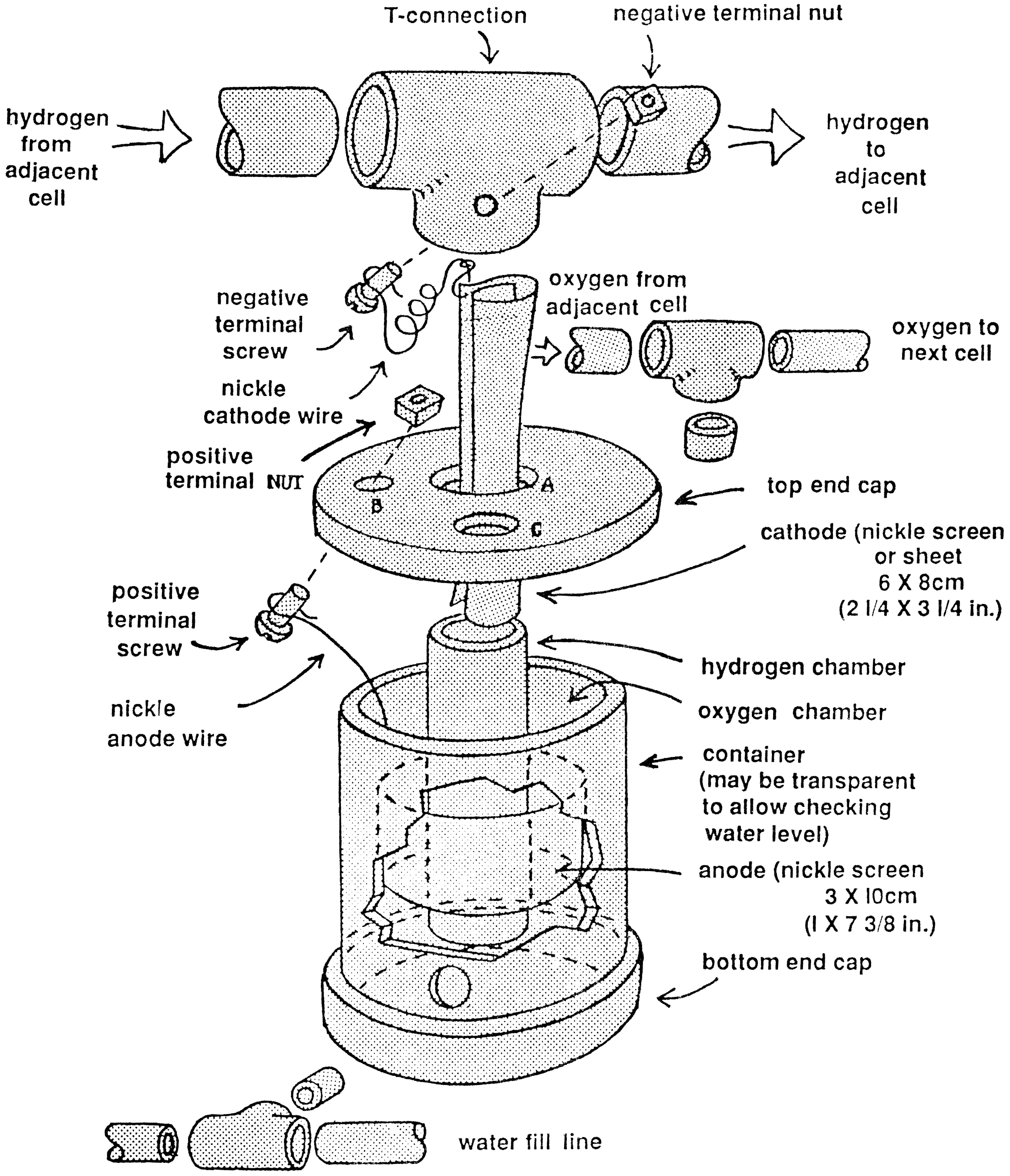
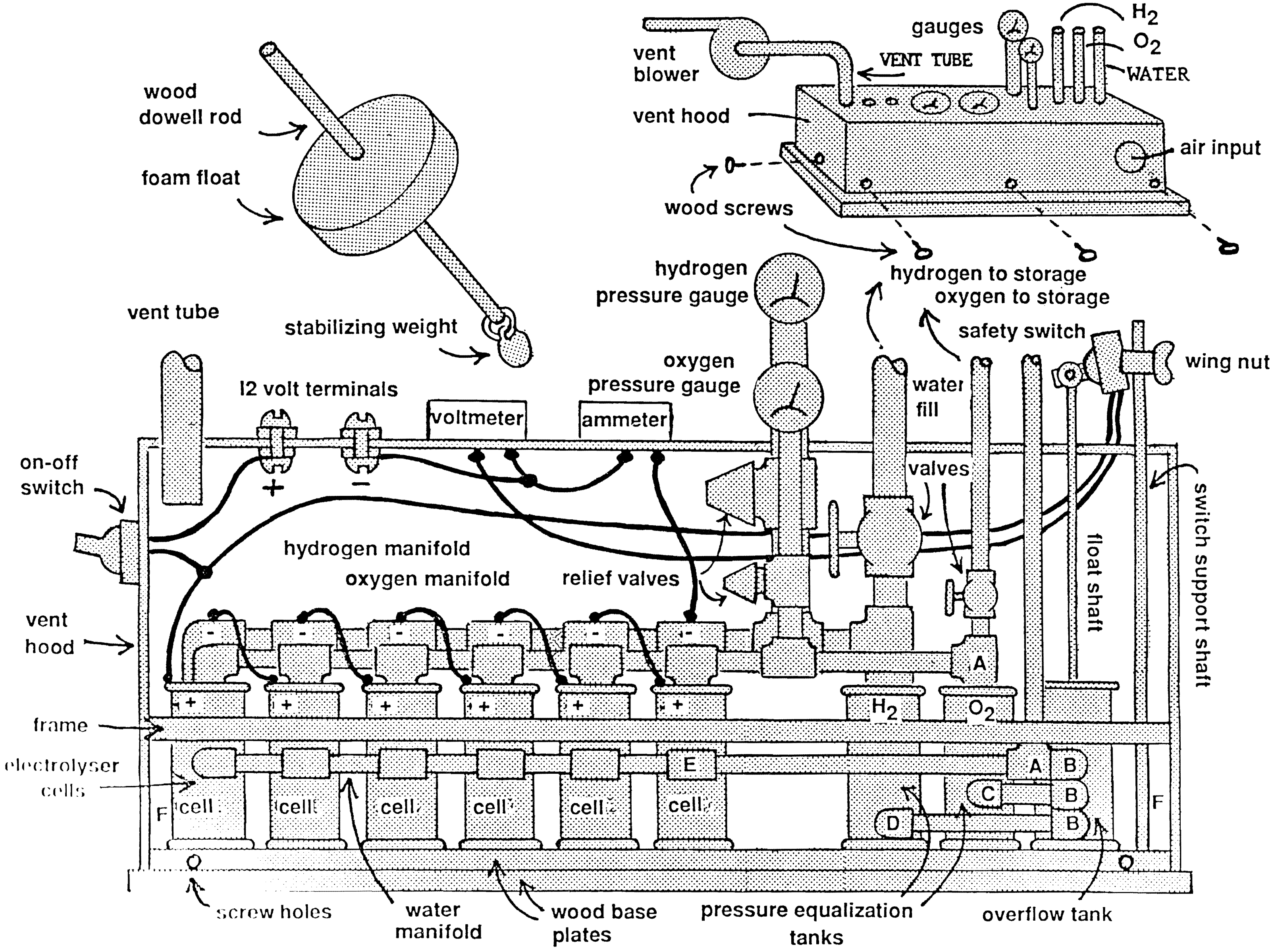


EXHIBIT 9
Side View of Electrolyser



WARNING: Never reverse the terminals. This would cause hydrogen to be generated at the oxygen electrode, and oxygen to be generated at the hydrogen electrode. The gasses would mix causing an explosion hazard.

Adding the Electrolyte

Using an ohm meter to measure the electrical resistance of the electrolyte, add potassium hydroxide until the resistance equals 0.3 ohms, or a 30% solution, whichever comes first. Note that the higher the current of the cell, the less electrolyte needs to be used.

WARNING: When the electrolyser is first used, hydrogen and oxygen may be mixed. Discard the first hour's production.

Output

At 100% efficiency, 12 volts and 40 amps, 480 watts (0.6 horsepower) per hour of hydrogen fuel is produced. In practice, efficiency is usually about 25%. This means that output is one-fourth of what it would be if the unit were 100% efficient.

WARNING: Place the electrolyser at a safe distance from habitable buildings. Change the electrolyte every 1,000 hours of oepration. Ground all circuits. Keep feet dry when touching the electrolyser.

The above design may be scaled up for higher output by increasing the height and width of the elecrolyte containers, the area of the electrodes, or increasing the number of cells. Larger designs with higher current may employ cooling fins around the cells so that the blower may dissipate heat more readily to avoid damage to the electrolyte materials.

If 115 volts of alternating utility current is used for electrolysis, a transformer and rectifier are neededto convert the current to 2 volts direct current with boosted amperage.

HIGH PRESSURE CELL

The following is a general description of a relatively high pressure electrolyser. **(9)** It is designed to operate at 200°C (485°F) and 98.7 atm (10 MPa, 1,450 psi). The gap between the electrodes is 3 mm (0.12 in). These design features combine to give the device a 75% efficiency. Other features include:

- Sanded nickle electrodes to increase surface area.
- 30 to 50% KOH electrolyte.
- 1.6 volts and 1 amp per square centimeter ($0.16A / in^2$) at 200°C (392°F).

Since asbestos is corroded in caustic solutions at temperatures above 100°C (212°F) the diaphragms are made of metal screens covered with oxide ceramic. These are corrosion resistant and have a high hydraulic resistance with small pores. This feature eliminates the probability of passing significant amounts of gas bubbles. The separators also have a low electrical resistance of 0.05 to 0.10 ohm/cm^2 (0.016 ohm/in^2). Nickle electrodes will corrode in caustic solutions at high temperature. The anode in this design corrodes at the rate of 0.03 mm/year (0.002 in/year) at 0.01 amp/cm^2 (0.07 amp/in^2) and 0.10 mm/year (0.04 in/year) at 1.0 amp/cm^2 (7 amp/in^2). The cathode deterioration rate is 0.01mm/year (0.004 in/year) at 0.01 amp/cm^2 (0.07 amp/in^2). The cathode corrosion rate increases to 0.0003 mm/year (0.0012 in/year) at 1.0 amp/cm^2 (7 amp/in^2).

In the high temperature region plastics cannot be used. In these areas all bodies and tubings are made of steel-lined with nickle because nickle does not absorb hydrogen as many other metals do. Steel is needed for its strength but must not come into contact with the hydrogen.

The electrodes are made of coarse screen: 0.6 mm (0.24 in) diameter wire layed out in a 0.52 mm (0.02 in) mesh. A 1 mm (0.04 in) perforated nickle plate may be substituted. The electrode may also be corrigated to increase surface area even further. Each corrigation has a 3 cm (1.2 in) radius.

High temperatures combined with caustic solutions destroy many high temperature plastic materials. Nafion (R) was found to be destroyed in days at 150°C (302°F) and in a 50% KOH solution.

An exploded view of the electrolyser cell "sandwich" is shown in **Exhibit 10.** Hydrogen is produced at slightly above the thermoneutral voltage shown in **Exhibit 5.** At this voltage, heat is produced in the electrolyser along with hydrogen. This cell can be connected to the meters, valves and storage tanks as shown in **Exhibit 7.**

Free electricity may be used to power the electrolyser. These can take the form of photovoltaic cells or windpower plants, such as the 32 volt, 40 amp Jacobs model. Connect the wind driven generator to batteries and then connect the batteries to the electrolyser to insure constant current supply.

SOLID POLYMER ELECTROLYTE

A basic problem in designing electrolysers is to allow *ions* to travel between the electrodes while at the same time excluding gas molecules. Liquid electrolytes transfer both the gas bubbles and the ions. Since the distance between electrodes must be small to minimize electrical resistance, the problem of keeping the evolved hydrogen and oxygen gasses separate becomes even more acute. Solid porus barriers known as *separators* are used with liquid electrolytes to keep the evolved gasses separate but to allow ion transfer.

With the advent of *solid electrolytes* the separator is no longer needed. The electrolyte alone performs this function. The electrodes are immersed in water but are separated by the solid electrolyte. See **Exhibit 11.**

Thinner solid electrolyte cells may be designed to accomplish the same task as a liquid electrolyte cell. This reduces internal resistance. Because the solid electrolyte typically has a high melting point, the cell may operate at elevated temperatures, thereby increasing efficiency.

General Electric has developed a solid electrolyte made of *perfluorinated sulfonic acid polymer* 0.1 mm (0.004 in) thick and capable of operating at temperatures between 120 to 150°C (248 to 302°F). Current densities of 20,000 amp/m^2 (1,872 A/ft^2) allow a 90% thermodynamic efficiency. Capital costs are $200 to 280/kWh. Hydrogen production costs range from $4.10 to 7.00/1,000 kWh assuming electric power costs of $0.06 to 0.23/kWh. **(10)**

By contrast, a current state of the art machine, the Teledyne alkaline liquid electrolyser, requires a capital investment of $260 to 320/kWh. A high temperature separator withstands a 150°C (302°F) operating temperature. Current density is 4,000 to 6,000 A/m^2 (432 to 575 A/ft^2). Hydrogen production costs are comparable to the GE electrolyser.

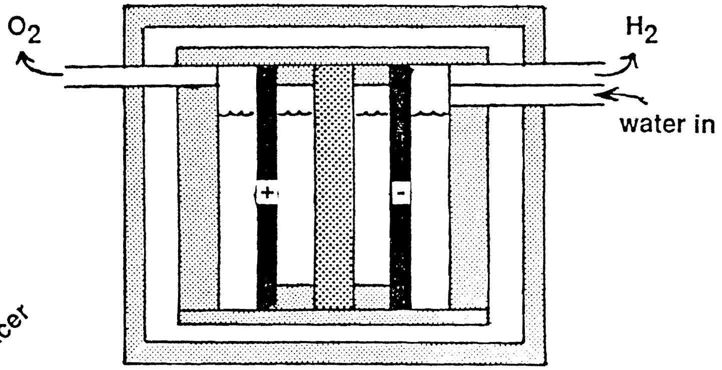
Exhibit 12 shows a Westinghouse solid polymer cell. It is configured as a tube. Water is injected as steam at one end of the tube and hydrogen gas comes out the other end. Oxygen emerges from the outside wall (anode) of the tube. The cathode forms the inner wall of the tube. The solid polymer separates the inner and outer walls of the tube. **Exhibit 12** shows that the cell tube is connected in sections and reveals the details of the joints.

CELL CONNECTIONS

A pair of electrodes and a container of electrolyte make up one elctrode *cell.* Several cells can be combined for greater output. Cells may be electrically connected in *parallel* or in *series.*

EXHIBIT 10

High Temperature Electrolyser "Sandwich"



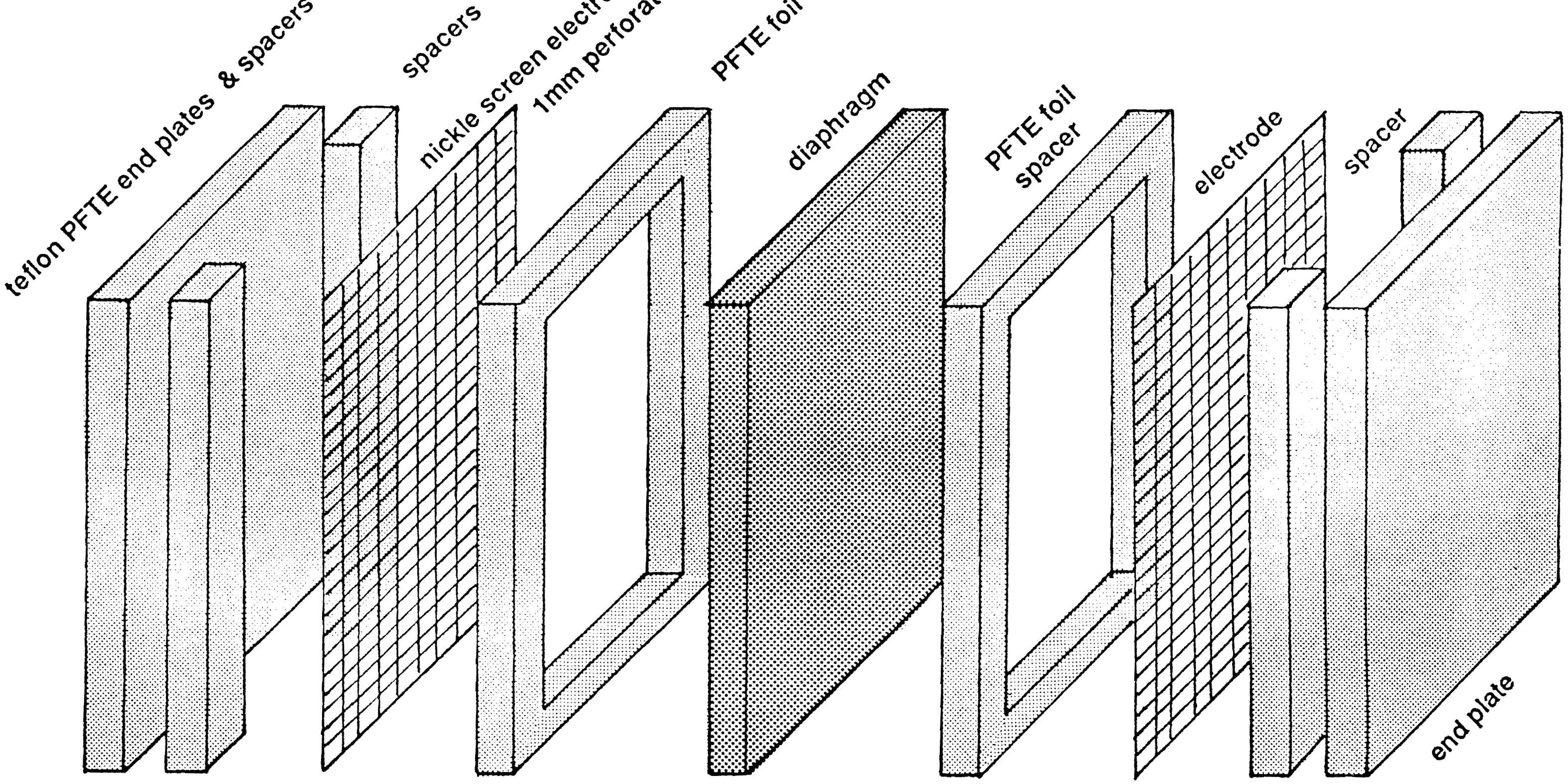


EXHIBIT 11
Solid Electrolyte Cell

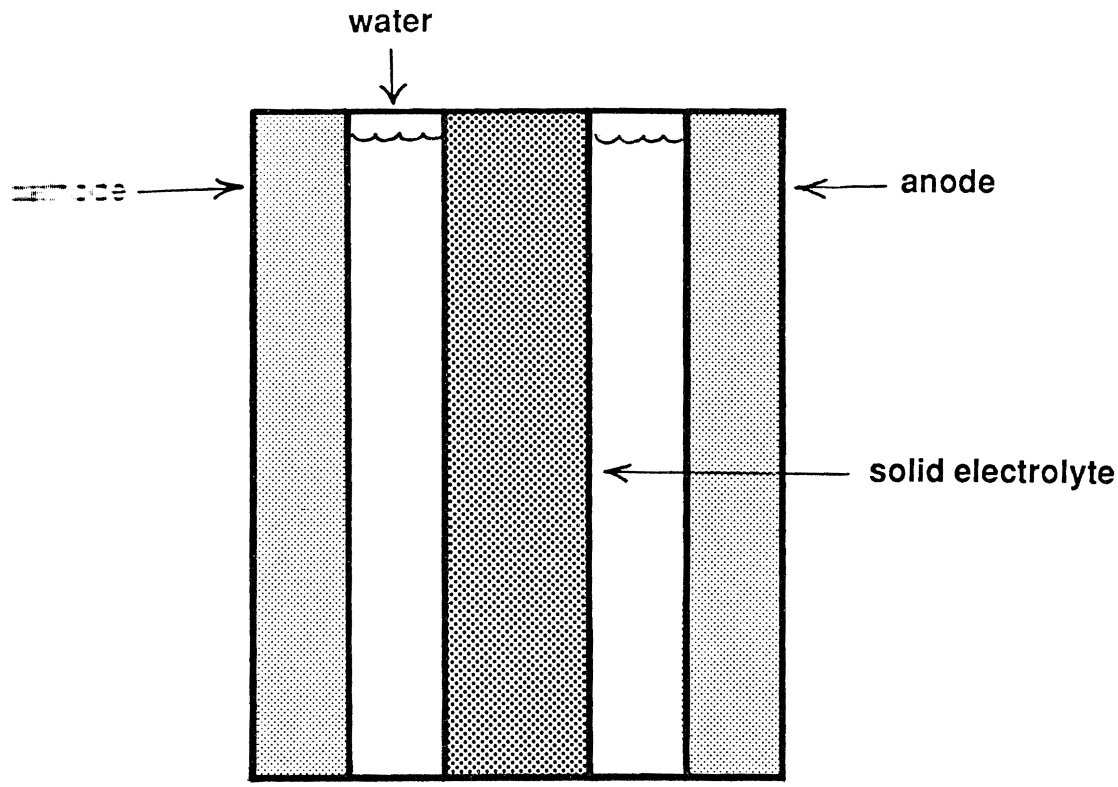
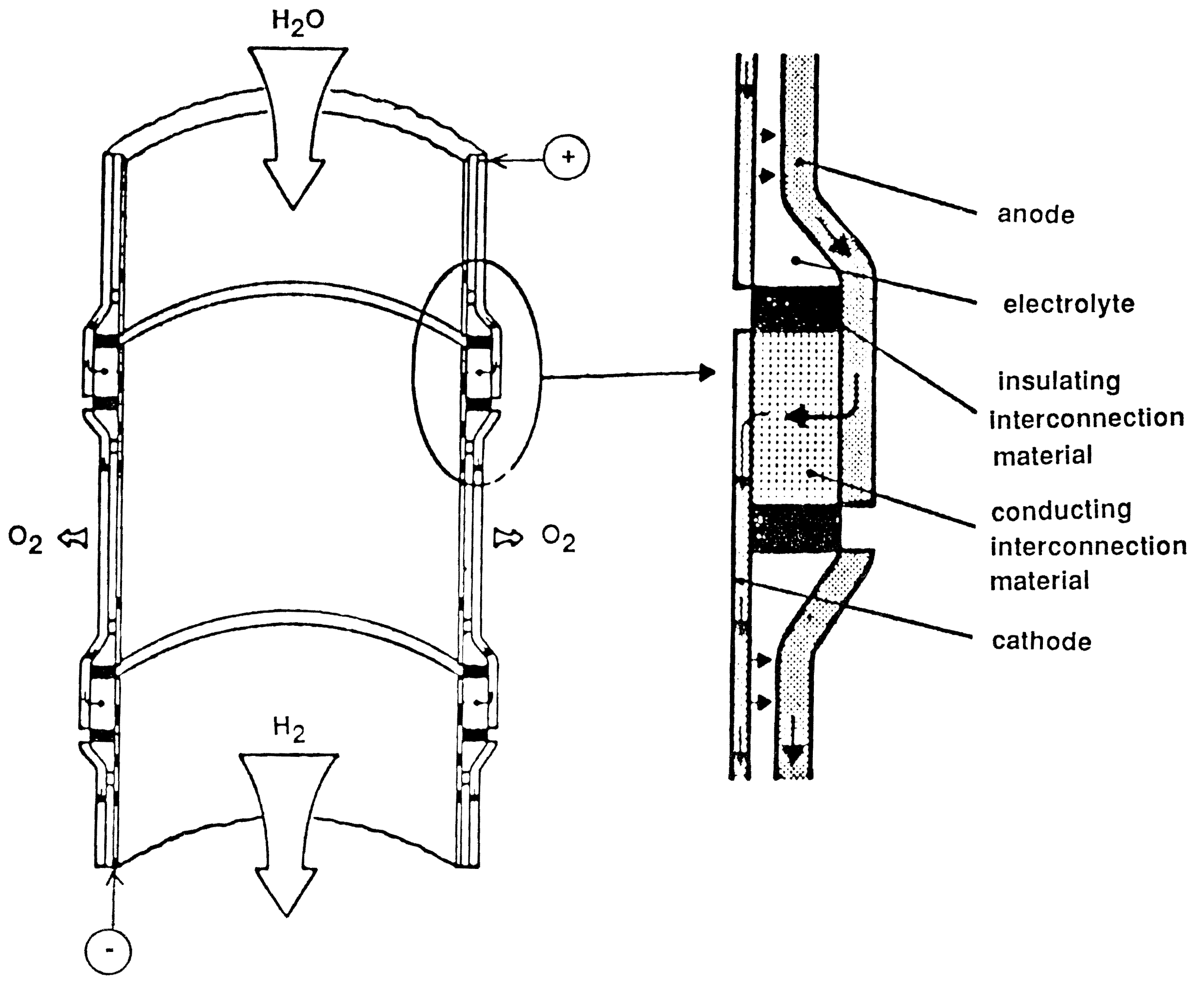


EXHIBIT 12

Crossection of S.P.E. Cell and Joint Detail



In the *parallel (or unipolar)* connection shown in **Exhibit 13**, each anode is connected separately to the positive terminal of the electric source. Each cathode is similarly connected to the negative terminal. Each cell can be switched off without effecting the neighboring cells. The electrolyte container for each cell is also kept separate from the other cells. This means that each cell can be removed and repaired individually without shutting down the whole unit. The voltage requirement for the entire unit is equal to that of one cell. However, the current requirements of this array are higher than for a single cell. The total current needed is figured as follows.

Current needed = current requirements of each X number of cells.

The *series (bipolar)* electrolyser is made up of cells each sharing an electrode with the next cell. Each electrode has a positive and a negative side. The positive side serves as the anode and the negative side serves as the cathode. The removal and repair of one cell means that the entire electrolyser must be shut down. Unlike the parallel electrolyser, the voltage needed for the entire electrolyser is:

Voltage needed = voltage requirements of each cell X number of cells.

The current consumed for the entire electrolyser is the same as the current consumption for any one cell.

Advantages of Parallel Compared to Series Electrolysers

- Individual cells may be isolated without effecting neighboring cells.
- Higher current density is possible, resulting in higher current efficiency approaching 100%. **Exhibit 14** Shows a four cell unit. Notice how the voltage requirements taper off when operating over 2,200 A/m^2 (200 A/ft^2).
- Longer service life is possible (25 years or more) with maintenance-free operation for the first 10 years.

Disadvantages of Parallel Compared to Series Electrolysers

- Low voltage and high current is needed resulting in the need for large conductors (bus bars) to keep electrical resistance low. Large current consumption also requires large transformers and rectifiers.
- Because each cell is separate and the components are not shared, as in the series type, more floor space is needed. Liquid electrolyte must be kept in motion in each cell to control heat and remove waste gasses. A manifold circulates the electrolyte in each cell separately, as shown in **Exhibit 15.** In **Exhibit 16** notice how the hydrogen manifold delivers gas to the overhead tank for collection "over water" as in small scale lab experiments. This prevents reverse gas flow.

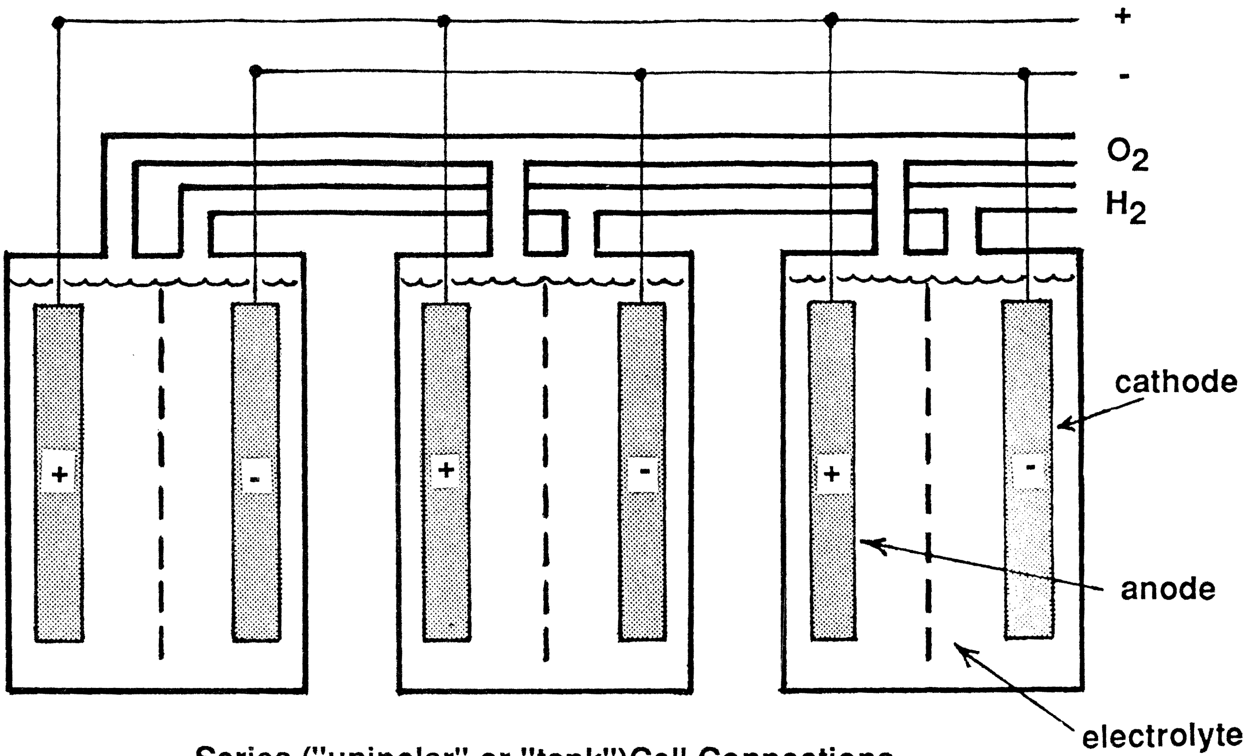
Advantages of Series Compared to Parallel Electrolysers

- High voltage and low current means more efficient AC-DC rectification.
- Less floor space is needed due to thinner cells.
- All cells share a common electrolyte bath allowing freer circulation of the electrolyte. Gas production also helps circulate the electrolyte.

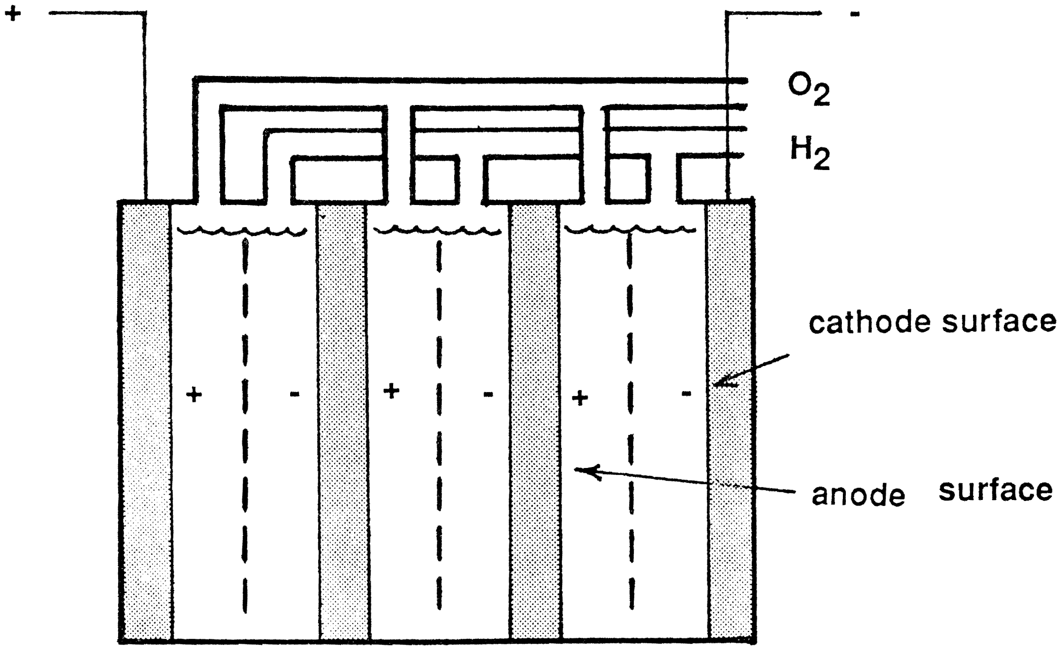
Disadvantages of Series Compared to Parallel Electrolysers

- High voltage and low current input combine to give lower current efficiencies of 95% or less.
- Each cell must be engineered to be identical to all the other cells in the electrolyser to

EXHIBIT 13
Electrolyser Cell Connections (Series and Parallel)



Series ("unipolar" or "tank")Cell Connections
Total voltage = number of cells X voltage for each cell.



Parallel ("bipolar" or "filter press") Cell Conections
Total voltage = number of pairs of electrodes X voltage for each cell.
= number of cells X voltage for each cell.

EXHIBIT 14

Design Performance of Four-Cell Unit

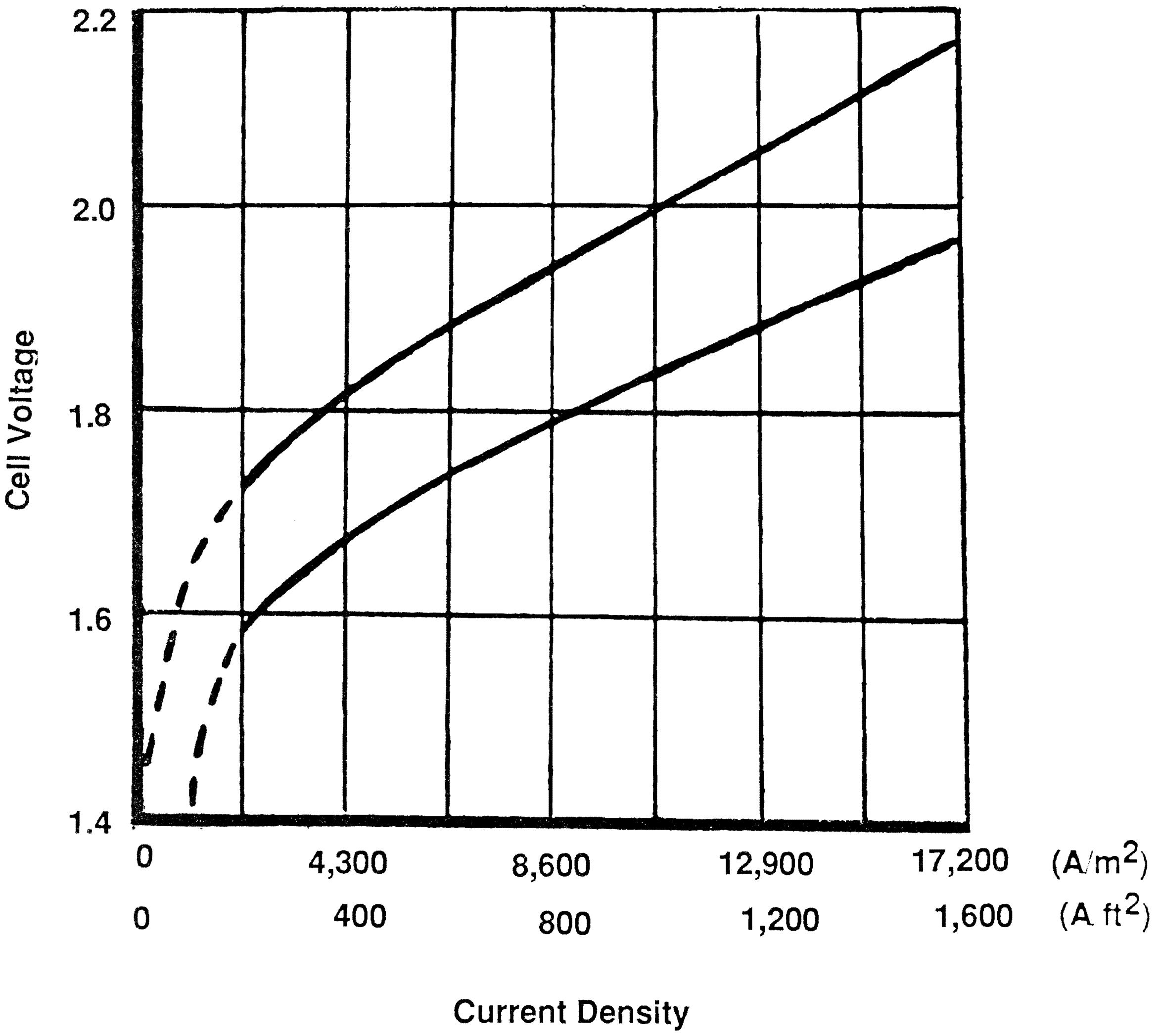


EXHIBIT 15

Crossection of Single Parallel Cell Showing Electrolyte Circulation

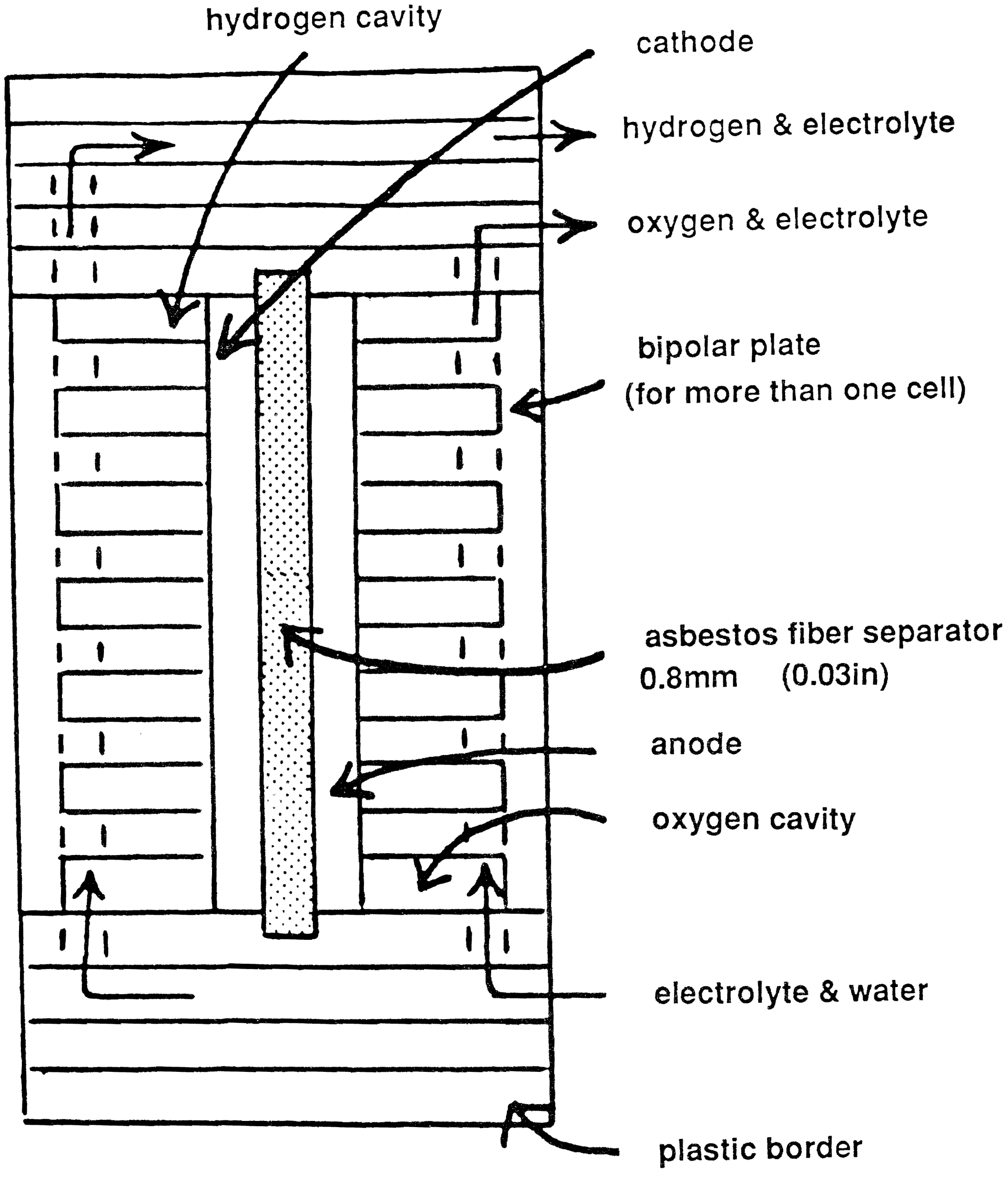
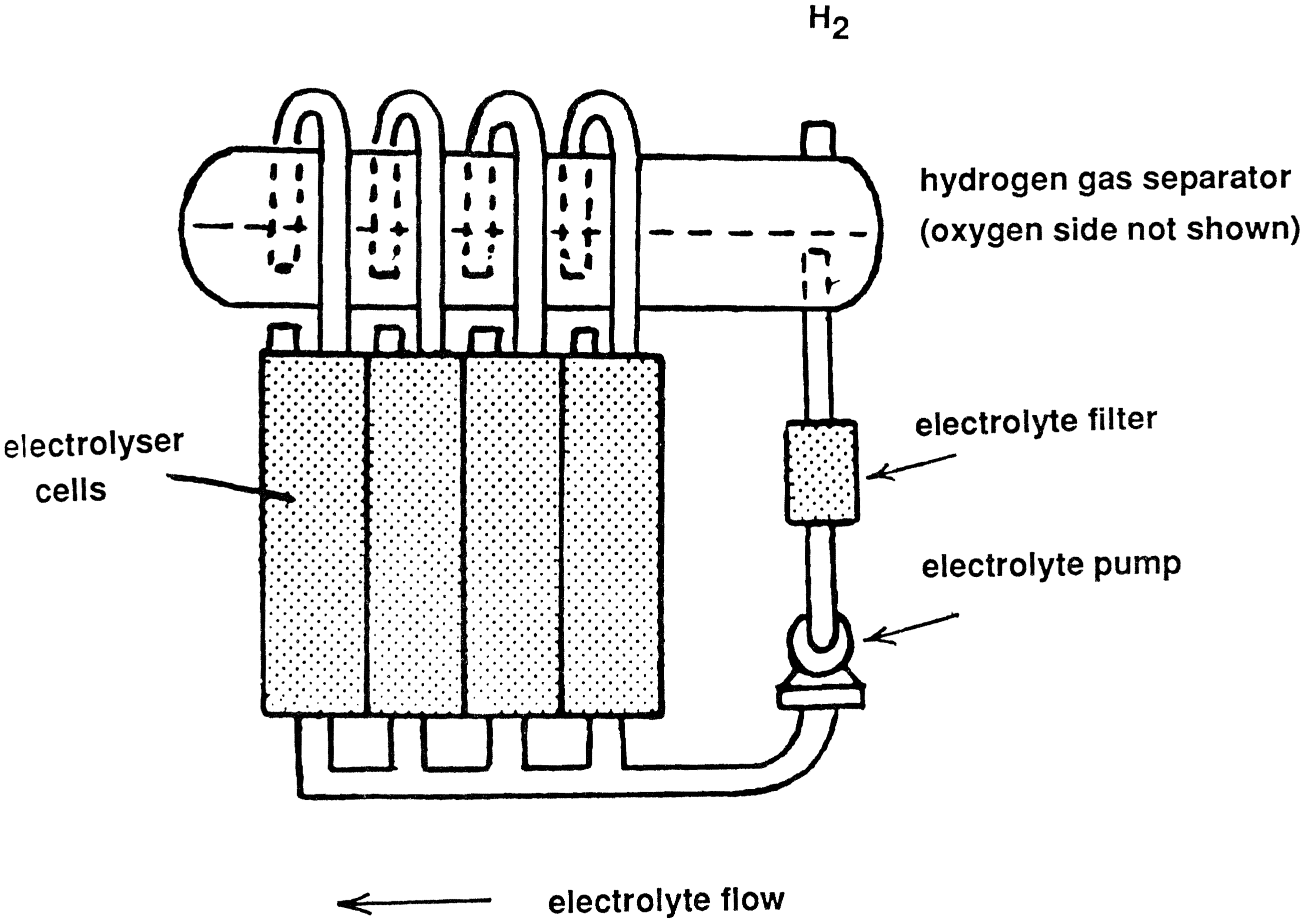


EXHIBIT 16

Electrolyte Circulation in a Four-Cell Parallel Unit



avoid overloads. Capital costs, therefore, are usually higher.

With a solid polymer electrolyte the need for electrolyte circulation may be avoided. **Exhibit 17** shows how the experimental solid polymer tubes, described earlier, may be connected in a single electrolyser module. The ends of the tubes are capped. Steam under high pressure enters one end of the tube and is converted to hydrogen. Oxygen is vented outside. The hydrogen gas at the capped end, still under pressure from the rising steam, is forced down a smaller diameter tube inside each electrolyser cell. Manifolds deliver steam to each tube and remove hydrogen as shown.

The material used for the gas ducts is a high temperature-resistant alloy while the base frame for the cells is made of aluminum. At high temperatures aluminum, the manifold, and the cell bodies all expand at different rates. Special joining techniques had to be devised to insure tight connections at prevent gas leaks. Their reliability has been prooven in tests. **(11)** This and other problems illustrate the difficult of engineering high temperature electrolysers.

Commercial electrolyser may combine both series and parallel connections of cells to achieve the right combination of features and current-voltage characteristics. One such hybrid connection is shown in **Exhibit 17.** A typical electrolyser installation might have a row of cells connected in series. Auxilliary parallel connections allow each cell to be shut down without effecting the other cells.

COMMERCIAL ELECTROLYSERS

Electrolysers made for industry usually operate at high temperatures and pressures to increase efficiency and reduce operating costs. The optimum voltage decreases about 0.83 millivolts per degree centigrade of temperature increase. For standard liquid electrolyte cells, as shown in **Exhibit 18** and **19**, at an operating pressure of 20 atm (2.1MPa, 300 psi) and at a temperature of 121°C (250°F) hydrogen is produced at about 0.04 m^3 per m^2 (0.07 ft^3/ft^2) per minute. Half as much oxygen is produced in the same time. Typical performance and components of commercial electrolysers can be illustrated by describing the Stuart Cell manufactured in Canada by the Electrolyser Corporation.**(12)**

- Hydrogen output: 818 m^3/hr (28,900 ft^2/hr). 99.9% pure.
- Energy input: A.C. 4.70 kWh/m^3 (0.13 kWh/ft^3).
  D.C.4.52 kWh/m^3 (0.13 kWh/ft^3).
- Current density: 1,350 A/m^2 (125 A/ft^2). State of the art for some electrolysers permits up to 5,00 A/m^2 (465 A/ft^2).
- Cell voltage: 2.04 volts.
- Current efficiencies: 100%.
- Thermodynamic efficiency: 72%. State of the art ranges up to85%.
- Electrolyte: 30% potassium hydroxide.
- Water feed rate: 25 liter/hour (6.6 gallon/hour).
- Cooling water feed rate: 1,098 liters/hour (290 gallon/hour).
- Electrode material: low carbon steel.
- Anode material: low carbon steel, nickle-plated.
- Separator material: woven asbestos cloth.
- Operating temperature: 70°C (158°F).
- Operating pressure: 1 atm (0.1 MPa, 14.7 lb/in^2).
- Teflon gaskets, stainless steel cell frames and end plates.

For typical electrolyser installations hydrogen production costs range from $680 to 4,250/kW for small plants and from $350 to 680/kW for large plants. Capital costs are about 30% of total costs. The operating costs not directly related to power generation are 10% of the above figures. **(13)**

Few plants are larger than 5 megawatts (5 MW). A proposed plant in Canada would have an output of 3,000 kg (6,600 lb). This equivalent to 3,000 kW. This plant would

EXHIBIT 17
A Module of S.P.E. Cells

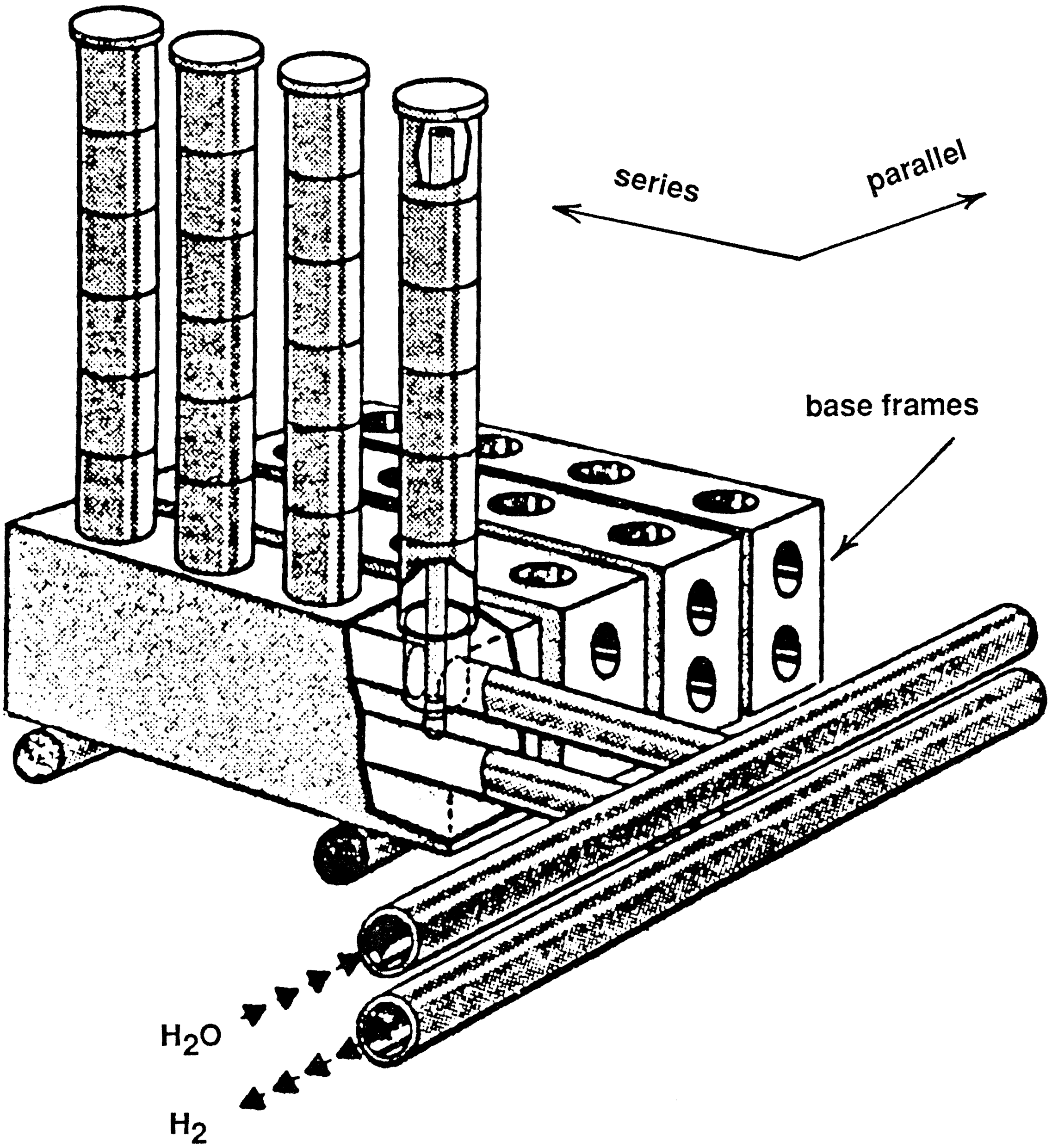
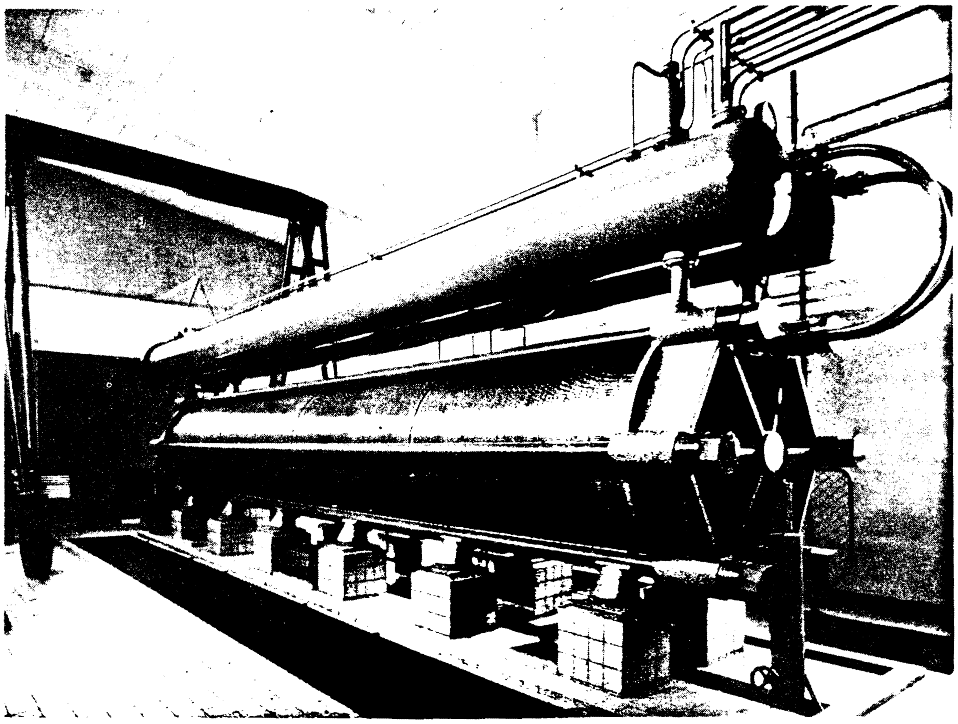


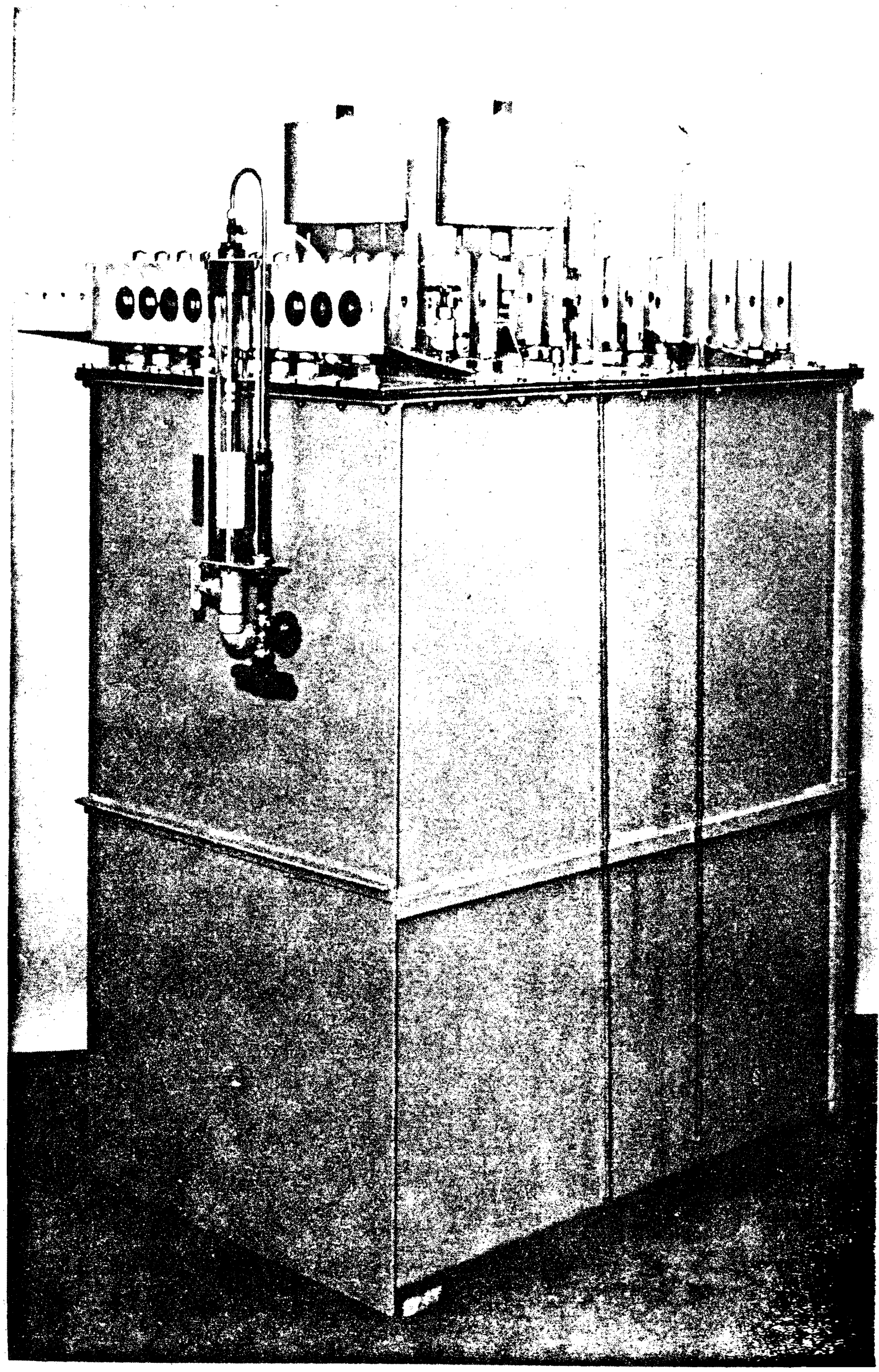
EXHIBIT 18

Lurgi Parallel Electrolyser



The "Electrolytor" is capable of producing 740 m^3/hour (26 100 ft^3/hour) of hydrogen gas. (Courtesy of Lurgi-Apparate-Technik GmbH.)

EXHIBIT 19
Stuart Series Electrolyser



This electrolyser produces 818 m^3/hour (28 900 ft^3/hour) of hydrogen gas. (Courtesy of The Electrolyser Corporation, Ltd.

need an input of 7 MW. Described as the "the largest of its kind" **(14)** the plant will provide gaseous hydrogen for a liquid hydrogen fuel production facility to service customers in Canada and the northeastern U.S. Cheap, readily available electricity from Hydro Quebec will be supplemented by surplus hydrogen from a nearby chloralkali plant. The $32 million cost is shared by the Canadian government ($4.1 million), the Quebec provincial government ($3.2 million) and private sources.

Electrical power fed to a commercial electrolyser plant from the utility must be converted from *alternating* to *direct* current (A.C. to D.C.). For the Candian plant described above 25,000 volt, 3 phase, 60 cycle A.C. power is converted to D.C. by two rectifiers into 100,000 A at 74.6 V.D.C.

HIGH PRESSURE ELECTROLYSIS

Some manufacturers specify operating pressures from 5 to 30 atm (0.5 MPa, 74 psi to 3 MPa, 441 psi). The advantages of operating at high pressures are given below.

- Reduced power consumption.
- Compressors used to prepare the product gasses for storage may operate at lower pressure if the electrolyser supplies some of the input pressure.
- Reduced cell size.
- Reduced voltage losses.

Dissadvantages of high pressure operation also become apparent.

- Increased costs of pressure vessels.
- It becomes more critical to maintain a precarious balance between oxygen and hydrogen gas pressure to prevent separator failure.
- Increased dissolved gasses appear in the electrolyte. This may be overcome by using pressurized feed water.

Despite the engineering challenge the cost-benefit tradeoffs still weigh in favor of high pressure operation. The DeNora company of Italy produces units operating at 30 atm (3 MPa, 441 psi). **(15)**

HIGH TEMPERATURE ELECTROLYSERS

Increased Performance

As was seen in **Exhibit 5**, a large increase in the operating temperature of the electrolysis process requires only slight increases in voltage but provides a substantial increase in efficiency. Energy in the form of heat is partially substituted for the electrical energy needed to split water. According to K.H. Quandt, *"One has the possibliity of providing part of the splitting energy by thermal energy instead of electrical, thus achieving higher total efficiency".* **(16)** This is particularly true if water is fed into the electrolyser as steam. Less energy is needed to split water in the vapor phase because of reduced demand for electricity at the electrode and the possibility of using increased current densities.

A high temperature electrolysis (HTE) development program called *Hot Elly* was begun in 1977 by the German Federal Ministry of Research and Technology. The technology, it is reported, *"has reached an advanced status".* **(17)** High temperature operation allows a 30% reduction in energy input for each volume of hydrogen produced - from 4.5 to 3.2 kWh/m^3 (0.13 to 0.09 kWh/ft^3). For 1,000^{o}C (1,800^{o}F) experimental results are summarized below for two different energy inputs.

- 1.33 volts, 5,000 A/m^2 (465 A/ft^2).
- 1.07 volts, 3,000 A/m^2 (279 A/ft^2).

85% of the steam is converted to hydrogen.

For commercial applications, commercial requirements call for an steam conversion of 70% and current densities of at least 3,700 A/m^2 (344 A/ft^2) and voltages of no more than 1.33 volts. **Exhibit 20** compares the performance of three classes of electrolysers.

- Conventional commercial electrolysers using an alkaline electrolyte.
- Experimental advanced low temperature electrolysers including both liquid and solid electroltyes.
- Water vapor electrolysis with a temperature of around 1,000^{o}C (1,800^{o}F).

The second group has a clear advantage over conventional commercial electrolysers. The lower the voltage the higher is the efficiency. High temperature electrolysis (HTE) has an even greater advantage over experimental low temperature electrolysers.

Materials

At high temperatures other materials must be substituted for asbestos in the separator. Two materials, potassium titanite or perfluorinated sulfonic acid polymer, Nafion (R), may be used instead.

The General Electric solid polymer electrolyser, mentioned in a previous section, is designed to split 1,000^{o}C (1,800^{o}F) steam. The solid electrolyte serves a double function as a charge conductor and a gas separator. High temperature materials used were: **(18)**

- Base frame: alumina.
- Gas ducts inside tubes: high temperature-resistant alloy (Iconel 601).
- Electrodes: yttria-stabilized zirconia.

The main problem in working with such materials at high temperature is in joining materials with different expansion properties.

Modes of Operation

Electrolysers both consume and produce heat. For any electrolyser, operating at a specific temperature, there is a certain voltage (the *thermoneutral voltage)* at which as much heat is consumed as is produced. Above this voltage, the electrolysis reaction produces heat, and below the voltage, it consumes heat. **Exhibit 5** shows the electrolysis voltage-temperature relationship graphically.

In a presentation of a design for a high temperature electrolyser various modes of operation were analysed. **(19)**

A high temperature electrolyser operating exothermally (above the thermoneutral voltage) needs no external high temperature heat source. Only 200^{o}C (390^{o}F) steam is needed to insure a gas output temperature 70^{o}C (160^{o}F) greater than the input. This lowers both investment costs and thermal efficiency (39.3%).

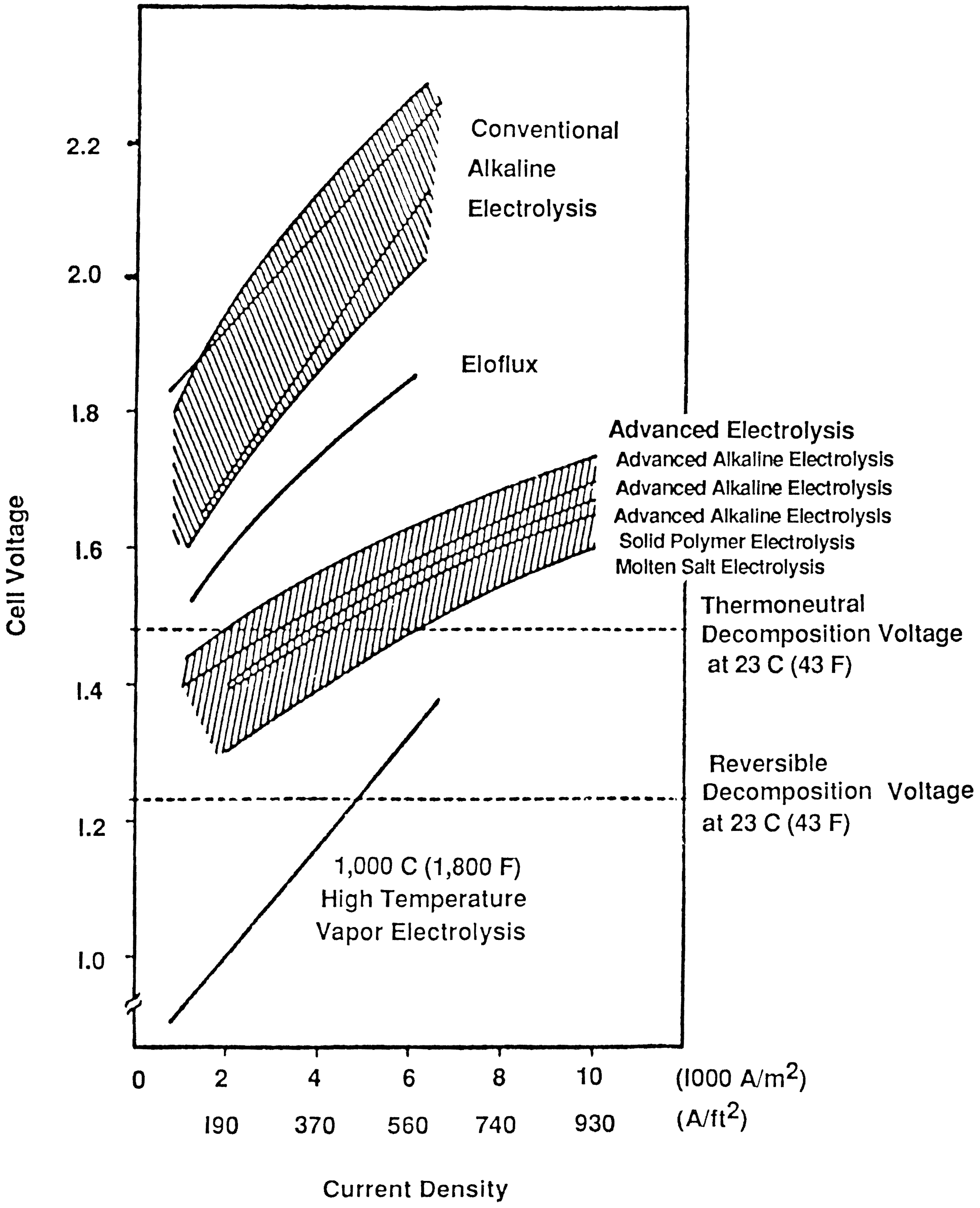
In the thermoneutral mode the temperature of the output gasses equals the temperature of the input steam. At a 1.3 volt cell potential, 3.12 kWh/m^3 (0.09 kWh/ft^3) of energy was consumed. It was found that this balance of temperatures did not make the best use of the superheating equipment.

Operating below the thermoneutral voltage (endothermally), the electrolyser exhibited the highest efficiency. But the reduced voltage (below 1.3 volts) also reduced the allowable current density and the hydrogen output. At 1.07 volts and 3,000 A/m^2 (279 A/ft^2) the energy input needed is 2.6 Wh/m^3 (0.07 kWh/ft^3) for each volume of hydrogen produced. Increased capital costs were anticipated for coupling the electrolyser to a high temperature heat source. A heat input of 0.6 kWh provides a thermal efficiency of 44.7% at 19% less electrical power cost.

In all modes of operating pressures above 24.7 atm (2.5 MPa, 262.6 psi) incurred

EXHIBIT 20

Cell Voltage-Current Density Characteristics of Conventional and Advanced Electrolysis



higher operating costs. Cell pressures at 3 to 5 atm (0.3 MPa, 43.5 psi to 0.5 MPa, 72.5 psi) are more economical even when the output gas had to be compressed to a more useful 24.7 atm (2.5 MPa, 363 psi) storage pressure.

Costs

HTE can make use of waste heat from a veriety of sources including coal and nuclear power plants. Nuclear fusion is a form of nuclear energy, currently under research, that promises a nonpolluting and virtually endless supply of energy. Fusion derives its energy from fusing pairs of hydrogen atoms to form helium. Copious amounts of heat are also produced. *"The technical integration of fusion and high-temperature electrolysis appears to be feasible and that overall hydrogen production efficiencies of 50 to 55% seem possible."* **(20)**

With current technology, the waste heat from coal-fired plants can be used for HTE, but problems remain. *"Based on performance and cost figures available in 1983, high-temperature electrolysis coupled with thermal electrical energy derived from coal is not yet competitive with processes which make hydrogen from hydrocarbons. If natural gas prices were to double (from $0.012/kWh to $0.027/kWh) catalytic steam reforming and high temperature electrolysis would have comparable hydrogen production costs."***(21)**

An HTE plant converting 90% of the steam to hydrogen at a computed 38.2% thermal efficiency exceeds the 15% steam conversion and 30.6% efficiency of a comparable capacity coal gasification plant.

Exhibits 21, 22, and **23** show when the cost of hydrogen from HTE is economical compared to the cost of hydrogen from other methods of production. **(22)** **Exhibit 21** compares HTE with conventional forms of electrolysis. The higher the price of electricity becomes the more competitive HTE gets. **Exhibit 22** compares HTE with hydrogen from the steam reforming of natural gas. With the costs of electricity and natural gas shown on the two axes of the graph the "break even" line shows at what price of the two inputs the costs of HTE equals steam reforming of natural gas. At price combinations of electricity and natural gas above the line HTE is advantageous. Below the line natural gas steam reforming is more cost effective. **Exhibit 23** shows the cost relationship of coal gasification and HTE at various prices of coal and electricity. In the U.S., the current cost of electricity is too high (above $0.05/kWh) and the price of coal is too low ($0.007 to $0.008/kWh) for HTE to be economically competitive at the present time.

The initial costs of building conventional electrolysis plants is about $12/m^3/hr ($0.34/ft^3/hr) of hydrogen production capacity. With HTE this cost could be reduced by various means.

- Using circular vessels, thus eliminating the need for reinforcing ribs.
- Incorporating vertical stacks of modules into the design. This would reduce capital costs as much as 50%.
- Selling the pure oxygen produced at the current rate of $0.05/m^3 ($0.0014/ft^3) to reduce costs 15%. **(23)**

M.A. Liepa has completed a study of HTE fed by electricity and heat derived from coal or natural gas. **(24)** He estimates hydrogen production costs of $0.07 to $0.22/m^3 ($0.0048 to$0.0062/ft^3). This is equivalent to $0.04 to $0.06/kWh for electricity. About 12% of this comes from thermal energy, the rest from electrical energy. These low estimates were based on the following assumptions.

- Operating temperatures: 1,000°C (1,800°F) on average.
- Maximum temperature drop: 200°C (300°F).
- Cooling water temperature: 15°C (59°F).
- Hydrogen output temperature: 25°C (77°F).

Cost of coal:	\$0.007/kWh.
Cost of natural gas:	\$0.012/kWh.
Cost of electricity:	\$0.050/kWh.
Cost of fuel oil:	\$20/barrel
Annual capital cost recovery:	20%
Thermodynamic efficiency of electrical power generation:	35%
Gas to gas average heat transfer coefficient:	60 W/m^2/^{o}C (3 W/ft^2/^{o}F).
Expansion gas to water heat transfer coefficient:	230 W/m^2/^{o}C (12 W/ft^2/^{o}F).
Condensation gas to water heat transfer coefficient:	850 W/m^2/^{o}C (44 W/ft^2/^{o}F).

J.A. Fillo estimates even lower costs if waste heat from nuclear fusion reactors is used. According to his estimates the costs might be: \$0.0017/kWh (\$5.87/million BTU) at 1,300^{o}C (2,370^{o}F) and \$0.002/kWh (\$7.14/million BTU) at 1,150^{o}C (2,100^{o}F). *"Thus in the long term, the electrolytic process may well be able to compete with hydrogen production from fossil fuels, particularly in view of the expected raw material shortage after the year 2000, expecially of natural gas."* **(25)**

PHOTOVOLTAIC-POWERED ELECTROLYSIS

Hydrogen as an Energy Carrier

Hydrogen is often erroneously regarded as a *source* of energy similar to petroleum or coal. This would be true if hydrogen were available naturally in large quantities. However, much of it is derived from hydrocarbons and water or by electrolysis. Hydrogen is similar to the energy storage characteristics of an electrical storage battery. Energy is needed to obtain hydrogen from either water or hydrocarbons. This is because hydrogen is rarely found in a pure state on earth. The energy used to obtain hydrogen from water is recovered when the gas is burned. Hydrogen is a carrier of the energy used to obtain just as an electrical battery carries the energy used to charge it.

Energy from sunlight can be converted to electricity by photovoltaic (PV) cells. This electrical energy can then be stored in batteries or as hydrogen from electrolysis. Hydrogen has much more energy per unit weight than electric batteries. In practical terms, *"A solar energy economy is not conceivable without hydrogen being used for storage and energy distribution."* **(26)**

At the earth's surface about 1 kWh/m^2 (317 BTU/ft^2) of solar energy is available. If it could all be harnessed it would supply 10,000 times the current annual world energy consumption. (27) Solar energy can be converted to useful energy by various technologies that harness the sun's radiation.

- *PV powered electrolysers.* PV cells convert sunlight to electricity.The electricity is then used by an electrolyser to produce hydrogen.
- *Photoelectrodes.* Electrodes immersed in water and an electrolyte combine PV cells and an electrolyser in one device. However, it is difficult to match the current voltage output of the electrodes with the demand of the electrolysis process. At present, it is more efficient to carry out each of these processes separately.
- *Photochemical processes.* The energy of solar radiation is absorbed by various chemicals in solution and is used to drive hydrogen-producing reactions.
- *Biological sources.* Microorganisms in water absorb light to split water in the process of making their own "food" and in respiration. The use of similar processes to synthesize methane, methanol or ethanol is currently cheaper and more efficient than the process of producing hydrogen from microorganisms. **(28)**

EXHIBIT 21

Cost of Electrolytic Hydrogen

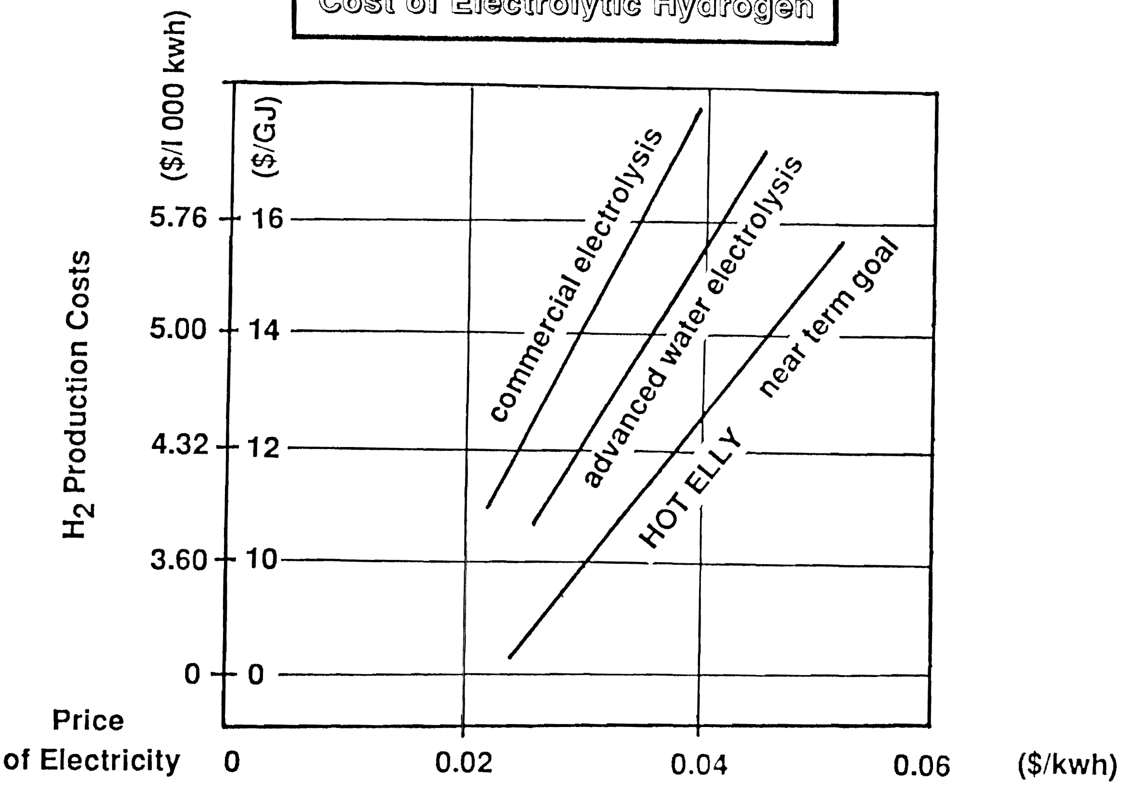


EXHIBIT 22

Cost Comparison of Electrolysis and Natural Gas Conversion

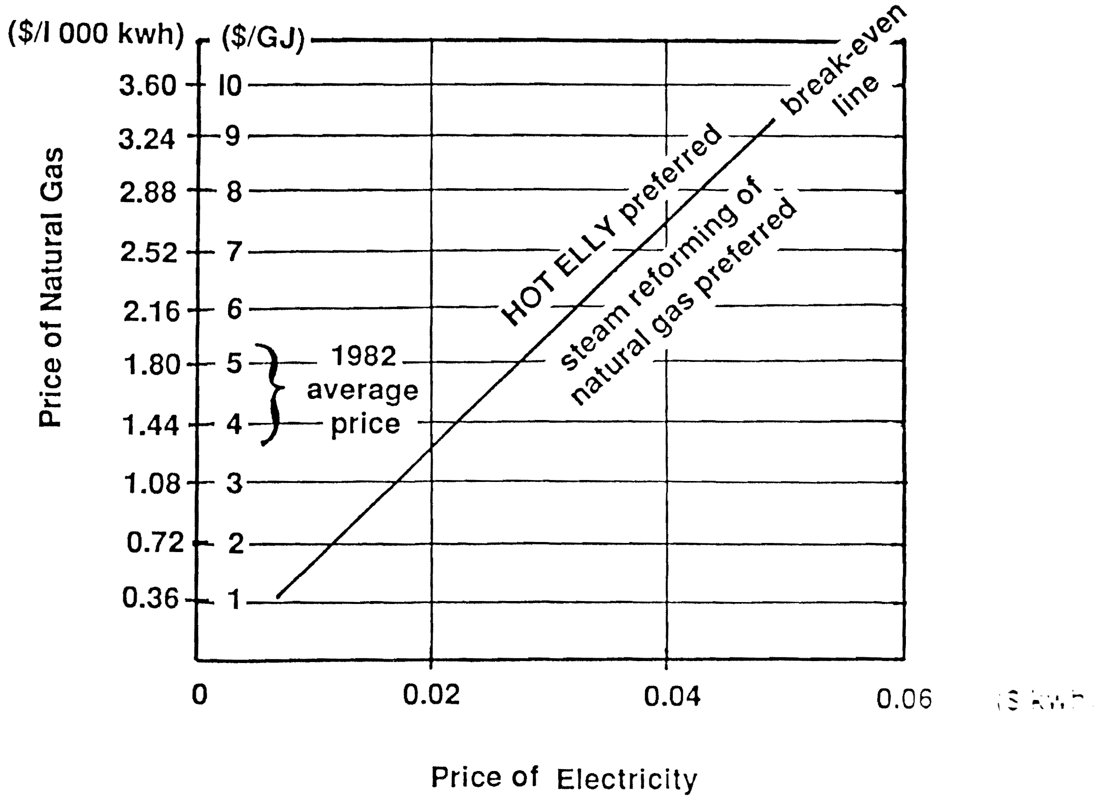
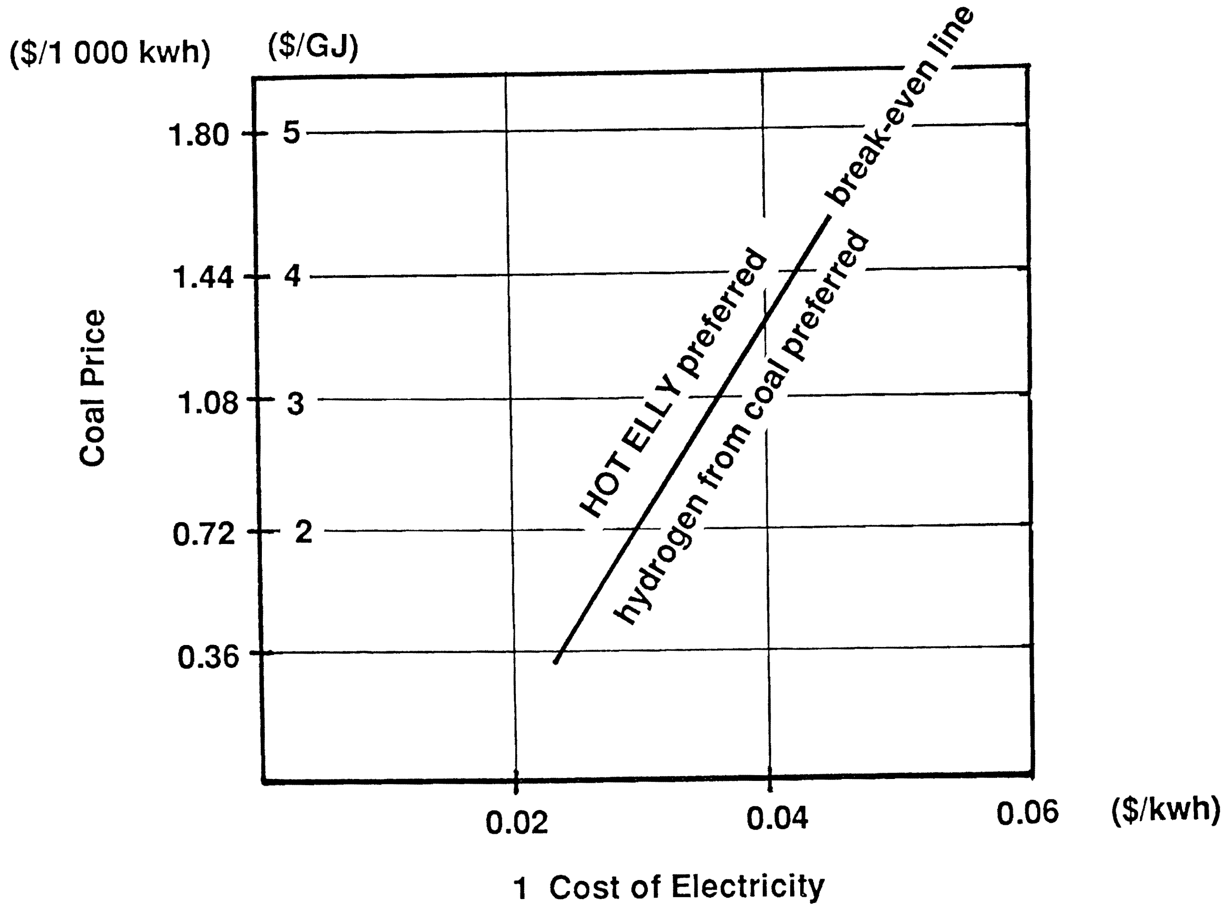


EXHIBIT 23

Cost Comparison of Electrolysis and Electricity



- *Direct thermal water splitting.* At 2,500°C (4,500°F) water decomposes into hydrogen and oxygen. A lens or reflector is employed to concentrate sunlight to supply heat. The problem here is to prevent the oxygen and hydrogen from recombining at the high temperatures used in the process.
- *Thermochemical cycles.* Relatively low temperature heat, 1,000°C (1,800°F), is used to drive reversible chemical reactions. These processes are promising but very experimental at the present time.

From Sunlight to Hydrogen

State of the art PV cells operate at about 10% efficiency. Nevertheless, one square kilometer can produce 26,000 kW. One square mile can produce 67,000 kW. A 120 by 120 km (75 X 75 mile) square array in sunny Arizona could produce 1,000,000 megawatts. This is equivalent to the projected electrical needs of the U.S. in the year 2000 AD. **(29)**

A PV cell converts light energy to electrical energy at a specific voltage and current level. The more light the cell receives the greater the energy output. However, the current and voltage do not increase equally. **Exhibit 24** shows that at various light levels the current doubles, from 10 to 23 milliamps, while the voltage remains around 0.5 volts. The temperature is constant.

To make the best use of single photocell or any array of cells, the load must operate at an optimal combination of current and voltage known as the *maximum power point* (M.M.P.). This point is shown on each of the curves in **Exhibit 24**. This point is where the tangent to the curve is 45°.

Changes in either the light intensity or cell temperature will shift the power curve and the M.M.P. **Exhibit 25** shows this shift in response to three different temperatures. In general, the power output of a PV cell increases with lower temperatures and higher light levels.

When PV cells are coupled to an electrolyser, light energy can be converted, indirectly, to hydrogen production. The current output of the PV cell is expressed in milliamps per square centimeter (mA/cm^2). The higher the current density, the higher the rate of hydrogen production and the lower the operating costs per unit of hydrogen produced.

The electrolyser electrode area determines the current requirements while the number of electrolyser cells (at 2 volts each) determines the voltage needed.

The amount of light striking the PV cell will vary with different times of day, weather conditions and season. The operating temperature of the cells will also vary when the cells are exposed to the weather. For these reasons, the electrolyser will not always be operating at the maximum power point for the cells.

Power conditioning equipment constantly adjusts the voltage and current characteristics of the cells so that the electrolyser always operates at the M.M.P. The efficiency of the power conditioning device is typically in excess of 90%. With power conditioning the rate of hydrogen production is higher than without such continual adjustments. However, the equipment needed is complex and costly. Direct coupling of the cells to the electrolyser (with a fixed voltage-current transformer) is cheaper and simpler even though hydrogen output is slightly lower. The simplest and cheapest power tracking method is a switching interface that changes the parallel and series connections of the cells to give relatively coarse changes in voltage and current from the cells. **(30)**

According to a recent study, in New Mexico, at a latitude of 35°C (95°F) and a hydrogen production rate of 4.4 kg/m^2 (0.9 lb/ft^2) of cell area per year is possible. This is an average annual value. The summer peak rate is calculated to be 0.002 kg/m^2 (0.0004 lb/ft^2) per hour. The average annual efficiency is about 7%. **(31)**

At a latitude of 48° , in central Europe, the hydrogen production rate is about half that for New Mexico.

A PV-powered electrolyser was constructed and studied at the Florida Solar Energy

EXHIBIT 24

Solar Cell Performance with Different Light Intensities

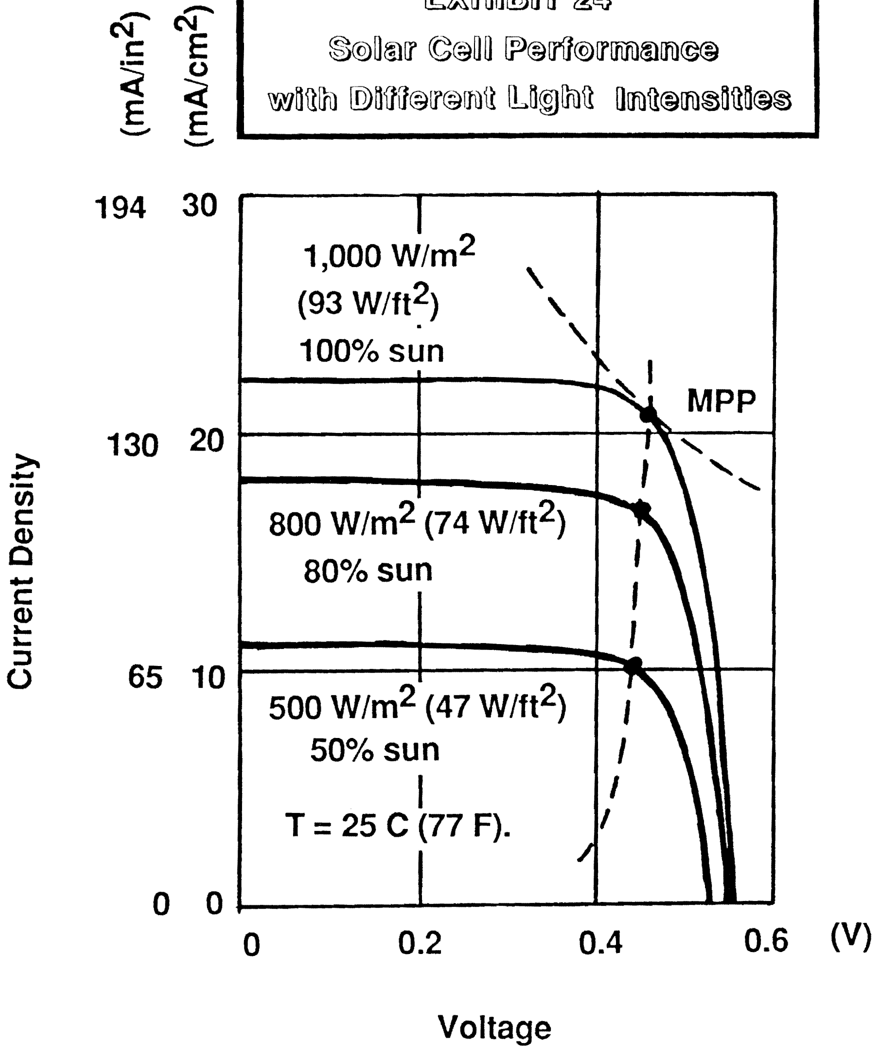
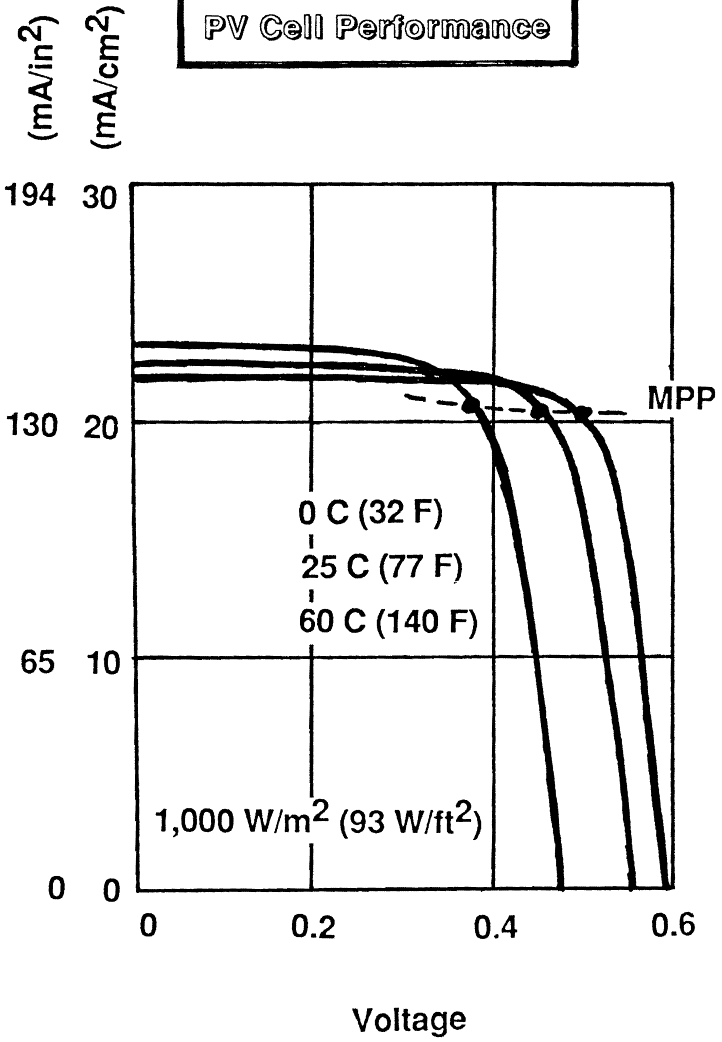


EXHIBIT 25

PV Cell Performance



Center under a NASA grant. **(32)** The experimenters were interested in hydrogen as a means of storing solar energy. They noted the disadvantages of batteries.

- Low energy stored compared with high weight.
- The use of scarce resources in their construction.
- Leaking of stored energy due to heating and long periods of nonuse.
- The need for standby charges.

The specifications for the experimental hydrogen plant were as follows.

- *Electrolyser cells:* 15 cells, each 5.19 cm (2 inches) in diameter and with an current output of 600 mA/cm^2 (3,870 mA/in^2).
- *Peak power output:* 1 kW.
- *Electrolyser power input:* 4 kWh, 500 kWh per month, in Florida.
- *Electrolyser pressure range:* 0 to 1.7 atm (0.28 MPa, 40 psi).
- *Electrolyser type:* Series (bipolar, or "filter press").
- *Separator:* asbestos fabric.
- *Electrolyte:* 25% by weight KOH.
- *Photovoltaic array:* 50 Solec Model 3135 modules.
- *PV efficiency:* 6.1%.

No power tracking was used. The peak power of the PV cell array was matched to the electrolyser demand. In 15 days the plant could generate 29.7 kWh of hydrogen (101,600 BTU) equivalent to 3 liters (0.75 gallon) of gasoline. A summary of the plant's performance is given in **Exhibit 26.** The result of a computer study concluded that the most power conditioning equipment could boost hydrogen output was 6% (assuming that the power conditioner was 100% efficient - a technical impossibility). The researchers concluded that, *"Maximum power trackers are probably not desirable in PV-electrolyser systems".* **(33)**

Solar Hydrogen Aircraft

PV cells have always been used in the space program because of their simple maintenance-free operation. The cost of the PV electrolysis is relatively high for a house, but is small compared to the total cost of a spacecraft.

For an application closer to earth, Lockheed has proposed a high altitude aircraft powered by photocells mounted on the skin of the craft. It is designed as a robot reconnaissance plane able to stay aloft for a year or more. The cells power an electric motor that turns a large diameter, low rpm propeller. The same cells also generate hydrogen by way of an on-board electrolyser. At night, the stored hydrogen is used to feed a fuel cell that supplies electricity to the motor. The oxygen from the electrolysis is also needed because of the thin atmosphere at 20 km (65,000 ft) altitude.

The *Solar High-Altitude Powered Platform,* as it is called, is designed to carry a 113 kg (250 lb) payload of communications relays or surveillance cameras. Although designed for continuous powered flight, it is expected to cost less than a communications satellite. The wingspan will be 91 m (300 ft) while the fragile craft will weigh only 907 kg (2,000 lb). **(34)**

Costs of Solar Electrolysis

The Solar Power Corporation in San Diego, California has built a 7 kW solar cell plant. Tracking solar concentrators focus sunlight on 76 m^2 (2,603 ft^2) of PV cells. The reflector also produces 45.8 kW of heat.

Relying on current data and future research and development activities, the company anticipates costs of $0.0285/kWh for a 1,000 Megawatt plant. This is comparable to

EXHIBIT 26
Electrolyser Performance Summary

Day	Power Input (Ah)	Hydrogen Produced (l)	(ft^3)	Output Efficiency (real/ideal)	Energy Equivalent (Wh)	Energy of P.V.Array (Wh)	Energy Efficiency (%)	Gas Pressure (MPa)	(psi)	Electrolyte Temperature (C)	(F)	Length of Day (hours)
1	121	733	26	97.0	2,511	3,426	73.3	0	0	55	131	8.25
2	139	759	27	87.3	2,601	4,093	63.5	0	0	70	158	11
3	123	726	27	94.4	2,488	3,382	73.5	0	0	70	158	8.25
4	131	744	26	90.6	2,549	3,796	67.1	0	0	60	140	11
5	123	616	22	80.2	2,110	4,022	52.5	28	40	70	158	8.25
6	98	607	21	98.4	2,080	2,798	74.3	28	40	35	95	8.25
7	126	661	23	83.7	2,265	3,600	62.9	28	40	70	158	8.25
8	101	462	16	72.9	1,583	2,903	54.5	28	40	70	158	8.25
9	121	592	21	78.0	2,029	3,421	59.3	28	40	70	158	11
10	122	607	21	79.0	2,080	3,454	60.2	21	30	70	158	11
11	109	582	21	84.4	1,994	3,009	66.3	14	20	70	158	8.25
12	124	608	22	77.9	2,084	3,653	57.0	14	20	75	167	11
13	101	486	17	77.0	1,665	2,871	58.0	14	20	60	140	11
14	80	397	14	79.6	1,360	2,391	56.9	14	20	60	140	8.25
15	29	108	4	59.3	370	1,493	24.7	0	0	40	104	8.25

EXHIBIT 27
Estimated Cost of Residential Hydrogen

Cost element	**1983-1984$**	**1995$**
PV array, 4 kWh	48,000	12,000
Electrolyser, 4kWh	15,000	5,000
Maintenance charges & electrolyte replacement	3,500	2,300
Replace module	3,200	1,500
Property tax	14,900	3,300
Insurance	7,300	500
Total present value	91,900	24,600

current costs of electricity from hydropower or natural gas. This also compares favorably with \$0.0775/kWh for nuclear power and \$0.0993/kWh for coal-fired plants. **(35)**

A study of the solar electric plant at the Florida Energy Center developed a program to estimate the costs of future solar hydrogen plants. The data in **Exhibit 27** summarizes the estimated cost of residential hydrogen from a PV array.

NASA has experimented with a 1 kilowatt commercial solar cell array. The experimenters used no power conditioning. They selected the number of electrolyser cells, and designed the electrolyser cells for the peak power output from the array. The electrolyser had 15 cells designed for a current density of 600 mA/cm^2 (3.9 A/in^2). Each electrode was 5.19 cm (1 in) in diameter. Each cell had an asbestos separator. The energy value of the hydrogen produced had 50 to 75% of the solar cell energy input. The overall system efficiency from sunlight to hydrogen was about 4%. The experimenters calculated that for a 500 kWh/month plant located in Florida, the operating costs would be \$0.73/kWh. The average residence in Florids consumes 1,000 kWh/month.

By 1995, with production of solar cells increased 100 times, the cost of solar electricity from a plant similar to the one studied, would be reduced to \$0.17/kW. If present developments in solar cell technology become commercially feasible, further cost reductions can be expected.

Stanford University is demonstrating a new silicone-based solar cell with a textured surface that has a efficiency of 27.5%. **(36)** Combined with an electrolyser with 90% efficiency, the overall efficiency would be = 0.275 X 0.90 = 25%.

J.E. Nitsch, in a study of future solar electric costs, anticipates capital costs to decline to one-tenth the current levels over 20 years and by one-half to one- third over the next 10 years. Capital costs for electrolysis equipment are expected to decline one-third over next 40 years. **(37)**

Electrolytic hydrogen is expected to become cost competitive with fossil fuels in the 2005 to 2010 time period, assuming favorable conditions, which are:

- Interest rates on capital of no more than 6%
- Increasing plant life up to 30 years, due to technical improvements
- Increasing prices for fossil fuels by 4 to 5% per year.

Wind Power

The total windpower in the 48 contiguous states of the U.S. averages about 13 kW/hectare (5.2 kWh/acre) or 400 billion kW. This is about equal to the total U.S. residential electric consumption from 1970 to 1985. Residential electric consumption is about one-third of the total electric consumption. On average, each house in the contituous 48 states consumes 30,000 kWh/year and is 200 square meters (2,150 ft^2) in area. To be useful, the wind must be blowing at over 10 km/hr (16 miles/hour). In Oklahoma this occurs 80% of the time. To supply 30,000 kWh/year to a house on a continuous basis a wind energy plant must store 20% of 30,000 kWh or 6,000 kWh/year for use on relatively calm days. For two successive windless days, 165 kWh must be stored. This can be done in any of several ways. These alternatives can accomodate a peak home load of 15 kW. **(38)**

- A water tower 10 m (33 ft) high storing 20 cubic meters (706 ft^3) of water.
- A volume of gaseous hydrogen stored at 1 atm (0.1 MPa, 14.7 psi) in a 1 cubic meter (35.3 ft^3) volume.
- One liter (1/4 gallon) of liquid hydrogen.

S.B. Lalvani reports that the presence of sulfur in the anode during electrolysis reduces oxygen output and converts sulfur (S) to sulfate (SO_4^{-2}). The cell voltage needed to produce a volume of hydrogen is reduced by one-third, compared to conventional electrolysis. A minimum of 0.36 volts is required. At 1.2 volt the reaction proceeds as follows at the anode:

$$S + 4H_2O \text{ -----> } 8H^+ + SO_4^{-2} + 6 \text{ electrons.}$$

At the cathode the reaction is:

$$6H^+ + 6 \text{ electrons -----> } 3H_2.$$

The overall reaction is:

$$S + 4H_2O \text{ -----> } H_2SO_4 + 3H_2.$$

Hydrochloric acid, the most suitable electrolyte, is added to the water in the electrolyser. Sodium sulfate (Na_2S) is also suitable. According to Lalvani, *"Preliminary investigations indicate that sulfur-assisted water electrolysis has the potential of becoming a viable economic process for co-generation of hydrogen and sulfuric acid".* **(39)**

High material costs include an expensive platinum mesh electrode. The sulfur forms a layer and reacts with the electrolyte.

This process is similar to the *Westinghouse Cycle,* a process for producing hydrogen and sulfuric acid from sulfur dioxide and water.

$$SO_2 + 2H_2O \text{ -----> } H_2SO_4 + H_2.$$
$$H_2SO_4 \text{ -----> } H_2O + SO_2 + 1/2O_2.$$

The overall electrolysis reaction is:

$$H_2O \text{ -----> } H_2 + 1/2O_2.$$

Ideally, the process has a 45% thermodynamic efficiency and requires less than 0.6 volts. For practical applications high concentrations of sulfuric acid are used, thereby increasing the voltage required. This process takes place at higher temperature than the pure sulfur process. In contrast, sulfur-assisted electrolysis requires a temperature of less than 75^{o}C (167^{o}F). Hydrogen production is also higher than with the Westinghouse process.

In comparison with conventional electrolysis, the hydrogen production rate for sulfur-assisted electrolysis is three times higher with electrical consumption one-half that required for ordianary electrolysis. Sulfuric acid is produced instead of oxygen, but the acid can be reacted with metals to produce still more hydrogen.

It is easy to see how it is possible to start with sulfur or sulfur dioxide and produce hydrogen, then add metal, like iron, and get still more hydrogen. Both sulfur dioxide and scrap iron are products of an industrial society that can be recycled into fuel production.

Either of the following two reactions produces hydrogen and sulfuric acid.

$$S + 4H_2O \text{ -----> } H_2SO_4 + 3H_2.$$
$$SO_2 + 2H_2O \text{ -----> } H_2SO_4 + H_2.$$

Sulfuric acid also reacts with iron to produce hydrogen.

$$Fe + H_2SO_4 \text{ -----> } FeSO_4 + H_2.$$

For all three reactions no separator is needed because the reactions produce only one gas. Only liquids or solids form at the oxygen electrode.

PHOTOVOLTAIC PROCESSES

Solar Electric Hydrogen

Various research projects demonstrate how the functions of solar cells and electrolysers can be combined in one device. These experiments involve two main components.

- Mone or more photoelectrodes or photocatalysts.
- An electrolyte in solution with water.

Light striking the photoelectrode generates an electrical potential (voltage) at the surface of the semiconductor and the electrolyte. This potential then splits water into hydrogen and oxygen in an electrolysis process. The gasses are generated together. Some means of separating them is necessary.

Strong ultraviolet light can directly split water. As the water molecule absorbs this wavelength of light the energy is sufficient to overcome the molecular bonds holding the hydrogen and oxygen together. Since ultraviolet light makes up only 8% of solar radiation, this process is inherently inefficient.

Photoelectrodes

Certain chemicals can convert a wider spectrum of light to electrolytic energy. Each of these makes more efficient use of the solar spectrum. Candidate materials include some salts, organic dyes, semiconductors absorbing a wider spectrum of light (these need a gandgap over 2.3 electronvolts). Some species of algae also serve this function. **(40)**

Photoelectrode materials generally share one or more of the following problems.

- *Phtotcorrosion* that causes the material to decompose under the influence of light reduces electrode life.
- *Temperature mismatch:* photovoltaic processes are more efficient at low temperatures while maximum electrolytic production occurs at higher temperature.
- *Voltage mismatch:* the voltage output of the photoelectrode (1.5 volt) does not approximate the voltage input needed for the electrolytic reduction process (2.2 volts). **(41)**

These problems have led some researchers to conclude that a separate solar cell array is preferable. **(42)** Undaunted, other researchers continue the search, tempted by the elegance of a single process that converts light directly to hydrogen fuel. In the search, oxides of sulfur and phosphorous have already been excluded from the role of photoelectrodes. **(43)**

Mixing ferric oxide and titanium dioxide with silicone produces a *phtotanode.* Ferric oxide and magnesium oxide comprise a photocathode. The two electrodes placed in a neutral electrolyte solution with water and in the presence of light yield electrolytic hydrogen and oxygen without the need for any input voltage. **(44)** However, a process which is *technically* possible is not necessarily *economical. "A Cheap accessible industrial process for producing titanium dioxide is not now available."* **(45)**

Experiments compared relatively cheap zinc and cadmium sulfide precipitated onto Nafion (R) film then precipitated onto silicone dioxide with more expensive platinum mixed with cadmium sulfide. The conclusion was that:

- *"Relatively efficient photoassisted catalytic hydrogen generation can be realized without a noble metal catalyst."*
- The nature of the support for the surface coating of zinc and cadmium sulfide *"is not a crucial element"*.
- *"Intimate contact of zinc sulfide and cadmium is required for good activity."***(46)**

In other experiments 1.0 grams (0.002 lb) of zinc sulfide in suspension in an electrolyte solution produced 16 liters (0.6 ft^3) of hydrogen in 35 hours with *"no observable deactrivation of the photocatalyst"*. **(47)** There was no need for platinum to improve the charge transfer.

Electrolysis of Hydrogen Sulfide

Some hydrogen-containing compounds are easier to split than water. Hydrogen sulfide is an example. It is a derivative of natural gas, coal, and petroleum refining. It requires only 1/7 the amount of energy to electrolyse hydrogen sulfide as it does to electrolyse water. The energy required to split hydrogen sulfide is sufficiently low to allow the use of light as a source of energy to split the molecule.

In one set of experiments light in a specific band of wavelengths stimulates cadmium sulfide to release an electron that splits hydrogen sulfide into hydrogen and sulfur.

$$H_2S + 2 \text{ photons of light} \text{ -----> } 2H^+ + S.$$

A small amount of rubidium dioxide (0.1% by weight) was mixed with the cadmium sulfide to form the catalyst. The catalysts were dissolved in a 0.1 mole solution of sodium sulfide illuminated with a 250 W halogen lamp shining through a 15 cm (6 in) water column to remove the infrared portion of the spectrum. This avoids heating the solution. The 25 ml (0.006 gal) solution produced 2.3 ml/hour (0.00008 ft^3/hr) of hydrogen. 90% of the hydrogen sulfide was converted to hydrogen. Doubling the rubidium dioxide increased the hydrogen output 50%. **(48)** The experimenters didn't need platinum as an electrocatylist. Other experimenters, using the same chemical constitutents, discovered thermodynamic efficiencies of 2.85%. **(49)** The experimenters concluded:

"Apart from its importance for solar energy research, the process might be used in industrial procedures where H_2 S or sulfides are formed as a waste product whose rapid removal and conversion into a fuel, ie. hydrogen, are desired. Also, in intriguing fashion, these systems mimic the function of photosynthetic bacteria that frequently use sulfides as electron donors for the reduction of water to hydrogen." **(50)**

Texas Instruments Solar Energy System

Texas Instruments has the *"only reported commercial photoelectrochemical* *program"* . **(51)** Hydrobromic acid is used as the photoelectrode while a sulfuric acid and water solution serves as the electrolyte. The photoelectrode coats microspheres 0.25 to 0.40 mm (0.010 to 0.020 in)in diameter. They use two types of microspheres: *photoanodes* and *photocathodes.* The photoanodes evolve bromine while hydrogen emerges at the photocathodes. The electrolyte-microsphere suspension is contained between two sheets of glass, one with a conductive backing. Sunlight shines through the transparent side and produces hydrogen with 7% thermodynamic efficiency. Further developments are expected to increase this to 8 to 10% by 1990.

Summary

Photoelectrodes employ either semiconductor powder suspensions or photosensitizers that transform electrons to and from water molecules. Compared to solar cell powered electrolysis, the current technology of photochemical processes for producing hydrogen have conspicuous disadvantages.

- The product gasses, hydrogen and oxygen are mixed.
- Light energy corrodes the electrode material.
- The process has lower efficiency.

BIOLOGICAL SOURCES

Plants as a Carbon Source

All means of producing hydrogen from water are not man-made. Green plants and algae (microscopic one-celled plants) convert carbon dioxide, water, and sunlight to carbohydrates, water, and oxygen.

$$CO_2 + 2H_2O \text{ -----> } CH_2 + H_2O + 3/2O_2.$$

Plants can then be used by man as a source of carbon-based fuel. This can be substituted for coal in the steam reforming process.

$$C + H_2O \text{ -----> } CO + H_2.$$

At 550°C (1,022°F) 24% of the carbon is "used up" in producing hydrogen. At 600°C (1,112°F) the rate jumps to 89%. A cobalt molybdate catalyst increases the hydrogen production rate at all temperatures.

Certain bacteria, in the absence of oxygen, will convert organic matter into methane. Municipal sewage can be used or algae can be grown and harvested specifically for this purpose.

In growing an algael "energy crop" heat is needed to boost the growth rate. The wast;e heat from the cooling towers of a 100 MW nuclear reactor will support a 4,047 hectare (10,000 acre) algae pond. The land around nuclear plants is wasted, anyway, because it must be kept clear for safety reasons. This pond will yield 4.5 kg/m^2 (20 tons/acre) of organic matter. Supplying extra carbon dioxide increases the rate 50%. 22,680 kg (25 tons) of algae can reasonably be converted to 10 kWh (34, 143 BTU) of methane. **(52)**

Biological Production of Hydrogen

Hydrogen can be produced by intercepting a plant's production of carbohydrates during photosynthesis. During photosynthesis the plant absorbs green light (a 500 nm wavelength). This is only about 16% of the visible solar spectrum. Hydrogen is briefly formed by water splitting and then used to construct carbohydrates that are used by the plant.

Researchers are trying to find a way to intercept the hydrogen before it is used to form carbohydrates. Work on this process is at an early stage. No working models have been developed and tested yet. In *Scientific American* (January 1986) two basic approaches are discussed.

- Using the active ingredient of photosynthesis in water (as a thylakoid membrane of ruptured chloroplasts).
- Preparing a solution of platinum and hexachloroplatinate in water.

When properly set up, light shining on either of these solutions will produce a brief electrical potential. The resulting electrolysis splits water molecules liberating hydrogen.

Some microorganisms produce hydrogen naturally. One species (*Rhodobacter sphaeroides* 8703) converts 7.9% of the light input energy at 50 W/m^2 (4.6 W/ft^2) to hydrogen gas. At 75 W/m^2 (7 W/ft^2) of light intensity the conversion efficiency drops to 6.2%. **(53)**

In experiments using different growth media for hydrogen producing microorganisms a salt water blue-green algae (*Oscillatoria sp. Miami* BG7) was found to produce 30% more hydrogen when the cells were grown on a thick jelly and mobility was restricted. **(54)** Similar results were found with hydrogen-producing bacteria **(55)**

Exhibit 28 shows the results of experiments with various hydrogen-producing microorganisms. Both algae and bacteria are represented. Since algae is a green plant it produces hydrogen in the process of making carbohydrates. Some bacteria, on the other hand, give off hydrogen as a by-product of digesting carbohydrates. The algae have to be subject to artificially contrived conditions to be "tricked" into producing hydrogen. This involves interrupting their photosynthetic activity. From the standpoint of the aglae, making hydrogen is a "waste of time". Certain bacteria will produce hydrogen under more natural conditions. For this reason, bacteria produce more hydrogen than algae.

Some researchers are trying to get around the problem of raising these fussy organisms by developing synthetic photosynthesis. **(56)** In one process under consideration, 70% of visible sunlight could be converted to electrical voltage and made available for electrolysis **(57)**

Summary

The practical use of microorganisms remains a distant vision due to the current problem of low energy conversion rates, exacting biological requirements, and the periodic replacement of the microorganisms and their substrate.

DIRECT THERMAL WATER-SPLITTING

At a temperature 2,730°C (4, 946°F) water decomposes into hydrogen and oxygen. Solar energy focused by a parabolic reflector or a lens can achieve this temperature.

50% of solar energy is in the infrared spectrum - the heat producing part of solar energy. Based on this observation, direct thermal water splitting would seem to be the simplest method of producing hydrogen from water. However,

EXHIBIT 28
Biological Sources of Hydrogen

Organism	**Hydrogen Production**		
	ml H_2/g of cells	**(ft^3/lb)**	**ml/l culture**
Photosynthesis (producing glucose)			
Oscillatoria sp. Miami BG7	15	0.24	10
Anabaena cylndrica	50	0.80	30
Rhodopseudomonas capsulata	202	3.2	131
Rhodosprillum rubrum	96	1.5	74
Fermentation (digesting glucose)			
Clostridium butyricum	270	4.3	---
Citrobacter intermedius	360	5.8	272
Enterobacter st. E. 82005	420	6.8	520

there are two main problems.

- Keeping the hydrogen and oxygen separate.
- Finding high-temperature materials.

The latter problem is slowly being solved by materials engineers. Another general approach is to use a *fluid wall.* This is a boundary layer of gas injected into the container so as to keep the high temperature water vapor from the container wall.

"*The work of these groups demonstrates that solar direct splitting of water can be accomplished in a reactor constructed of currently available materials.*" (58)

Various means of keeping hydrogen and oxygen separate have been proposed.

- *Centrifuging:* Oxygen is heavier than hydrogen. Spinning the gas mixture in a centrifuge will tend to fling the oxygen out farther toward the rim, in a shorter time than it would require for hydrogen.
- *Magnetic separation:* Some hydrogen molecules may be deflected in a magnetic field while others are not. This may be a partial solution.
- *A membrane:* Vanadium or paladium will transmit hydrogen selectively at temperatures above 730°C (1,350°F). The expense of this material and its intolerance of high temperatures makes this impractical.
- *Quenching:* Cooling the gas before it can recombine. The gasses then are carefully separated at lower temperature by other means. (59)

The most effective means used to quench the temperature of the hot product gasses before combustion takes place are the following.

- *Injection quenching:* injecting the hot gas as bubbles into water and collecting them at the top of the water container. **(60)** As the bubbles rise, the gasses can be separated by gravity. Hydrogen, being lighter and more bouyant, rises faster than oxygen.
- *Impingement quenching.* A jet of a high temperature gas mixture is forced under pressure against a flat plate. **(61)**

With impingement quenching, the jet strikes the "wall" at a flow rate of from 2 X 10^{-5}m^{3}/s (7X 10^{-4} ft/s) to 6.7 X 10^{-5}m^{3}/s (2.4 X 10^{-3} ft^{3}/s). The portion closest to the wall is the coolest and gets hotter closer to the nozzel. The stream flares out as it hits the wall. There is a stagnation zone in the center of the stream as it impacts against the wall. This stagnation zone was thought to cause the gasses to recombine but an experimental device using this principal worked better than expected. "*Such a fast exchange* (heat transfer) *within the wall jet of the stagnation zone may be efficient enough to prevent back recombination by both rapid cooling and dilution of the cold medium.*" **(62)**

Exhibit 29 shows the percent of water that is dissociated at various temperatures.

Inspite of current breakthroughs problems remain. Given the higher temperatures and materials problems involved we can conclude that "*this direct thermal decomposition of water is not feasible at an industrial level with the present technology.*" **(63)**

EXHIBIT 29
Water Dissociation at Various Temperatures

Temperature (°C)	(°F)	Amount Dissociated (%)
1,730	3,146	0.69
2,030	3,686	2.64
2,430	4,406	10.35
2,730	4,946	22.40
3,230	5,846	57.43

THERMOCHEMICAL CYCLES

Isothermal Steps

Avoiding the high temperature requirements of direct thermal water splitting requires more complex chemical processes. "*According to the thermodynamic restraints, pure thermodynamical cycles operating at temperatures below 1,000°C (1,800 °F) consist of three steps or more.*" **(64)**

Unlike electrolysis, heat energy is used to directly decompose hydrogen-containing compounds. These compounds are easier to thermally split than water and the thermochemical process is generally more efficient than electrolysis. **(65)** Some processes are designed to utilize both a thermal and an electrical input and are referred to as *electrothermochemical* processes or as *hybrid thermochemical* cycles. **(66)**

In general, higher temperatures increase the chemical reaction rate and help lower plant costs. Higher temperatures also reduce the number of steps needed for a chemical process. By taking bigger thermal steps, fewer steps are needed to arrive at the desired product. **(67)** The temperature required at each step must also match the heat input available. For example, future fusion reactors will produce 1,250°C (2,280°F) cooling water. This could support a sulfur-iodine thermochemical cycle at 45% efficiency because the thermochemical process can use the exact temperature ot the waste heat as it comes from the reactor. **(68)**

Efficiency

The efficiency of a thermochemical process is defined as:

$$79.42\ \mathrm{Wh}/Q.$$

Where:

- 79.42 = combustion energy of 1 gram (0.0022 lb) of hydrogen.
- Q = total energy required for decomposition at 100% efficiency.**(69)**

Costs

In comparing alternative processes, economic costs, as well as the efficiency, of various choices must be considered. The costs of high temperature electrolysis with solid polymer electrolytes is comparable to the best thermochemical cycles - approximately $0.05 to 0.06/kWh. **(70)** "*The costs are close enough so that no clear choice can be made among the processes.*" **(71)** Coal gasification, however, remains a cheaper source of hydrogen. "*Hydrogen from water splitting will most probably be more expensive than hydrogen or other synfuels produced from coal gasification. Therefore, water splitting , either by electrolysis, or by thermochemical cycles is a long term energy conversion process.*" **(72)**

A nation with sufficient deposits of coal doesnot have to be vitally dependent upon foreign sources of energy. The *Sasol* process developed in South Africa turns 5.4 billion kg (6 million tons) of coal per year into various oils, alcohols, and gasses at relatively low temperature and pressure making that nation 80% *indpenedent of imported fuel.* **(73)**

Exhibit 30 shows the comparative costs of various commercial and experimental processes of generating hydrogen. **(74)**

EXHIBIT 30

Hydrogen Production Costs

Process			**Cost per Unit Voltage**	
			(\$/m^{3})	**(\$/ft^{3})**
Catalytic Steam Reforming			0.10-0.12	0.003
Partial Oxydation of Fuel Oil			0.12-0.16	0.003-0.005
Koppers-Totzek Coal Gasification			0.17-0.20	0.005-0.006
Conventional Electrolysis			0.34-0.41	0.01- 0.012
Advanced SPE Electrolysis			0.22-0.24	0.006-0.007
High Temperature Steam Electrolysis				
	Energy Input			
	(Wh/m^{3})	(Wh/ft^{3})		
	3,125-3,186	88.5-90.2	0.19-0.22	0.005-0.006
	3,064-3,124	86.8-88.4	0.18-0.21	0.006-0.0062
	2,711-3,064	76.8-86.7	0.17-0.18	0.005-0.0052
Sulfur-Assisted Conventional Electrolysis			125.7-170.9	3.56 - 4.48
Sulfur-Assisted SPE Electrolysis			43.8- 87.9	1.24 - 2.49
Formate-Bicarbonate Cycle			2.32+	0.008+

Demonstration Plants

A study was conducted of over 1,000 possible thermochemical cycles which use materials that can be recycled. In hydrocarbon reforming processes the input materials are used up. The only inputs for each of these thermochemical cycles were water, heat, and electricity. From the study three promising cycles were selected and three small demonstration plants were built. The three cycles were:

- The Westinghouse sulfur cycle.
- The iodine-sulfur cycle devised by the General Atomic Company.
- The bromine-sulfur cycle, *Mark 13,* developed by the Joint Research Center in Ispra, Italy.

The first two require heat and electricity. The latter process has only heat as an energy input. The Westinghouse cycle is based on the following reaction at 300° to 375°C (572° to 707°F).

$$SO_2 + 2H_2O \text{ -----> } H_2SO_4 + H_2.$$

$$H_2SO_4 \text{ -----> } H_2O + SO_2 + 1/2O_2.$$

The last reaction represents a simple splitting of the sulfuric acid molecule by heat at 1,200°C (2,190°F). Decomposition of 84% of the reactants can occur at 1,080°C (2,190°F).

The iodine-sulfur cycle involves thermally splitting surfuric acid and hydrogen iodide. The latter compound can be split at low temperatures and energy input.

$$2H_2O + I_2 + SO_2 \text{ -----> } H_2SO_4 + 2HI.$$

$$H_2SO_4 \text{ -----> } H_2O + SO_2 + 1/2O_2.$$

$$2HI \text{ -----> } H_2 + I_2.$$

The process gives low yields and presents difficulties in separating the sulfuric acid from the hydrogen iodide. **(75)**

The experimenters found that the most promising of the three processes to be the bromine-sulfur cycle. In May 1978 the demonstration of this process was the first complete thermochemical hydrogen production process by water decomosition.

$$2H_2O + Br_2 + SO_2 \text{ -----> } H_2SO_4 + 2HBr.$$

$$H_2SO_4 \text{ -----> } H_2O + SO_2 + 1/2\ O_2.$$

$$2HBr \text{ -----> } H_2 + 2Br.$$

The sulfuric acid in the first reaction is easily separated in a column still. It constitutes 75% of the total weight of the mixture. The acid is split at a temperature from 900°C to 1,200°C (1,650° to 2,230°F) at a low pressure of 3 atm (0.3 MPa, 43.5 psi). Steel is used as a catalyst. No heat exchangers were required.

Hydrogen bromide is electrolysed in the third reaction at 0.80 volts. Hydrogen is produced at the rate of 0.1 m^3 (0.003 ft^3/hr). Because hydrogen is lighter than bromine, the two gasses are easily separated. No separator is needed. The following is a summary of the output and operating conditions of a plant that begun operation in 1984 and was run for 18 months.

- Hydrogen output: 1,000 m3/hr (353 ft3/hr).
- Sulfuric acid processed: 43.7 kg/hr (96 lb/hr).
- Operating pressure: 24.7 atm (2.5 MPa, 362.6 psi).
- Maximum operating temperature: 950°C (1,740°F).
- Electrical input: 100 kW.
- Efficiency: 30 to 40%.
- Cost: $1.00/m3/hr. ($0.03/ft3/hr).

The efficiency compares with 28 to 32% for high temperature solid polymer electrolysis, but the overall costs are similar. According to G.E. Beghi, a researcher connected with the project:

"The operation of the plant showed no problems of major instabilities, and no formation of by-products or side reactions. The starting-up was also easy and rapid once the required levels were reached, the plant could be put on stream immediately at its normal hydrogen and oxygen production flow rate. Industrial pilot plants can already be built with the present knowledge, chemical engineering data and commercial materials are available, no critical breakthrough is necessary.... Thermochemical production of hydrogen is demonstrated and feasible." **(76)**

The Nitric Acid Process

Newell C. Cook has developed a process for recycling nitric oxide compounds and acid while splitting water to produce hydrogen. Nitric oxide is advantageous because of its low boiling point, low ionization potential, and its high thermal stabiltiy. A variety of acids may be used but phosphoric acid is shown in the following reaction.

$$2NO + 2HPO_3 \text{ -----> } 2NO^+PO_3^- + H_2.$$

The phosphoric acid decomposes, releasing hydrogen, and forming nitrosonium phosphate (a salt). When water is added to the salt, the acid and one-half of the nitric oxide is reconstituted. Heat is given off.

$$2NO^+PO_3^- + H_2O \text{ -----> } 2HPO_3 + NO + NO_2.$$

The NO_2 is reduced by heat and recycled to the first reaction.

$$NO_2 \text{ -----> } NO + 1/2O_2.$$

The overall objective is to "split" nitric oxide into a positive ion (NO^+) and a free electron (e^-). This reduction process is more efficient than electrolysis. The energy input required is 58.2 Wh at 20°C (68°F) and 1 atm (0.1 MPa, 14.7 psi). 60 to 80% of this can be fed back as heat from the later reactions.

Despite the low hydrogen yield the process is promising. It is simpler than other chemical cycles for making hydrogen, has fewer steps, and uses cheaper and more readily available chemicals.

"The reactions described above suggest that if yields can be improved, a cyclic process for making hydrogen from water and low-level energy may be possible through the use of the NO/NO+ redox system." **(77)**

Summary

Regarding the costs of these and other thermochemical processes the observations of L.P. Bilelli are not so optimistic. *"Owing to the many problems involved, it is diffucult to predict whether one of these hydrogen production processes, which are extremely complex from a technical viewpoint, will ever reach a commercial stage."* **(78)**

These costs are offset by the *environmental and health costs* of using fossil fuels and the *military costs* of in defending our precariously overextended energy supply lines. Perhaps a crash program to develope all energy resources that can make us energy independent would be cheaper both now and in the long run.