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ELECTROCHEMICAL-THERMOCHEMICAL CYCLES FOR THE
PRODUCTION OF HYDROGEN FROM WATER**

**David Herbert Munger
(M. S. thesis)**

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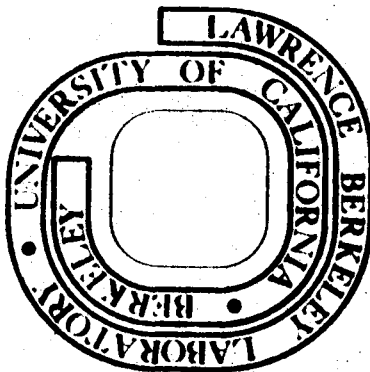
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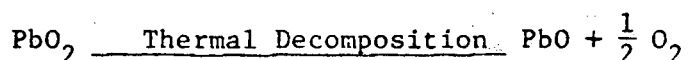
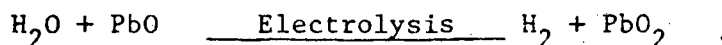
A PRELIMINARY EVALUATION OF HYBRID ELECTROCHEMICAL-THERMOCHEMICAL CYCLES FOR THE PRODUCTION OF HYDROGEN FROM WATER

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ABSTRACT

Water decomposition cycles, of the hybrid type, involving an electrochemical cell producing hydrogen, and an oxide, and a subsequent thermochemical process loop which liberates oxygen and regenerates the lower oxide (or metal), are evaluated. A prototype cycle based on the oxides of lead:



is presented. In principle, such cycles would allow the positive characteristics of conventional water electrolysis and those of thermochemical water-splitting cycles to be exploited to give higher energy efficiencies. An equation correlating the energy efficiency to several of the process operating parameters has been developed. The calculated efficiencies of 28% to 46% for the hybrid cycles compare favorably to the 20% to 25% range for conventional water electrolysis. The reasons for this proposed higher efficiency are: Low reversible cell voltages required, lower level of irreversibilities incurred during electrolysis because of lower ohmic losses and a more reversible electrode reaction; and efficient thermal decomposition.

The hybrid processes are reported to offer comparable energy efficiencies to the thermochemical cycles. However, the hybrid processes offer increased flexibility since many reactions can be performed in electrolysis which could not ordinarily be accomplished by thermal means. Less difficult separations and fewer corrosion problems may be additional advantages offered by hybrid cycles.

Certain physical and economic limitations of hybrid cycles are identified and discussed. The major problems facing the hybrid processes are the short supply and expense of the reactant material, high solubility of the anodic reactant (or product), incomplete reactions, difficult material handling, poor heat exchange characteristics, and difficult filtration due to degradation of the solid material.

Although the hybrid cycles presented in this study are theoretically equal or superior to the other methods for water decomposition, their technological feasibility and economic promise are, nevertheless, not sufficient to contemplate their practical implementation.

I. INTRODUCTION

A. Hydrogen Economy Concept

In recent years, due to the pressure of expanding energy demands, people have become aware of a limit to our energy resources. This "energy crisis" has necessitated an evaluation of the problem. It is generally concluded that an alternative to the petroleum-based economy must be found in order to relieve the pressure.¹⁻⁷

Much of the world's energy reserve is a direct result of radiation from the sun. This resource is stored primarily in the form of natural gas, coal, and petroleum. If the high level of consumption of these nonrenewable reserves is to be maintained, it will be necessary to develop other means to provide for future energy demands. The two most plausible substitutes for the fossil fuels are solar and nuclear power generation.⁸⁻¹⁷

Another primary energy source is geothermal activity. However, geothermal steam, hot rock, and hot water are capable of only minimal contributions towards the total energy supply and create several environmental hazards.^{18,19} Hydroelectric, wind, tidal, and ocean thermal gradient energy sources, all natural extensions of solar energy, are limited in their availability and, in part, are aesthetically questionable.²⁰⁻²³

The efficiency of conversion of the primary energy sources into useful forms of power, or products, is presented by Austin, et al.²⁴ They estimate the total efficiency of energy utilization to be $> 50\%$ for 1970,

and the projected efficiency for the year 1985 is ~44%, implying that the increased electrical generation at 35% efficiency is the cause for this decrease. Since the hybrid cycles for hydrogen production involves the use of electricity, the low efficiency of electrical generation can have serious implications when evaluating the feasibility of a proposed hybrid cycle.

The high efficiency of energy utilization by industrial, residential, and commercial sectors reported by Austin, et al. is doubtful since the study of these sectors is based only on the first law of thermodynamics. An American Physical Society study²⁵ shows that, based upon the second law of thermodynamics, the efficiency of industrial processes rarely exceeds 20-30%. Moreover, the efficiency of space heating, air conditioning, and refrigeration in all sectors of the economy is $\leq 6\%$. Since electrolytic processes generally operate at electrical efficiencies exceeding 50% (see Chapter I, section B), the proposal for the development of hybrid cycles which have electrolytic process steps is valid.

The life-style of the American people should be a major consideration in actual efficiency estimations. The excessive and wasteful use of high quality energy carriers (electricity, natural gas, gasoline, and oil) is a result of poor energy planning (unutilized byproduct steam and solar radiation could substitute for many of the uses) and a lackadaisical approach to conservation. The lack of conservation is exemplified by our "planned obsolescence" economy in which most American homes are riddled with disposable, mass-produced products of low-quality.

Even if the problem of misspent technology is alleviated, there is still the need to supplement the present and future energy distribution systems with a more compatible energy carrier. The question of how solar or nuclear energy can be converted to a more flexible energy carrier has given impetus to the "hydrogen economy" concept. The use of hydrogen as a fuel is attractive because it offers superior performance over electricity in the areas of total energy efficiency, transmission, storage, and utilization. As a replacement for fossil fuels, a hydrogen energy carrier has the particular advantage that man's menace to the environment is minimal. It took nature three billion years to convert the original atmosphere of reducing gases to oxygen and nitrogen. In the last 75 years man has managed to increase the carbon dioxide level by 25 ppm (8.5%).^{26,27} The real effect of this increase on the weather patterns and ozone level is still not fully understood, but it is quite probable that it upsets the balance of the natural processes. Since both the raw material and combustion product of hydrogen is water, the implimentation of hydrogen as a fuel provides an appealing alternative.

A number of studies and discussions concerning various aspects of the "hydrogen economy" have been published.^{7,28-30} These studies discuss a variety of considerations including hydrogen production, transmission, storage, utilization and implimentation. Safety, legal, environmental, economic, political and social aspects are also considered. The conclusions reached are generally supportive of the basic idea, but it is stressed that much more research and development is necessary in order to achieve the goal of a hydrogen economy.

The two most frequently discussed methods of hydrogen production are water electrolysis and thermochemical water decomposition cycles. The third route for hydrogen production involves a hybrid cycle that utilizes the positive characteristics of both electrolysis and thermochemical schemes. All three of these processes require heat as an intermediate energy carrier, eg. from either nuclear or solar sources. Conversion of the heat into electricity is also necessary for operation with the water electrolysis or hybrid processes.

The question of whether to transport energy as electricity or chemical potential (hydrogen) is discussed by Leeth.³¹ He shows that it may be more efficient and economical to use nuclear heat to produce hydrogen instead of electricity. The high power losses in electrical transmission leads to the conclusion that hydrogen could be produced and transported more economically for delivery distances greater than 100 kilometers. If underground electrical cables are used, the distance is reduced to 10-20 kilometers. From an aesthetic standpoint, the underground electrical cable or hydrogen pipeline are infinitely more desirable than over-ground electrical cables.

The probability that power-generating facilities will be located in regions remote from the high-population-density areas lends weight to Leeth's observations. Solar farms are practical only in isolated sectors of the country where land is inexpensive and sunlight is plentiful. Nuclear power plants will be sited at costal or deep-sea locations because of the necessity for the dissipation of large amounts of waste heat. Since most cities are removed from these locations,

it is important that the line losses in transmission of energy be kept to a minimum.

The flexibility of a hydrogen fuel is further demonstrated by the capacity of hydrogen to be stored as a gas, cryogenic liquid, or metal hydride.³² The net effect is a load leveling of the power generating facilities. Designers of present day electrical generating plants must allow for a "load use factor". This requirement results in a higher capital investment for equipment that is used for only a few hours a day, during the peak demand periods. The storage capabilities of hydrogen will eliminate this problem by providing a buffer capability to offset the power consumption surges.

The utilization of hydrogen is anticipated to take place in stages.⁷ Initial impact is expected in applications where large amounts of natural gas are presently consumed, such as ammonia synthesis, industrial uses, and home needs. The use of hydrogen as a fuel for powering engines for transportation purposes is the final step for full realization of a hydrogen economy.

The nonpolluting characteristics of hydrogen fuel makes its use attractive, especially in high-population-density areas. The exhaust from a hydrogen fueled furnace or engine has no unburned hydrocarbons, no carbon monoxide or dioxide, and possibly less NO_x pollutants. There have been several successful automobiles powered by hydrogen built recently that demonstrate these important advantages.^{33,34}

The use of hydrogen as a fuel can also lead to improved design of existing processes and end uses. For instance, liquid hydrogen fueled

aircraft will show to have improved performance over the use of kerosene fuels. Studies at NASA^{35,36} claim that using liquid hydrogen in supersonic jets will increase fuel efficiency and speed by providing better cooling and a high energy density.

The hydrogen economy concept has been receiving growing support from the scientific community over the past few years. This is evidenced by the number of national and international symposia³⁷⁻⁴¹ dealing with the advances in the technology of a hydrogen economy. The major thrust of these conferences is toward finding an efficient, economically-viable process for the production of hydrogen. The predominant features of the three proposed schemes for large scale hydrogen production are presented in the following discussions.

B. Water Electrolysis

Electrolysis is presently the only commercial process used to decompose water into its elements. Water electrolysis accounts for about 1.4 million kilograms of hydrogen per day, world-wide.⁴² This quantity is only about three percent of the total amount of hydrogen used in one day in the United States.⁷ Most of the electrolytic production is found in areas of the world where the cost of natural gas is high and the cost of electricity is relatively low. These areas include Norway, Chile, Egypt, and India.

Generation of hydrogen by electrolysis has many advantages over the proposed thermochemical schemes. The two most apparent features are the low maintenance required and the lack of chemical by-products. The undesirable features of electrolytic hydrogen are the low energy

efficiency and the high capital cost.

The overall energy efficiency of hydrogen production by electrolysis suffers from the low efficiency of converting heat into electricity, and from losses in the operation of the electrolytic cell. Electrical energy efficiency is defined as the ratio of the theoretical water decomposition voltage (1.23 volts at 1 atm and 298°K) to the actual cell operating voltage assuming 100% current efficiency. Present day cells⁴³ operate in the 1.8 to 2.2 voltage range, with a corresponding electrical energy efficiency of 68% to 56%. Combining these values with the 35% efficiency of electricity generation, the electrolysis cell is capable of producing hydrogen at a 20 to 25% overall energy efficiency.

The power losses due to the increased cell voltages are dependent upon three factors: activation overpotential of the electrode processes, ohmic resistance across the cell, and concentration overpotential.

The activation (or kinetic) overvoltage is a result of the slow rate of the electrode reaction. The type of metal used for the electrode surface has direct bearing on the catalytic nature of the reaction. Practical replacement for the noble metal electrode include the use of Raney nickel catalysts^{44,45} and porous electrodes. The overvoltage is reduced by operating at elevated temperatures and pressures, and is increased as the current density of the electrode reaction is increased.^{43,46}

Ohmic losses occur as a result of low conductivity across the cell. The resistance is a combination of resistances caused by slow mobility of the ions in the solution, gas bubbles formed at the electrode, and the presence of a dividing diaphragm. Methods of relieving the ohmic

losses include agitation of the electrolyte, and raising the temperature or pressure of the cell.

Concentration overpotential results from the changes in the composition of the layers of electrolyte close to the electrodes. This change in composition is characterized by a depletion of ions and the supersaturation of oxygen and hydrogen within these layers. These effects are minimized by elevating the operating temperature and optimizing ionic and gas transport by agitation, or by the use of porous electrodes. Electrolyzers of advanced design are showing promising trends towards higher current densities, higher efficiencies and lower cost of operation. Various designs use aqueous or solid-phase electrolytes, liquid or vapor water input, closer electrode spacing, greater agitation, and higher temperature and pressure ranges to achieve the improved performance.

Allis Chalmers has developed a high current density electrolyzer utilizing improvements achieved in the fuel cell technology of the 1950-60's. Porous electrodes allow the gas bubbles formed on the face of the electrode to be pushed out the back of the electrode by the higher pressure in the cell. This arrangement allows for lower ohmic voltage drop due to closer electrode spacing and smaller void fraction from the evolving gas bubbles. The cell also operates at a higher temperature. This operation at elevated temperatures reduces the cell voltage losses even further by lowering the activation overpotential, the theoretical cell potential, and the resistance of the electrolyte. Costa and Grimes⁴⁷ have presented a design paper on this system based

on work done at the Oak Ridge National Laboratory.

General Electric⁴⁸⁻⁵⁰ has proposed a high temperature electrolyzer using an ionic conducting solid electrolyte (calcium yttrium zirconate) operating at 800-1000°K with a water vapor feed. The high temperature, and its associated advantages, is possible in the cell because the lack of free acid or alkaline electrolyte minimizes the corrosion problem usually associated with elevated temperatures.

The most important consideration in the evaluation of the electrolytic process is related to the production of electricity. Michel⁵¹ reviewed the economics of hydrogen production and concluded that 84% of the cost of electrolytic hydrogen is due to the cost of the electricity consumed. Consequently, there is incentive for the development of more capital-intensive electrolyzers that will have lower electrical energy requirements.

C. Thermochemical Water Decomposition Cycles

A search for systems that would allow production of hydrogen more economically than by electrolysis has lead to the proposal of numerous thermochemical cycle schemes for water-splitting. The basis of the improved economics is that there is no electrical generation step involved in the process; the process is not inherently limited by the 35% efficiency of generation of electricity.

The direct thermal decomposition of water can only be accomplished at extremely high temperatures ($> 4000^{\circ}\text{K}$). This is not possible on a large scale at present due to the lack of a practical heat source, and serious problems with containment and separation of gases.

An alternative to direct decomposition of water is to run a series of coupled reactions at lower temperatures. The highest temperature expected from advanced nuclear fission reactors is about 1300°K,⁵² implying that none of the chemical reactions can be proposed to occur above that temperature. The thermodynamic strategy for the formulation of energy efficient cycles is presented in Chapter II. It is imperative that these reactions form a closed cycle in which water is the raw material, hydrogen and oxygen are the products, and all other chemical species are completely recycled within the system. To date there have been numerous thermochemical cycles proposed.⁵³⁻⁶⁸

The problems associated with the thermochemical cycles range from fundamental to practical. Formerly, a majority of the reactions in the proposed cycles have had very little useful importance. This has led to a lack of basic information about the feasibility of the reactions. Because of the dearth of thermodynamic and kinetic data, any estimates of the feasibility of the proposed processes must be regarded with caution. Evaluations of some of the more promising cycles are given in papers by Abraham and Schreiner,⁶⁹ Glandt and Myers,⁷⁰ and others.^{71,72}

It is stressed that most of the research on thermochemical water decomposition cycles is in the preliminary stages. The problems to be solved are numerous. Nuclear reactor interfacing, intercycle heat transfer, corrosion, slow kinetics, separation of like phases and high capital cost of equipment and reactants head the list of the most pressing problems. To date there have been no thermochemical processes developed which are capable of producing hydrogen economically.

D. Hybrid Electrochemical - Thermochemical Cycles

A hybrid electrochemical-thermochemical water decomposition cycle is a scheme in which at least one step is performed by electrolytic means, and the remaining steps are driven thermally. The goals for such a process are to utilize the positive characteristics of both the electrolysis and thermochemical systems in order to obtain an economically viable, and energy efficient method for producing hydrogen.

A prototype scheme proposed by this research involves the substitution of lead oxide for the oxygen electrode. During operation of the electrolysis cell, hydrogen is evolved at the cathode, and lead oxide is oxidized to lead dioxide at the anode. The lead dioxide is subsequently removed from the electrolysis cell and thermally decomposed to lead oxide and molecular oxygen. The schematic for the process is presented in Fig. 1. The advantages of the hybrid process over either the electrolysis of water or thermochemical decomposition of water are:

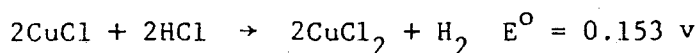
1. The serious irreversibility of the oxygen electrode^{46,73,74} is avoided by substitution with a more reversible couple.
2. A reaction, which is unfavorable in respect to thermodynamic or kinetic criteria, can be made feasible by adding the electrochemical step.
3. The hydrogen can be delivered at high pressures.
4. Corrosion problems are minimized.
5. The theoretical cell potential is lowered from the 1.23 volt value of water electrolysis.

6. Electrolytic cell voltage losses are reduced by improved cell design, and more favorable reactions.
7. Separation problems are eliminated.
8. Lower heat exchange requirements than thermochemical cycles.
9. Hydrogen is produced free of chemical by-products.

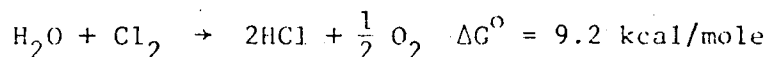
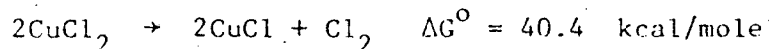
There are several different possibilities for anodic reactions in which the anode product can theoretically be regenerated by a thermal process outside of the cell. The thermal processes will involve either a simple thermal decomposition of an oxide, or possibly a series of coupled reactions. A listing of these possibilities with some examples includes:

1. Anodic oxidation of a metal or metal oxide with a simple thermal decomposition into the metal or metal oxide performed outside the electrolytic cell (see Fig. 1);
2. Metal redox couples which are oxidized in the electrolytic cell and then thermally reduced in single or multiple thermochemical steps:

Electrochemical reaction:



Thermochemical reaction steps:



3. Organic redox couples that produce the oxidized species within the electrolysis cell are regenerated by a single or multiple step thermochemical scheme:

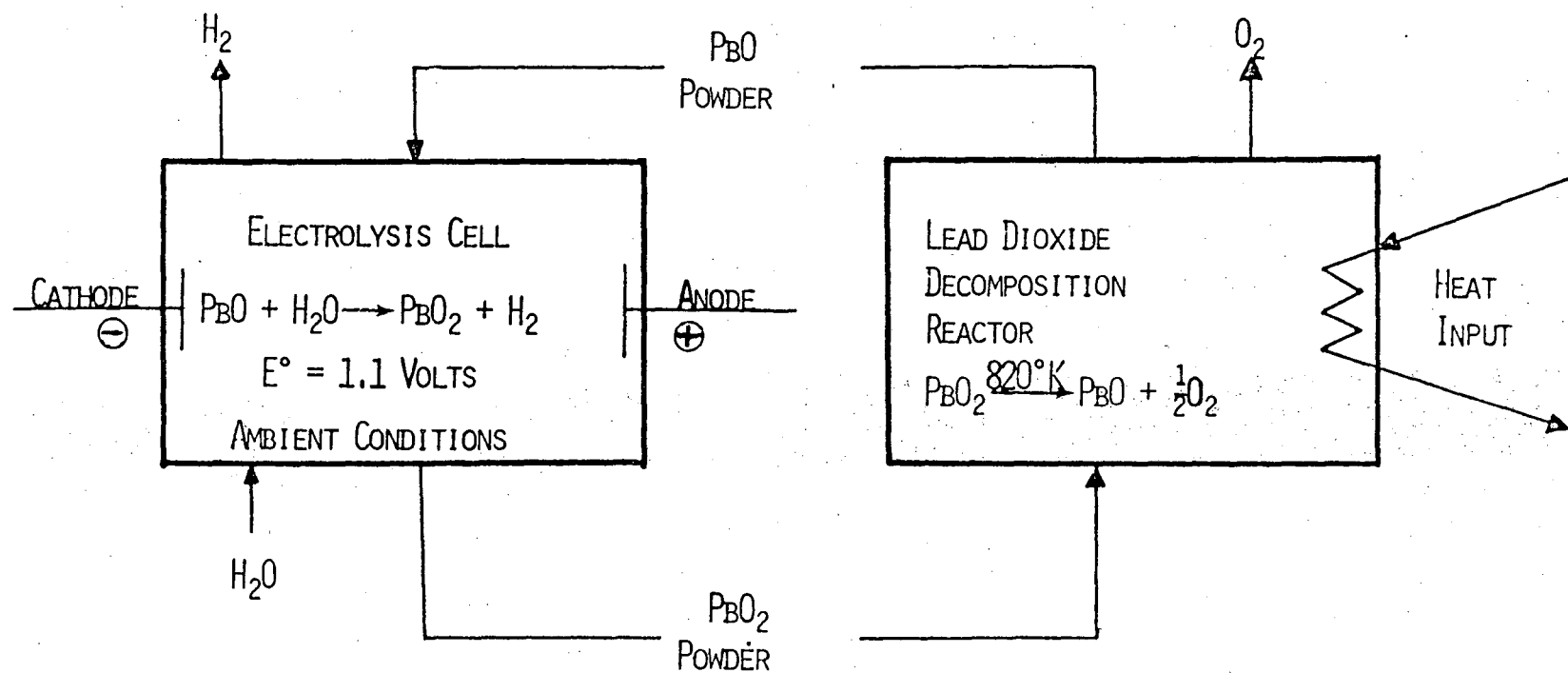
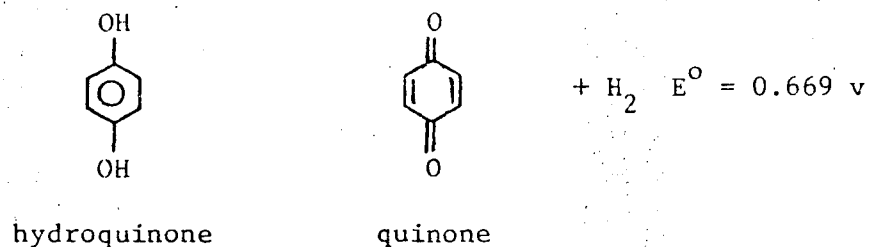


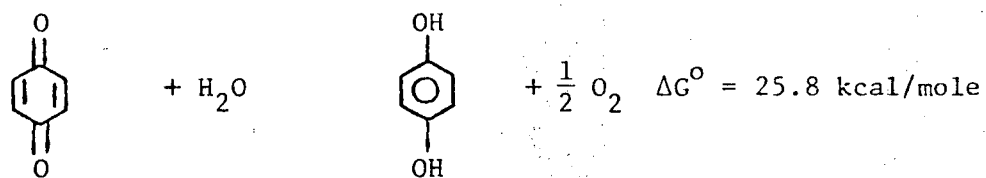
Fig. 1. Schematic of the Hybrid Cycle based on the Lead Oxide/Lead Dioxide Couple (Tobias (75)).

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Electrochemical reaction:



Thermochemical reaction step:



Conceptually, the hybrid systems exhibit many advantages over the use of either electrolysis or thermochemical cycles alone for the splitting of water. It is the purpose of this study to provide a preliminary evaluation of the proposed hybrid schemes from an engineering point of view.

II. THERMODYNAMIC CONSIDERATIONS

Since all of the hybrid cycles presented in chapter III are in the conceptual stage of development; it is extremely difficult to project accurately an actual efficiency for a given scheme. It is possible to use basic thermodynamic principles and data to calculate ideal maximum efficiencies for the hybrid processes. However, determination of the real inefficiencies of a proposed hybrid cycle would require extensive experimentation and detailed process design. The scope of the present study, a preliminary evaluation, did not allow undertaking the complex experimentation involved in the determination of kinetic and transport data on a wide range of materials and reactions of possible interest.

The discussion on irreversibilities exposes the reader to the major sources of inefficiencies in the actual process that might be involved in the production of hydrogen. The intent of the section is the estimation of the irreversibilities in order to make the calculation of the process efficiencies more realistic.

A. Reversible Thermodynamic Considerations

The definition of reversibility implies that, in a cyclic process, the initial and final states of that process, and the universe, are exactly the same. This situation can be realized only if the following reaction parameters can be maintained:

1. Work is generated at 100% of Carnot efficiency,
2. Chemical equilibrium is sustained,

3. Ideal work of separation is realized,
4. Ideal heat exchange (zero temperature driving force),
5. Work of expansion and compression is ideal,
6. Electrolysis processes are 100% efficient.

All processes in nature must follow the laws of thermodynamics given by the equation defining the standard-state Gibbs energy change for isothermal conditions:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (1)$$

where ΔG° is the standard-state Gibbs energy change, ΔH° is the standard-state enthalpy change, T is the absolute temperature, and ΔS° is the standard-state entropy change. This equation is used extensively as the basis for the calculation of the various reversible characteristics of the hybrid processes.

1. Efficiency of Reversible Cycles

There are four efficiencies generally used for the description of the performance of a reversible cycle.^{69-72,76,77} They are all derived from the equation describing the Carnot heat engine neglecting expansion work:

$$\Delta G = \left(\frac{T_H - T_C}{T_H} \right) Q_H \quad (2)$$

where ΔG is the chemical work produced by the cycle, T_H and T_C are the temperatures of the hot and cold heat reservoirs, and Q_H is the total heat absorbed from the high-temperature heat reservoir.

The thermodynamic work efficiency, ϵ , is the ratio of the chemical work produced by the cycle to the total heat absorbed from the high-temperature reservoir. Holding the inlet and outlet temperatures of the process to ambient, the work efficiency is defined as:

$$\epsilon = \frac{-\Delta G_f^0}{Q_H} = \left(\frac{T_H - T_c}{T_H} \right) \quad (3)$$

where ΔG_f^0 is the standard-state Gibbs energy of formation.

The second and third efficiencies relate the amount of heat obtainable from the product streams to the amount of heat supplied by the high-temperature reservoir. The quantity of heat available at standard-state from the products is the heat of combustion, ΔH_f^0 . Since the water produced as a result of this combustion will most likely be in the vapor or liquid phase, the thermodynamic heat efficiency, η , can be defined on two different bases. The lower heating value (LHV) for combustion to water in the vapor phase is 57.8 kcal/mole of water formed at 298°K and 1 atm. The higher heating value (HHV) includes the latent heat of condensation to a liquid. The HHV for water at 298°K and 1 atm. is 68.3 kcal/mole of water.

The heat efficiencies are related to the work efficiency, ϵ , by the ratio of the heat of formation to the Gibbs energy of formation for the reaction. Equations (4) and (5) are the definitions of the thermodynamic heat efficiencies:

$$\eta_{(LHV)} = \frac{-\Delta H_{f(V)}}{Q_H} = \frac{\Delta H_{f(V)}}{\Delta G_f^0} \epsilon \quad (4)$$

$$\eta_{(\text{HHV})} = \frac{-\Delta H_{\text{f(L)}}}{Q_{\text{H}}} = \frac{\Delta H_{\text{f(L)}}}{\Delta G_{\text{f}}^{\circ}} \epsilon \quad (5)$$

where subscripts (V) and (L) signify vapor and liquid, products respectively.

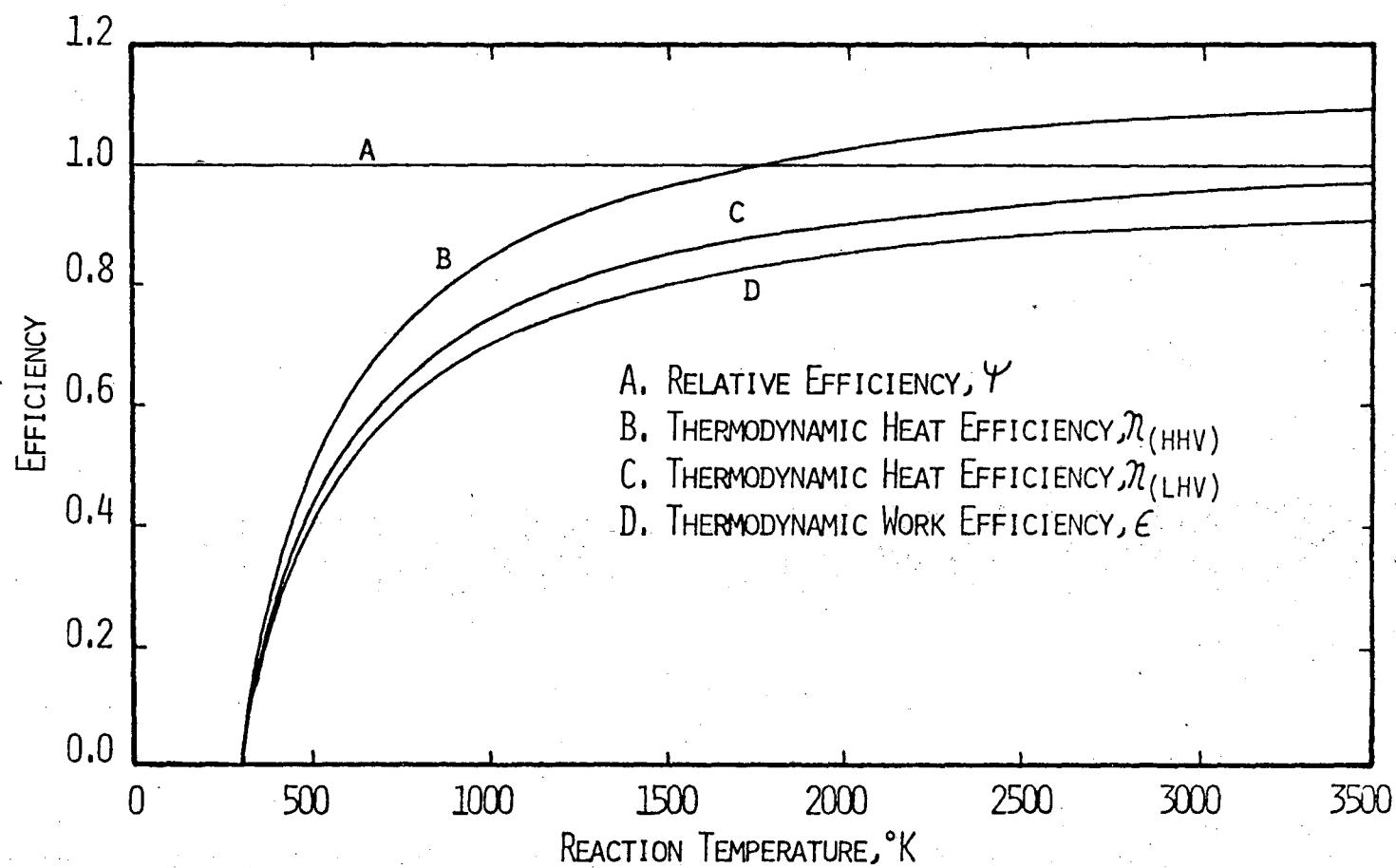
The relative efficiency, ψ , is the ratio of the chemical potential produced by a process to the ideal work that could be generated by a Carnot heat engine operating between the two temperature limits:

$$\psi = \frac{\Delta G}{Q_{\text{H}} \left(\frac{T_{\text{H}} - T_{\text{c}}}{T_{\text{H}}} \right)} \quad (6)$$

For a completely reversible reaction the relative efficiency will be unity because of the equality in Eq. (2).

The importance of the relative efficiency becomes apparent when considering the irreversibilities of a process. Since the actual work produced by a reaction is always less than the ideal work production of a Carnot heat engine, the relative efficiency is well suited as a measure of the deviation from reversibility.

Figure 2 is a graph of the temperature dependence of the four efficiencies. The work efficiency is preferred over the two heat efficiencies because most applications of hydrogen (fuel cells, transportation, etc.) will involve the production of work and not heat. The use of ϵ also provides for efficiencies between 0.0 and 1.0 which is less confusing than figures that range between 0.0 and 1.02 or 1.2. The principal advantage of using the heat efficiencies is that they



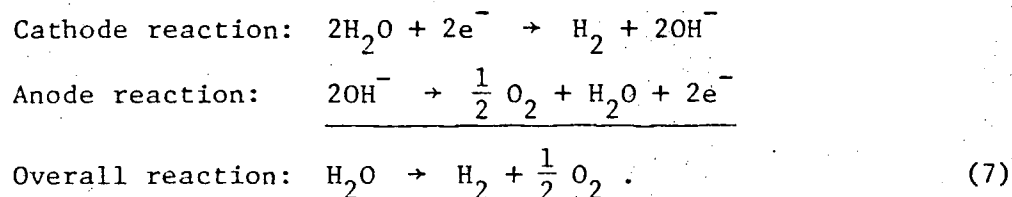
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Fig. 2. Temperature Dependence of the Reversible Efficiencies.

provide a more optimistic view of proposed cycles. The relative efficiency is a valuable tool because it provides a measure of irreversibility that is independent of the temperatures of the hot and cold reservoirs.

2. Equilibrium Electrolysis Cell Potential

The overall reaction in an electrochemical cell is the sum of the two individual reactions occurring at each electrode. For water electrolysis the overall reaction is the decomposition of water into oxygen and hydrogen (alkaline electrolyte):



Calculation of the standard potential⁷⁸ for the overall reaction involves the determination of the standard Gibbs energy change for that reaction according to Eq. (1). The relationship between the electrochemical potential and the chemical potential is:

$$E^{\circ} = \frac{\Delta G^{\circ}}{nF} \quad (8)$$

where E° is the standard cell potential, n is the valency for the reaction, and F is Faraday's constant (96,490 coulombs/equivalent).

The Nernst equation, which is an extension of the Van't Hoff isotherm,⁷⁹ is a statement of the effect that deviations from unit activity have on the reversible potential:

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{\pi_i(a_i)^{v_i}}{\pi_j(a_j)^{v_j}} \quad (9)$$

where E is the reversible cell potential, R is the gas constant, v is the stoichiometric coefficient, a is the activity, and subscripts (i) and (j) represent the products and the reactants, resp. For water electrolysis, the standard-state change in the Gibbs energy is 56.69 kcal/mole.⁸⁰ If the assumption of unit activity holds, then the equilibrium potential will be 1.23 volts. The additional 11.54 kcal/mole needed to satisfy conditions of enthalpy change in Eq. (1) are supplied by the transfer of heat into the cell ($T\Delta S$). Under equilibrium conditions the forward reaction is exactly balanced by the reverse reaction and there is no net change in any of the properties. In actual operation of a water electrolysis cell the necessary heat input to offset the entropy term is provided by dissipation of heat from the various inefficiencies of the electrolysis (e.g., ohmic potential drop and electrode overpotentials).

A theoretical development and a more complete application of the thermodynamics of electrolytic systems are provided by Newman,⁸¹ Potter,⁸² and Falk and Salkind.⁸³

3. Chemical Equilibrium Composition

All of the proposed thermochemical cycles involve at least one reaction at high temperature. The temperature dependence of the standard-state Gibbs energy change, $\Delta G_{(T)}^{\circ}$ at reaction temperature T , is determined by the changes of $\Delta H_{(T)}^{\circ}$ and $\Delta S_{(T)}^{\circ}$:⁷⁹

$$\Delta G_{(T)}^{\circ} = \Delta H_{(T)}^{\circ} - T\Delta S_{(T)}^{\circ} \quad (10)$$

Since the equilibrium constant, K_y , is related to the value of $\Delta G_{(T)}^{\circ}$:

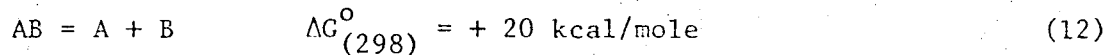
$$\ln K_y = \frac{-\Delta G_{(T)}^{\circ}}{RT} \quad (11)$$

at 1 atm. total pressure, to obtain a reasonable reaction yield, it is necessary that the value of $\Delta G_{(T)}^{\circ}$ has to be near zero. For the decomposition of water this temperature is approximately 4300°K. Clearly this temperature is too high for use in a practical thermochemical process.

Several reports have placed the maximum temperature attainable from gas cooled nuclear reactors at $T_h = 1300^{\circ}\text{K}$.⁵² This implies that the highest temperature available for a chemical reaction is less than 1300°K. The equilibrium constant for water at 1300°K is approximately 9.0×10^{-8} . The separation of the reaction components at partial pressures in the range of 10^{-8} atmospheres is obviously unfeasible.

The basis of the strategy used in the development of thermochemical water decomposition cycles is the introduction of chemical intermediates in a multiple-step process scheme in order to obtain reasonable equilibrium constants for each reaction at reasonable temperatures.⁷⁶ The sum of all the reactions would then be the decomposition of water into hydrogen and oxygen, with the chemical intermediates being recycled.

A hypothetical example of the strategy to decompose compound AB is presented below:



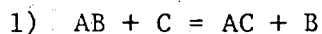
$$\Delta S_{(298)}^{\circ} = + 5 \text{ e.u. (0.005 kcal/mole}^{\circ}\text{K)}$$

It is possible to estimate the temperature at which this reaction will have a $\Delta G_{(T)}^{\circ} = 0.0$ by using the relationship between the changes of $\Delta G_{(T)}^{\circ}$ and T and $\Delta S_{(T)}^{\circ}$:

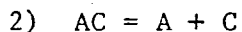
$$\frac{\partial \Delta G_{(T)}^{\circ}}{\partial T} = - \Delta S_{(298)}^{\circ} \quad (13)$$

Reaction 12 would require a reaction temperature of 4000°K in order to get a reasonable conversion yield.

If the reaction is split into two separate reactions using a component that is recycled, then it becomes possible to run the overall reaction at reasonable temperatures.



$$\Delta G_{(298)}^{\circ} = -10 \text{ kcal/mole; } \Delta S_{(298)}^{\circ} = -30 \text{ e.u.} \quad (14)$$



$$\Delta G_{(298)}^{\circ} = 30 \text{ kcal/mole; } \Delta S_{(298)}^{\circ} = + 35 \text{ e.u.} \quad (15)$$

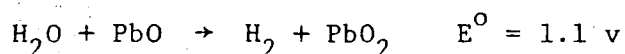
Reaction 14 is an exothermic reaction that occurs spontaneously at ambient temperatures. Reaction 15 experiences a rapid decrease in the Gibbs free energy change because of the large positive value for ΔS° . The reaction will proceed favorably at a temperature of 850°K where the Gibbs free energy change is zero.

Funk⁷⁶ showed that this strategy for the decomposition of water could very well be a practical method. He also demonstrated that there

are no possible two-step thermal water splitting cycles. Funk as well as others⁵³⁻⁷² express the hope that there are cycles composed of three or more steps that would prove to be economically viable.

The application of this concept is also valid for the hybrid cycles. The lead oxide-lead dioxide scheme (Fig. 1) is a good example of the use of an intermediate chemical species in a hybrid cycle:

Electrolysis step:



Thermal step:



56.7 kcal/mole of the work needed to split water is supplied by the electrochemical step. The remainder of the work is supplied by the thermal decomposition of the lead dioxide to lead oxide and oxygen. The decomposition temperature of lead dioxide is taken from Table 1 as 820°K. The hybrid cycle is proposed primarily as a method for decomposing water in which the work supplied by the electrolysis reaction is lowered from the value for conventional water electrolysis. The potential for a higher overall energy efficiency can be realized if the thermochemical portion of the hybrid cycle can be carried out at an efficiency greater than that for water electrolysis.

B. Irreversibilities in Hybrid Cycles

Operation of any cycle at finite rates leads to irreversibilities that result in the necessary lowering of efficiency from the reversible value. The magnitude of the irreversibilities is most directly dependent upon the physical environment provided by the manufacturer

Table 1. Table of Decomposition Temperatures of Metal Oxides for use in Hybrid Cycles. Sources: Brewer,⁸⁷ Kubaschewski and Hopkins⁸⁵

Metal Oxide	Reduced Metal Oxide	Decomposition Temp °K
MnO_2	Mn_2O_3	750
Mn_2O_3	Mn_3O_4	1170
Co_3O_4	CoO	1240
CuO	Cu_2O	1370
Ag_2O	Ag	455
CdO	Cd	$1240 @ 10^{-3} \text{ atm}$
HgO	Hg	700
Tl_2O_3	Tl_2O_3	760
PbO_2	Pb_3O_4	590
Pb_3O_4	PbO	820
Sb_2O_5	Sb_6O_{13}	670
Sb_6O_{13}	SbO_2	970
SbO_2	Sb_2O_3	1350
PtO	Pt	600

for the given reaction to take place.

Generally, the more capital a manufacturer is willing to put into a process, the more likely the process will perform with greater efficiency. In the water electrolysis process, for example, the use of a noble metal electrode instead of a nickel electrode results in a higher efficiency but also requires a higher capital cost. The other alternative is to operate the cell at a current density lower than usual in order to reduce the ohmic and overpotential losses. This method requires an increased electrode surface area, which results in a still higher capital investment for an equal production rate.

By identifying the sources of irreversibility in a process, it is possible for an investigator to estimate the approximate degree of energy losses that a system will exhibit. All of the processes mentioned in this report are in the conceptual stage of development, thus requiring that the estimates be arrived at by analogy to existing processes or by intelligent guessing.

1. Irreversibilities in the Electrochemical Step

In an electrolytic process the degree of irreversibility is directly measurable by the deviation of the operating voltage from the reversible cell voltage:^{81,83,46}

$$V = E + \eta_a + \eta_c + IR \quad (16)$$

where V is the total cell operating voltage, η_a is the activation overvoltage for both electrodes, η_c is the concentration overpotential for both electrodes, and IR is ohmic drop. The deviation is due to the fact that as a current is passed through the cell, there are forces

generated which tend to oppose the passage of the current. In order to sustain a finite reaction rate it is necessary to supply the cell with a potential of sufficient magnitude to overcome these forces.

All of the voltage losses are dependent upon the properties and design appropriate to the particular electrolysis cell. For this reason it will be assumed that the electrolysis portion of all the hybrid cycles will be carried out at the high efficiency of 80%. This is a reasonable figure when considering that the oxygen electrode,^{46,73,74} which is a major source of cell inefficiency, is to be replaced by another, presumably more reversible, electrode. Other design improvements are possible, such as closer electrode spacing and removal of the gas separating diaphragm found in ordinary water electrolyzers.

2. Irreversibilities in the Thermal Step

The irreversibilities associated with the thermochemical cycles have been reported by Flock.⁸⁶ He used the availability, ΔB , to relate the properties and conditions of any thermochemical process to the amount of available work actually produced by that process:

$$\Delta B = \left(\frac{T_H - T_c}{T_H} \right) Q_H - T_c \Delta S_{irr} \quad (17)$$

where ΔS_{irr} is the entropy production within the process due to irreversibilities.

The consequences of any irreversibility identified by the production of entropy are that the availability will decrease. This decrease in available work will result in an increase of actual work supplied to the process in order to bring about the desired change in

availability.

The redefinition of the relative and work efficiencies that includes the irreversibilities is:

$$\psi_{irr} = \frac{\Delta B}{\left(\frac{T_H - T_c}{T_H} \right) Q_H} \quad (18)$$

$$\epsilon_{irr} = \frac{\Delta B}{Q_H} = \left(\frac{T_H - T_c}{T_H} \right) \psi_{irr} \quad (19)$$

where ψ_{irr} is the relative efficiency including irreversibilities and ϵ_{irr} is the work efficiency including irreversibilities.

In his analysis of the inefficiencies associated with the proposed reverse Deacon reaction upon which many thermochemical cycles are based, Flock used the following basic processes to provide a measure of the irreversibilities:

1. Heat exchange - The energy loss in a heat exchanger is calculated by the difference of the entropy change of the high temperature heat reservoir and the low temperature heat reservoir:

$$dS_{irr} = \frac{dQ}{T_c} - \frac{dQ}{T_H} \quad (20)$$

The generation of entropy is increased as the temperature difference becomes larger and as the mean temperature becomes lower.

2. Unrecovered work of expansion - In an isothermal expansion the production of entropy is given by:

$$dS_{irr} = - \left(\frac{\partial V}{\partial T} \right)_P dP \quad (21)$$

where V is the volume.

3. Chemical potential - When there is a chemical potential gradient used to drive a reaction, then there will be a corresponding production of entropy:

$$\Delta S_{irr} = \Delta S - \frac{\Delta H}{T} - \frac{W'}{T} \quad (22)$$

The entropy will increase if the temperature of the reaction is lowered or the potential for the reaction is increased. It is the inability to utilize the potential for work that gives rise to the inefficiency.

4. Irreversible mixing of gases - The entropy production resulting from the irreversible mixing of gases is:

$$\Delta S_{irr} = - R \sum n_i \ln y_i \quad (23)$$

The inefficiency in this process is most severe when the concentrations of the components are very different.

5. Separation processes - Typical industrial separation processes involve many of the previously mentioned entropy production sources.

Flock concluded that the overall relative efficiency for the reverse Deacon process is approximately 13% assuming that heat at a

temperature below 400°K is considered unusable.

Historically, many separation processes have suffered from low efficiencies. For instance, the desalination of salt water is currently being accomplished only at efficiencies less than 10%.⁸⁷⁻⁸⁹

Again, it is emphasized that the intent of this thesis work is to identify candidate hybrid water decomposition cycles and to evaluate the schemes only in a basic sense. When this preliminary work is completed, the detailed analysis of the process of choice is then carried out. It is only during the process of the design of the actual cycle in which detailed calculations of the irreversible characteristics of the scheme are considered. With this intent, an estimation of the irreversibilities of several hybrid cycles will be made using assumed values for the relative efficiency and the electrical efficiency.

C. Estimation of the Work Efficiency for Hybrid Cycles

Since it is essential that the performance of a hybrid cycle be at least equal to that of water electrolysis to be considered feasible, it is necessary that the efficiency of the electrolysis portion of the cycle be at least as great as water electrolysis (70% for future water electrolyzers). As is pointed out earlier in this chapter, it is extremely difficult, without detailed design and experimental data, to forecast accurately the efficiency of any of the processes involved in a hybrid cycle. For this reason it is assumed optimistically that the electrolysis step is performed at 80% electrical efficiency.

The thermodynamic work efficiency for a hybrid water decomposition process can now be estimated:

$$\epsilon_H = \frac{56.69}{\frac{EnF}{(0.35)(0.80)} + \frac{\Delta G^\circ(298)}{\frac{T_H - T_c}{T_H} \psi_{irr}}} \quad (24)$$

Figure 3 is a graph of ϵ_H as a function of ψ_{irr} . The conclusion drawn from this graph is that above the value of 0.36 for ψ_{irr} the greater the portion of the Gibbs energy change for water decomposition that is supplied by the thermal steps of the hybrid cycle, the better the performance of the process will be. Below the 0.36 figure, the major portion of the work input should be supplied by electrolysis.

Abraham and Schreiner⁶⁹ and Appleby⁹⁰ optimistically estimate the relative efficiency for the proposed thermochemical cycles to be 0.56 and 0.67, respectively. For the purpose of the present estimation of the work efficiency for hybrid cycles, it is assumed that the relative efficiency of the thermal step is 0.60.

Figure 4 is a graph of the dependence of ϵ_H on the upper temperature of the thermal reaction. Above 600°K the efficiency is benefited by supplying most of the work during the thermal portion of the hybrid cycle. Below 600°K the favored process is electrolysis.

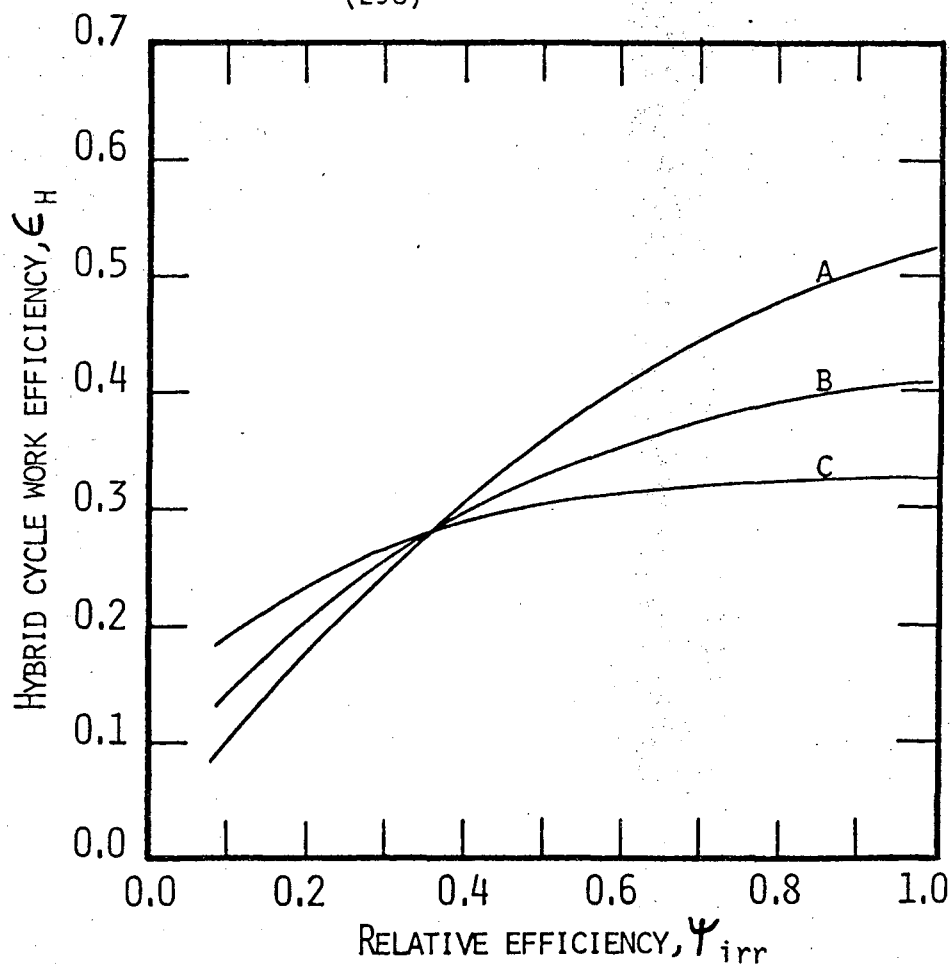
The value of considering the efficiency using the conclusions drawn from Figs. 3 and 4 is that the "tailoring" of high process efficiencies is possible by taking into account both the decomposition temperature and the free energy requirement for the thermal process. The lead, copper, and cadmium systems in Table 5 are examples of this concept. The 28.2% efficiency of the lead based cycle is calculated

DEPENDENCE OF WORK EFFICIENCY ON THE RELATIVE
EFFICIENCY AT CONSTANT REACTION TEMPERATURE = (1300°K)

A: 25% OF $\Delta G_{(298)}^{\circ}(\text{WATER})$ SUPPLIED BY ELECTROLYSIS

B: 50% OF $\Delta G_{(298)}^{\circ}(\text{WATER})$ SUPPLIED BY ELECTROLYSIS

C: 75% OF $\Delta G_{(298)}^{\circ}(\text{WATER})$ SUPPLIED BY ELECTROLYSIS



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Fig. 3. Dependence of Work Efficiency on Relative Efficiency.

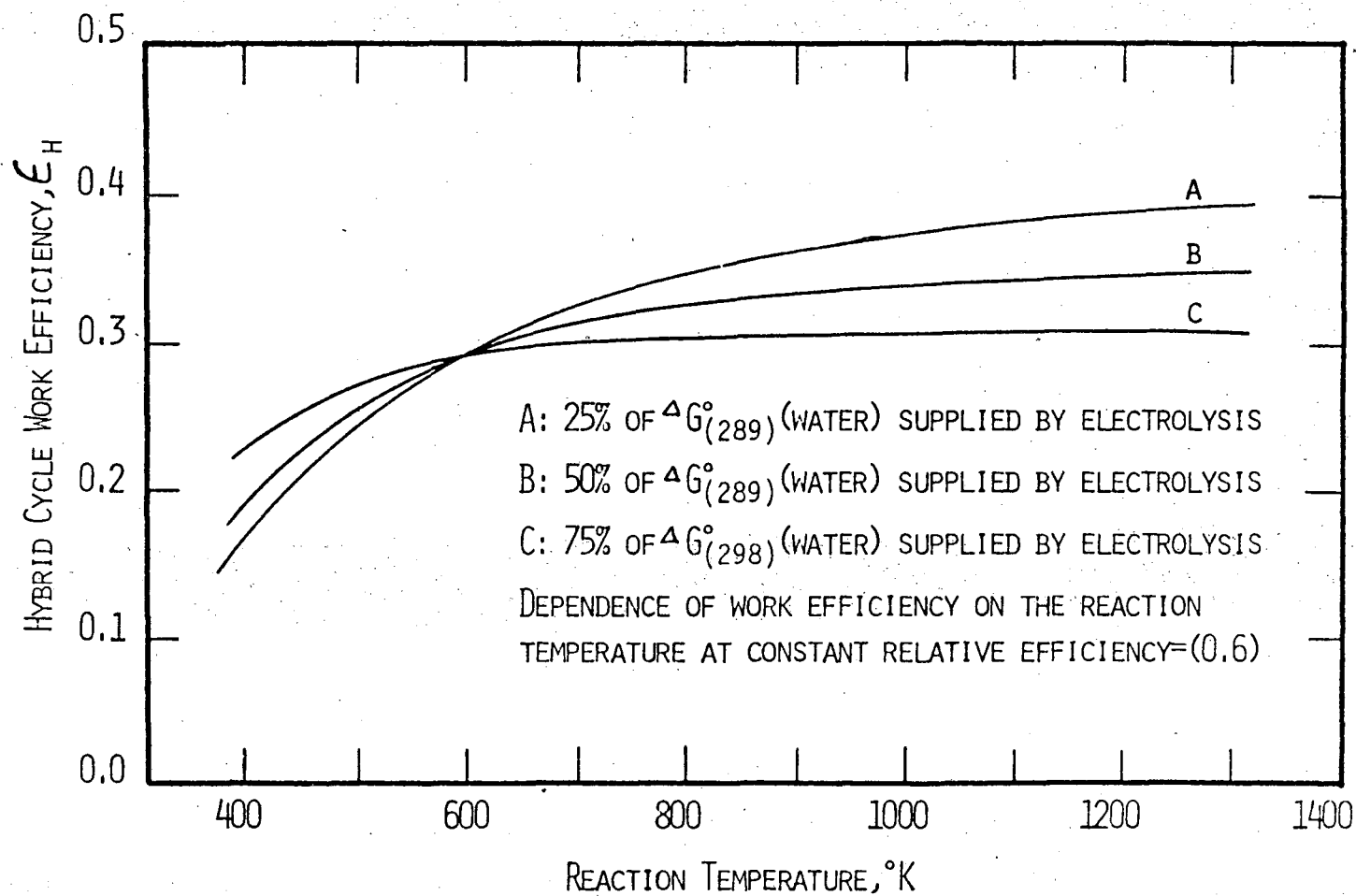


Fig. 4. Dependence of Work Efficiency on Reaction Temperature.

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from an upper temperature limit of 820°K and work input of 6.0 kcal/mole. The copper cycle, on the other hand, exhibits an efficiency of 38.1% due to the elevated temperature and increased work load on the thermal step of the process. The cadmium, cycle which actually has a lower decomposition temperature (assume that the 10^{-3} atm operating condition has negligible work input) than copper, has an efficiency of 46.0% because practically all of the free energy of water decomposition is supplied in the thermal step of the cycle.

Even the "low" efficiency of the lead oxide process can prove to be very attractive. The 28% efficiency of this cycle requires that 0.28 kW-hr/mole- H_2 be supplied by the total process. This compares very favorably with the 0.32 to 0.39 kW-hr/mole- H_2 range for water electrolysis.

The improved energy usage is further exemplified by considering the total energy consumption requirements for the U.S. in the year 2000 which is projected to be 175×10^{15} kJ/year.⁹¹ It is estimated that if the proposed hydrogen economy becomes a reality then approximately 25% of the energy would be supplied to consumers in the form of hydrogen.⁸⁶ This amount is equivalent to the output of 1100 one-thousand-megawatt electric power plants. If the hybrid process to produce hydrogen at a total thermodynamic work efficiency of 28% were used, there would be savings of 117 to 314 one-thousand-megawatt power plants relative to the use of electrolysis alone. It is clear that even a few percentage points in efficiency offers huge savings in energy.

III. DISCUSSION OF THE PHYSICALLY LIMITING FACTORS IN HYBRID CYCLES

Chapter III deals with the physical limitations of hybrid cycles proposed for the production of hydrogen from water. While Chapter II presented the thermodynamic considerations relevant to hybrid cycles, this chapter deals with the limitations of material availability, compatibility of the thermal and electrolytic process steps, and the elementary processes within each step.

This chapter also contains a summary of the hybrid processes considered in this study. Included are the estimated process efficiencies, limits of operation, and comments of specific interest to particular hybrid schemes.

A. Availability of Chemical Intermediates

An estimation of the cost and availability of the chemical species used internally by a proposed hybrid cycle is required to eliminate from further consideration those cycles that involve scarce materials, and/or that show no economic promise. For example, it would be clearly unrealistic to propose the use of gold, platinum, or silver in such a process.

The residence time of a given chemical intermediate in a cycle is necessary to estimate the projected inventory of that intermediate. Assuming a current density of 250 mA/cm^2 for a flat plate copper anode, the rate of oxidative growth will be approximately 0.10 cm/hour. If the design of the electrolysis cell calls for an oxide thickness of 0.10 cm., and the thermal portion of the hybrid cycle is fast, the

residence time for the chemical intermediate will be about 1 hour.

Since most of the proposed hybrid cycles involve one mole of reactant per mole of hydrogen produced, the total inventory of a chemical intermediate can be estimated by projecting the future annual production of hydrogen. Studies at Battelle⁹¹ forecast the U.S. energy consumption in the year 2000 as 175×10^{15} kJ BTU/year. In order for hydrogen to be considered a major contributor to the nation's power grid, at least 20% of energy consumption should be from the use of hydrogen as an energy carrier. Using these assumptions and projections, the inventory of a chemical intermediate proposed for use in a large-scale hybrid process is approximately 1.0×10^8 lb-mole.

To avoid a possible excessive capital investment in a proposed hybrid process, it is necessary to choose only those chemical intermediates that are relatively inexpensive and abundant. An arbitrary limit for material cost in a process is set at \$1000./lb-mole, corresponding to an initial capital outlay of 100 billion dollars for 1.8×10^8 pounds/year of hydrogen production. Table 2 is a compilation of all elements with a present day market value of less than \$1000./lb-mole. Obviously, a hybrid cycle based on a less expensive metal like lead or copper is preferred over the use of a more expensive material like cadmium.

The availability of an element is also an important consideration, since it is undesirable to strip the world's reserve of a chemical for use in a hydrogen production process. Of course, the cost of a chemical species is insufficient to estimate its relative abundance.

Table 2. List of Elements Costing Less than \$1000.00/lb-mole.
Source: Dept. of Interior⁹²

Element	Cost \$/lb-mole	Element	Cost \$/lb-mole
N	0.28	Sr	216
S	0.224	I	254
C	0.24	Ba	286
Cl	2.10	Cd	336
Fe	1.68	Mo	480
P	3.10	Hg	710
Na	4.37	V	714
Al	6.48	W	828
Si	7.00	Bi	832
As	7.50		
Mg	9.23		
Br	12.0		
Zn	13.0		
Mn	18.2		
Pb	31.0		
Cu	33.0		
F	35.7		
Ti	57.0		
Cr	59.8		
Sb	69.0		
K	78.0		
Ca	80.0		
Ni	90.0		
V	137		
Co	144		
Sn	210		

Skinner⁹³ has shown that minerals tend to follow a bimodal distribution of availability and ease of production. Because of this bimodal distribution, a judgement of availability based only on the present price of a mineral is erroneous. Therefore, the measure of a particular element's desirability should also be judged on the basis of total world reserves (Table 3). Any element that requires over a few percent of total world reserves should be considered unsuitable for large-scale use in a hybrid process. The elements eliminated from Tables 2 and 3 on this basis are uranium, mercury, cadmium, bismuth, and tungsten. Boarderline cases are cobalt, arsenic, strontium, molybdenum, tin, and antimony.

A further consideration of material availability is whether the U.S. is capable of supplying the needed chemicals, or if the element must be imported from other countries. Table 4 is a list of all raw materials that presently require substantial importation. It is, of course, highly desirable to propose hybrid cycles that would retain a sense of a national "self reliance". The use of manganese, for example, would require a minimum initial payment to a foreign country of 1.8 billion dollars.

B. Environmental Compatibility

The strict limitations put on a hybrid process are that the only chemical feed is water, and that the only products are hydrogen and oxygen. Use of volatile chemical species in a cycle, such as iodine, chlorine, and fluorine, might pose a serious problem due to the difficulty of separation from the two product gases. In this regard,

Table 3. List of % Depletion of World Reserves for Elements Costing Less than \$1000.00/lb-mole. Data Sources: Dept of Interior⁹²

Element	% of World Reserve Used	Element	% of World Reserve Used
N	Small	Sr	3.6
S	4.5×10^{-3}	I	Small
C	5.4×10^{-5}	Ba	0.21
Cl	Small	Cd	140.4
Fe	3.6×10^{-3}	Mo	3.0
P	1.2×10^{-4}	Hg	187.2
Na	Small	U	58.2
Al	1.5×10^{-3}	W	25.0
Si	Small	Bi	2613
As	4.2		
Mg	Small		
Br	Small		
Zn	0.09		
Pb	0.3		
Cu	3.6×10^{-2}		
Mn	1.6×10^{-2}		
F	5.1×10^{-2}		
Ti	5.4×10^{-2}		
Sb	5.1		
K	6.0×10^{-3}		
Cr	0.72		
Ca	1.5×10^{-2}		
Ni	0.15		
V	0.90		
Co	3.9		
Sn	4.8		

Table 4. List of all elements that are predominantly produced in other countries and imported into the United States.

Source: U.S. News and World Report⁹⁴

Element	Percentage of Use Imported in 1975
Columbium	100%
Strontium	100%
Manganese	99%
Cobalt	98%
Chromium	91%
Aluminum (bauxite and metal)	85%
Platinum group metals	80%
Tin	75%
Mercury	73%
Nickel	71%
Zinc	64%
Tungsten	54%

most metals would probably present minimal problems. Mercury, with its high degree of volatility, is a notable exception.

Two other potentially serious problems are posed by feed-water requirements and thermal pollution. These problems can at least be partially alleviated by suitable selection of plant sites, and by maximizing the total thermodynamic work efficiency for the process.

C. Characteristics of the Proposed Metal Oxide Based Cycles

1. Thermal Portion of the Metal Oxide Cycles

Since all of the hybrid processes outlined in Table 5 involve the decomposition of oxidized solids, it is important to consider the feasibility of their transport through the cycle, filtration to remove the entrained electrolyte, and heat exchange between solid materials (Fig. 5). Due to the electrolysis step in the hybrid process, the form of the solids in the thermal phase of the process will be dictated predominantly by the physical nature of the anode. The anode can be shaped as a solid plate, or it can be in powder or granular form, in either a packed, slurry, or fluidized bed. The characteristics of these forms of electrodes are presented in a later section.

a. Transport of solids. It is obvious that the transport of divided solids offers advantages over the handling of solid plates. The conveyance of divided solids can be accomplished by a number of systems including pneumatic, vibrating, screw drive, and belt (Perry⁹⁵). The transport of solid plates is limited primarily to hangers or conveyer belts. The solid plates will tend to be fragile, and rough handling in bulk processing could break up the plates. The other

Table 5. Hybrid cycles involving the anodic oxidation of a metal or metal oxide with regeneration of the anode material in the thermal portion of the cycle (Fig. 5).

Prime (') designates the electrolysis reaction in the cycle

Double prime (") designates the thermal reaction in the cycle

Basis: one mole of hydrogen produced

Reaction	E° or ΔG° (298) (78,80)	Decomposition Temperature °K	ε _H	Comments
1. a'				Potentially favorable characteristics in electrochemical cell ⁹⁷
Mn ₂ O ₃ + H ₂ O →	1.014 v			
2MnO ₂ + H ₂			0.28	98% of Mn is imported into the U.S. draws doubts about this cycle.
1a''				
2MnO ₂ → Mn ₂ O ₃ + $\frac{1}{2}$ O ₂	10.2 kcal	750		
1. c'				Expense and Scarcity of Ag excludes this cycle from further consideration
2Ag + H ₂ O → Ag ₂ O + H ₂	~1.2	-	-	
1. c''				
Ag ₂ O → 2Ag + $\frac{1}{2}$ O ₂	-	460	-	
1. d'				Boarderline case for material availability
3CoO + H ₂ O →	1.0 v	-		
Co ₃ O ₄ + H ₂				High Solubility (see Table 7)
1. d''				
Co ₃ O ₄ → 3CoO + $\frac{1}{2}$ O ₂	6.9 kcal	1240	0.32	

Table 5. (Cont'd)

Reaction	E° or ΔG° (298) (78,80)	Decomposition Temperature °K	ε _H	Comments
1.f'				High solubility (see Table 7)
Hg + H ₂ O → HgO + H ₂	0.93 v			Scarcity of Hg excludes this cycle from
1.f''				further consideration; Potentially toxic
HgO → Hg + $\frac{1}{2}$ O ₂	13.9 kcal	700	0.29	effects
1.g'				Scarcity of Cd excludes this cycle from
Cd + H ₂ O → CdO + H ₂	0.02 v	1240	0.46	further consideration
1.g''				
CdO → Cd + $\frac{1}{2}$ O ₂	56.6 kcal	10 ⁻³ atm		
1.h'				
Cu ₂ O + H ₂ O → 2CuO + H ₂	0.67 v	-	0.38	High solubility (see Table 7)
1.h''				High decomposition temperature
2CuO → Cu ₂ O + $\frac{1}{2}$ O ₂	25.8 kcal	1370		
1.i'				
PbO + H ₂ O → PbO ₂ + H ₂	1.1 v			High solubility (see Table 7)
1.i''				
PbO ₂ → PbO + $\frac{1}{2}$ O ₂	6.0 kcal	820	0.28	

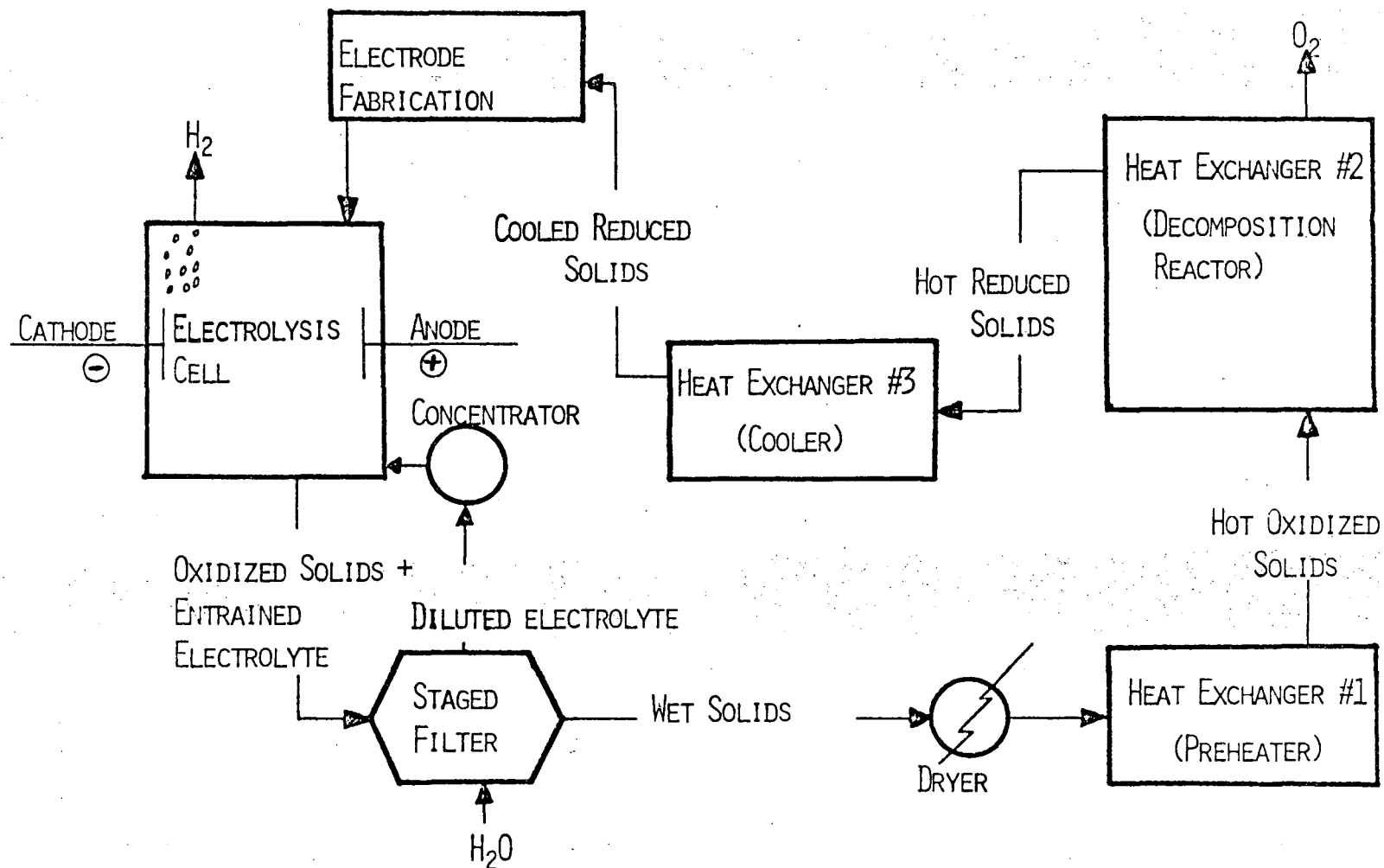


Fig. 5. Schematic for the Metal/Metal Oxide Hybrid Cycle Systems.

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choice is to grind the solid plates, run the resultant divided solids through the thermal phase of the cycle, and then refabricate the plate electrodes before returning them to the electrolysis cell. This method is a "last resort" alternative since it requires equipment that is both capital intensive and expensive to operate. For these reasons, the transport and use of solid plate electrodes will not be considered as a viable process option.

b. Filtration step to remove entrained electrolyte from the oxidized solids. Since there will be a continuous flow of anode material through the electrolysis cell, the electrolyte that is entrained must be separated from the oxidized solid product and recycled back through the electrolysis cell. If the electrolyte is allowed to complete the thermal portion of the cycle as an entrained substance, the performance of the hybrid cycle will be decreased. This is due to the increased loading of the heat exchangers, corrosive action of the electrolyte, and possible loss of expensive and environmentally harmful chemicals.

Filtration, with subsequent washings, of the solids appears to be the simplest approach to avoid the entrainment problem. The industrial production of phosphoric acid (wet process), for example, contains a large-scale filtration step. In this case the product phosphoric acid is separated from the by-product gypsum crystals using continuous vacuum filters. The Bird-Prayon tilting pan filter (Bird Machine Company) is described in Perry's⁹⁶ as having the advantages of complete wash containment, good cake discharge, and feasibility of construction

in very large sizes. The disadvantages of the filters include high capital cost and mechanical complexity.

The inability to produce a consistent gypsum crystal of the correct shape in phosphoric acid manufacture, is the cause of many problems in filtration. Specifically, if the crystal is too small, it will either pass through the filter cloth, or it will clog the pores of the filter cloth and reduce the speed and efficiency of filtration. This problem is also very likely to occur in a hybrid cycle filtration step. As a result of the high degree of agitation, and the repeated cycling of the solids in both the thermal and electrolysis portions of the hybrid cycles, a degradation of the solid material is foreseen. This degradation will lead to a wide distribution of solid particles ranging in sizes from relatively large to very small. Due to this phenomenon, degradation will lead to intolerable difficulties with the filtration step in the hybrid processes.

The reconcentration of the diluted electrolyte is another problem that must be dealt with in the filtration step of the hybrid process. The wash water will contain a diluted amount of electrolyte that, in turn, must be returned into the electrolysis cell in a concentration of sufficient magnitude to prevent high ohmic losses due to poor ionic conduction through the cell. The energy required for the reconcentration will be, of course, a serious source of energy inefficiency in the cycle.

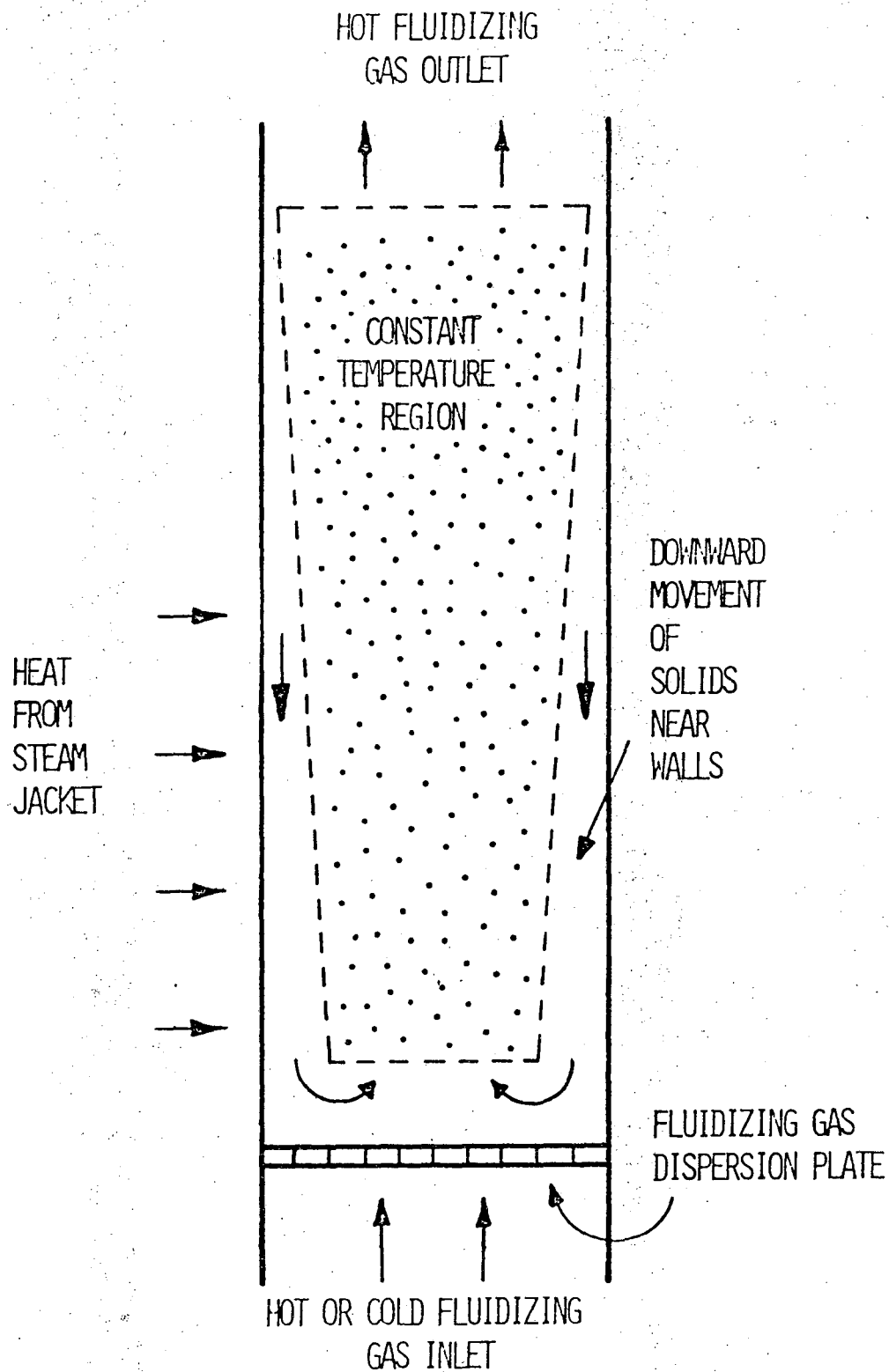
c. Heat transfer to divided solids. Practical continuous heat exchange to and from high tonnage rates of solid material poses a

formidable engineering problem. Again, only powder or granular solids will be considered because the solid plates will have high carry-over of unreacted electrode, material difficulties in conveyance, and slow rates of heat transfer due to the low thermal conductivity of most metal oxides, small surface area of the plate, and thickness of the plates.

The options for continuous heat exchange to powders or granules are limited. Basically, the two general types of heat exchangers available are the fluidized bed (either indirect or direct heating) or the agitated pan.

The use of the fluidized bed provides for the largest heat transfer coefficient for the indirect method of heat transfer. Figure 6 is a representation of the indirectly-heated, fluidized-bed heat exchanger. Typical heat transfer coefficients in this apparatus are from 100-150 BTU/(hr)(ft²)(°F) according to Holt.⁹⁸ The ft² term is the area of the inside exchanger jacket walls. Holt indicates that the downward movement of the solids near the walls can be likened to the falling film technique for fluids. Petrie, et al.⁹⁹ describes the addition of finned tubes to increase the effective area of the exchanger in calcining applications.

For most industrial applications, the indirectly-heated fluidized-bed is intended as a batch process because it provides a low rate of circulation of the solids within the exchanger. In continuous operation the indirect method has major difficulties in the areas of short circuiting and heat recovery from the exiting fluidizing gas.



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Fig. 6. Fluidized-Bed Heat Exchanger (Indirectly and/or Directly Heated).

The directly-heated, fluidized-bed heat exchanger is presented in Perry's (100) as having a vertical thermal conductivity of 20,000 - 30,000 BTU/(hr)(ft²)(°F)(ft). This process could be well suited for the drying step in Fig. 5. The direct contact of the heated fluidizing gas with the wet solids would facilitate relatively rapid dehydration. There will be little problem with short circuiting since the temperature of the fluidizing gas and the solids become very close only a few inches above the gas distributing plate.

Additional uses for the directly-heated, fluidized-bed heat exchanger could be during the heating of the solids in exchanger #1 and the reactor #2. As with the indirectly-heated, fluidized-bed heat exchanger, the utilization of this type of exchanger will present problems with heat reclamation of the fluidizing gas. The major disadvantage of using the directly-heated method is that the heat-exchange loop required to heat the fluidizing gas is capital intensive, and it represents an additional source of irreversibilities in the process.

The choice of air as the fluidizing medium is preferred since an inert gas would, in any case, become contaminated by water vapor and oxygen from the decomposition process. However, the use of air as the fluidizing medium would be practical only in the exchangers #1 and #2 in Fig. 5, due to the danger of recombination of oxygen with the reduced solids in exchanger #4.

The requirement of the exclusion of air in exchanger #3 as the fluidizing gas suggests the use of a heated-pan heat exchanger with mechanical agitation to facilitate heat transfer. Uhl and Root¹⁰¹ describe the continuous operation characteristics of a steam jacketed, rotary-spiral heat exchanger (Fig. 7). They report overall heat-transfer coefficients for varying conditions ranging from 10 to 50 BTU/(hr)(ft²)(°F) with an average temperature gradient of 100°F. If the operation of the proposed hybrid cycle equipment were to involve such a large temperature gradient at a low temperature (near ambient for exchanger #3), the contribution of irreversible entropy production (Eq. 17) by this process step would be quite serious.

The initial capital investment for both the fluidized-bed and pan type heat exchangers can prove to be of significant consequence. Figure 8 is a representation of the heat exchanger area required for the projected hourly production of hydrogen in the year 2000. Both exchanger types will require very large surface areas because of the low heat flux involved. Intuitively, the cost of the fluidized-bed heat exchangers is expected to be lower because of simpler construction and better heat-transfer characteristics.

The wearing out of equipment by the abrasive action of the solid material is also an important consideration. The problem with abrasion is probably less troublesome with the hybrid schemes than the analogous corrosion problems experienced by the thermochemical cycles that involve high-temperature reactions containing chlorine, fluorine, etc. However, the transport and heat exchange of intercycle material is

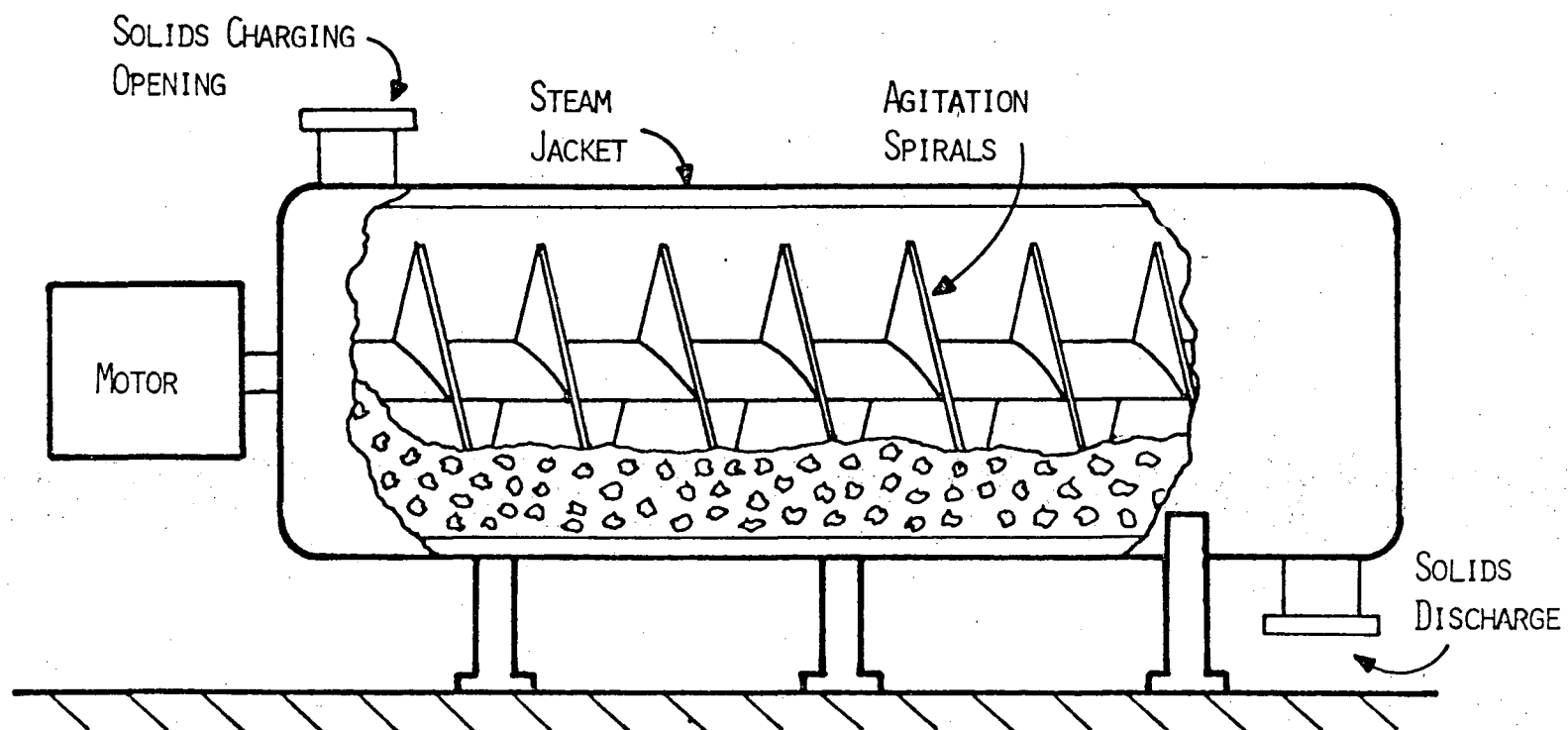
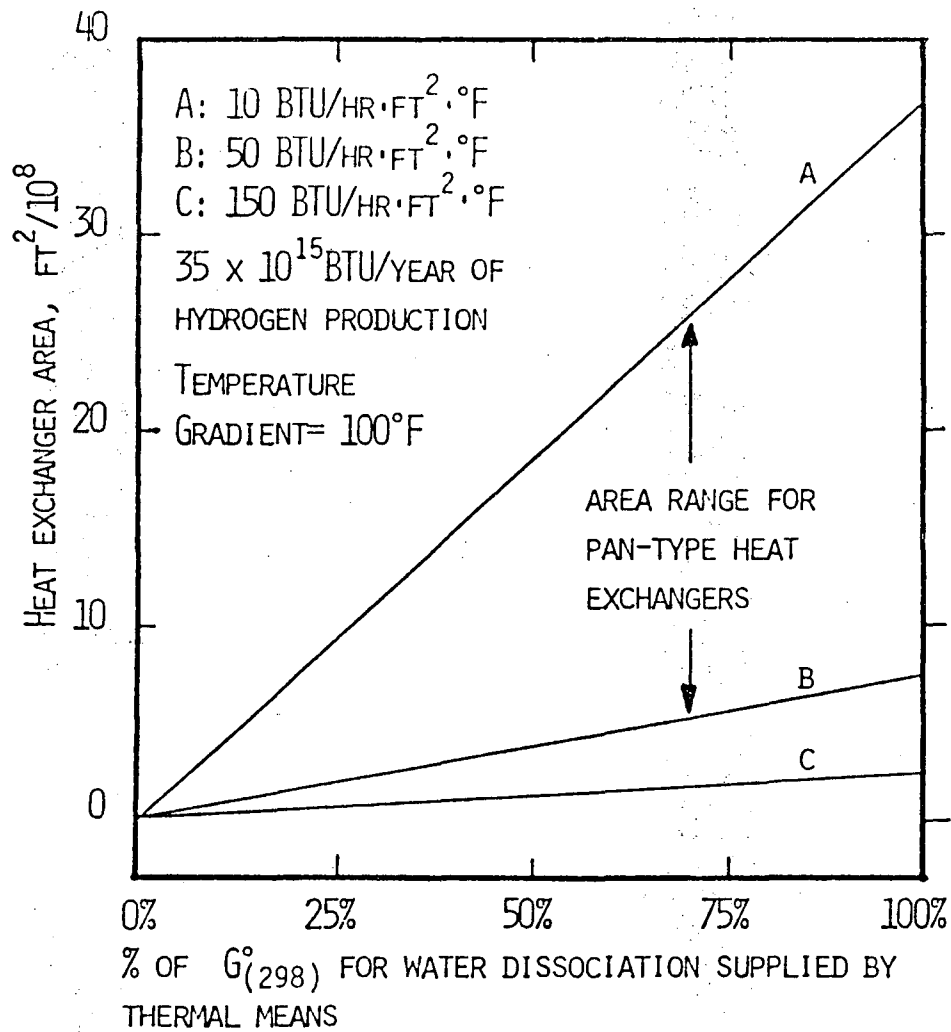


Fig. 7. Rotary-Spiral Heat Exchanger for Solids.

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Fig. 8. Estimated heat exchanger area required in hybrid cycles for the projected production of hydrogen in the year 2000.

superior in the thermochemical cycles that involve only liquids and gases.

Barring future technological developments in the area of handling and heat exchanging to solid materials, it is quite possible that the capital cost, operating expense, and inefficiencies associated with the systems involving solids processing will be the primary reasons for the elimination of the hybrid cycles from further consideration as a feasible option for large scale hydrogen production. It is noted that a majority of the proposed thermochemical cycles contain process steps that involve the handling and heat-exchange of solids. In this respect, the hybrid cycles and the thermochemical cycles seem to be equally questionable as alternatives to electrolysis.

2. Electrolysis Portion of the Metal Oxide Cycles

The oxidized product from the electrolysis cell must be in a compatible physical state of aggregation for successful integration with the thermal portion of the hybrid cycle. As shown in the previous section, the only practical form for the oxidized solids is a powder or fine granules. The proposed options to meet this requirement are to oxidize a powder or granular form of anodic reactant in the electrolysis cell, or to oxidize a solid plate anode, remove from the cell, and grind into a powder. Refabrication of the reduced powder is then necessary to reintroduce the plate into the electrolysis cell.

A third option would involve a scraping mechanism which would continuously separate oxide particles, as they are formed, from the surface of a solid plate electrode. As a solution to passivation problems, the scraping mechanism offers advantages, but feasibility on a large scale appears doubtful.

a. Yield of the anodic reaction. It is evident that the electrolysis product should contain as little unreacted or inert product as possible. The reason is twofold. First, the unreacted and inert material will cause an additional heat load on heat exchangers #1 and #3 in Fig. 5. Second, if a fluidized bed is used for exchanger #1, the combination of oxygen with the unreacted material will cause an increased heat load in reactor #2. Likewise, it is important that all of the material introduced into reactor #2 should be completely reduced there to avoid loading elsewhere in the cycle.

b. Protection of the anode surface. Since many of the proposed hybrid cycles involve the anodic oxidation of a metal or metal oxide, it is essential to determine the characteristics of the reactions taking place at the anode. Hopefully, in all of these cases there will be a formation of an oxide layer on the electrode substrate. However, this oxide layer will tend to alter the course of the reaction in most instances. The effect of this alteration is exemplified by the following cases.

Many metals will tend to form protective oxide layers that, when thick enough, will prevent the reaction from proceeding further. Aluminum, for example, forms hard and continuous oxide layers that have little pore structure, and after sufficient reaction the aluminum substrate will be protected from additional oxidation. This particular process is the basis for an important industrial method for forming protective oxide layers on aluminum.⁴³

Anodic oxidation of copper is another example of the formation of protective oxide layers on metal electrodes. Shoesmith, et al.,¹⁰² in their paper dealing with the anodic oxidation of copper in alkaline electrolytes, presented data pertaining to the thickness at which the oxide layer on the copper anode began to effectively decrease the rate of the preferred reaction. The results show a copper oxide layer thickness ranging from 0.1 to 1.0 microns. This would mean that in order to minimize the heat load in the heat exchangers, the original anode material would have to be not much thicker than 1.0 micron.

Since the electrode thickness cannot be thicker than 1.0 micron, the copper electrode system is considered as unfeasible. The pre-dominant reason is that the structural strength of even a 10 - 100 micron thick electrode is totally inadequate. Therefore, the copper system, and other systems of similar behavior, would require a slurry or fluidized bed electrode that would allow a more complete oxidation of the metal substrate.

Unlike the copper oxidation process, there are metal anodes which will not form continuous layers of pore-free oxide. For instance, the cadmium electrode will tend to form islands of cadmium oxide that will not effectively block the passage of ions to and from the electrode surface. This phenomenon is the basis of the nickel-cadmium battery in which the cadmium is oxidized to $\text{Cd}(\text{OH})_2$ at very high current densities while still retaining a large degree of reversibility.⁸³

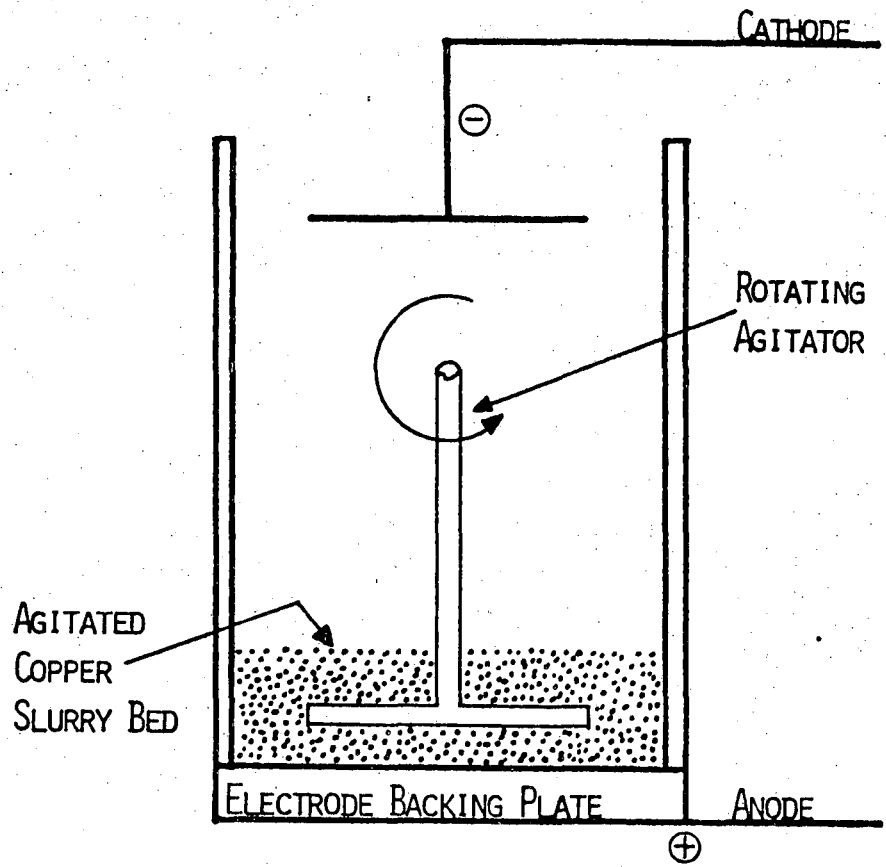
A third case to consider is an oxide layer which is relatively pore-free but electronically conducting. Platinum, for example, forms

an oxide layer that is highly conductive. When an anodic current is applied the platinum will not passivate further, but another reaction will take place, in this case most likely oxygen evolution will result from water oxidation.

The ideal situation for the anodic oxidation process in a proposed hybrid cycle is that the oxide which is formed should have many large pores. This would allow access of the ions in solution to the bare metal surface. If relatively free access is not allowed, the irreversibility of the anodic process (caused by high overpotential of dissolution) renders the entire hybrid process scheme uninteresting, since the very reason for the proposition of this alternative is to replace the oxygen electrode with a more reversible oxidation reaction.

c. Fluidized bed and slurry electrodes. Due to the need to employ powder or granular electrode systems, the feasibilities of these systems must be projected. In a slurry-bed electrode of copper powder (Fig. 9), for example, it is doubtful whether an effective reaction can be maintained to convert the copper completely to cupric oxide. The basis of this observation is that most likely the cell design will provide insufficient intimate contact between the powder particles and the backing plate, and that the high contact resistance between the particles, when there is intimate contact, will prove to be seriously detrimental for efficient cell operation.

The lack of contact between the powder particles is a result of the agitation of the electrode. This agitation tends to establish thin layers of electrolyte around each copper particle, thus requiring



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Fig. 9. Slurry Electrode for Copper Oxidation.

that ionic transport, instead of electrical conduction, be the pathway for the passage of current between the anode backing plate and the reaction site on the copper powder particle.

In order for the passage of current through the copper solids to occur, it is necessary that the reactions associated with the charge transfer on each side of the particles be completely reversible. But, after an initial period of cell operation, the particles will tend to form thin layers of surrounding oxide which will protect the copper from further oxidation at reversible potentials. Since further oxidation would require large potentials in excess of the reversible value, the current will simply pass through the electrolyte interstices between the copper particles. After this happens, all the reaction will occur on the solid electrode backing plate (this reaction will most likely be oxygen evolution or anodic deposition of a soluble metal oxide due to supersaturation at the backing plate surface).

When there is intimate contact between the particles and the backing plate electrode, the passage of current will be via electronic conduction. However, the high degree of contact resistance between the solids and the plate will limit the efficiency of the electrolysis, since an increase in cell potential is necessary to offset the increased ohmic resistance.

Table 6 is a list of the resistances of several of the oxides proposed for use in the hybrid cycles. Most of the oxides are very poor electronic conductors. The voltage drop experienced by the copper system, for example, with a current density of 250 mA/cm^2 and a $100 \text{ \AA}$

Table 6. List of the electrical resistance of several metal oxides at room temperature.

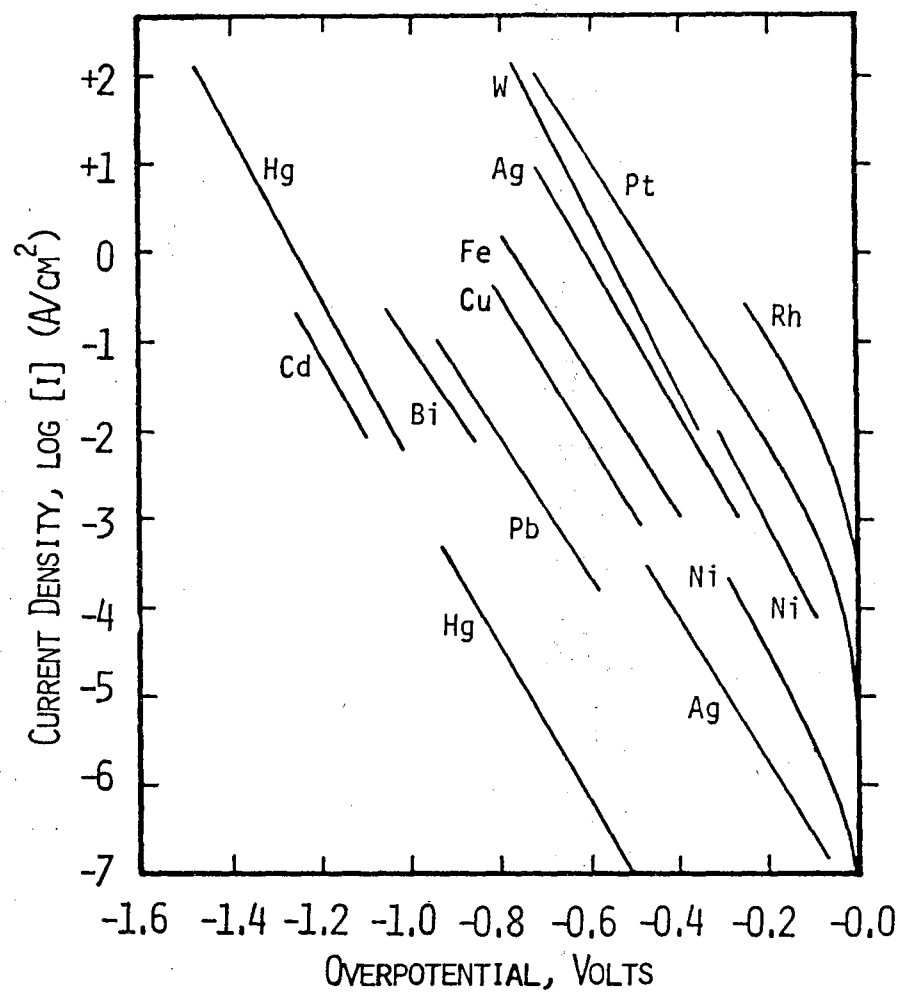
metal oxide	Resistance Ω -cm	Reference
Cu_2O	$\sim 10^{12}$	104
	4×10^7	105
CuO	$\sim 10^7$	106
MnO_2	85	107
Mn_2O_3	3.6×10^5	108
Mn_3O_4	$\sim 10^7$	109
CdO	4.7×10^{-3}	110
PbO_2	2×10^{-4}	111
PbO	$\sim 10^{10}$	112
CoO	7.4×10^5	106
ZnO	5.5×10^6	113
Zn(OH)_2	2.8×10^4	114
Ag_2O	10^8	115
AgO	1.2×10^{-2}	116

oxide thickness on each copper particle will be about 2.5 V.

Another source of inefficiency in a powder electrode scheme is due to the complexity of the mechanism for the oxidation reaction. If the additional irreversibilities contributed by each mechanism step are of sufficient magnitude, the process would be rendered uninteresting. For instance, Upada, et al.¹⁰³ attempted to produce a lead dioxide powder by anodically oxidizing lead oxide in a stirred slurry powder bed. They succeeded in producing the lead dioxide but only at the expense of much inefficiency in the electrolysis cell. Their results show that the electrical efficiency ranged below the 50% figure and the yields were also very poor. They attributed the reaction to a complicated dissolution and anodic deposition mechanism. The inefficiency of the cell was attributed to the irreversibilities associated with each of these steps.

The practical use of a fluidized bed or slurry electrode is seriously threatened by the foregoing considerations.

d. Solubility of anode material. The solubility of the metal anode reactant or the oxidized product, in the electrolyte is an important consideration. The consequence of a finite solubility is that the metal cation will tend to migrate and diffuse towards the cathode and plating of the metal will occur. Since the catalytic nature of the cathode is dependent upon the metals present on the surface of the cathode, it is critical that the activation overpotential not be raised by the poisoning of the cathode. Figure 10 is a graph of the hydrogen overvoltage on different materials. For example, if lead were to plate out on a platinum cathode during



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Fig. 10. Hydrogen overvoltage on Various Metals
(from Vetter 46).

electrolysis at a current density of 0.1 A/cm^2 , the associated increase in the overpotential would be about 0.9 volts.

Many of the proposed hybrid cycle involve metals or metal oxides that display a substantial degree of solubility (Table 7). Therefore, an anionic permeable membrane would have to be used in the electrolysis cell to eliminate the problem of poisoning the cathode surface. The effect of the membrane is to block the migration of all cations toward the cathode, and to allow only the anions to pass through to the anode.

However, the use of a semipermeable membrane in the electrolysis cell has several serious drawbacks. First, there is an increase in the ohmic potential drop across the electrolysis cell caused by the increased resistance to the passage of current. Du Pont's Nafion membrane,¹²³ a contemporary perfluorosulfonic acid, cationic-permeable membrane with an equivalent weight of 1200, exhibits a resistance of $2\Omega\text{-cm}^2$. If a cell were to operate at a current density of 0.25 A/cm^2 , the ohmic voltage loss due to the presence of the membrane would be 0.5 volts. This voltage drop, when added to the other losses in an electrolysis cell, would prove to be prohibitive for economical operation.

The second problem inherent to a semipermeable membrane is that the membrane is not 100% impermeable to the passage of the unwanted metal ions. The consequence is that gradually the metal ions will still pass through the membrane and poison the catalytic surface of the hydrogen evolving cathode.

Table 7. Solubility of candidate metals and metal oxides in water.

Metal/metal oxide	Species in Solution	mole/litre Solubility	Reference
CuO, Cu(OH) ₂	Cu ⁺⁺ , HCuO ₂ ⁼ , CuO ₂ ⁼	2.9 10 ⁻⁵	117
Cu ₂ O	"	2.5 10 ⁻³	118
Ag ₂ O	Ag ⁺ , AgO ⁻	6.7 10 ⁻³	118
CdO	Cd ⁺⁺ , HCdO ₂ ⁻	3.9 10 ⁻⁵	114
HgO, Hg	Hg ⁺⁺ , HHgO ₂ ⁻	3.5 10 ⁻⁴	119,120
PbO ₂	Pb ⁺⁺ , HPbO ₂ ⁻		118
PbO	"	5.0 10 ⁻²	121
ZnO	Zn ⁺⁺ , HZnO ₂ ⁻ , ZnO ₂ ⁼	3.8 10 ⁻²	122
CoO	Co ⁺⁺ , HCoO ₂ ⁻	2.0 10 ⁻⁴	118

The third problem with the use of a membrane is the high cost. Du Pont estimates the price of Nafion to be \$20/ft² with high production volume.

If a hybrid process is proposed which demands the use of a semi-permeable membrane, the likelihood that such a process would actually prove viable is dependent upon the development of an anion permeable membrane that is substantially less resistive, 100% impermeable to metal cations, and less expensive. To date, there are no such membranes available.

3. Cycles Based on Metal Redox Reactions

The cuprous/cupric metal redox cycle (Fig. 11) is considered because the electrolysis step can be performed without some of the limitations characteristic of the previous schemes (Table 5). The use of a dimensionally stable porous electrode¹²⁴⁻¹²⁶ offers high surface area and low maintenance problems due to the absence of complicated mechanisms.

The major stumbling blocks of the redox cycles appear in the thermal phase of the hybrid cycle. Figure 11 is a schematic of the cuprous/cupric redox process.

The evaporation and separation step in Fig. 12 is expected to be very inefficient. In this step, water is evaporated from the oxidized electrolyte solution to produce a crystalline cupric chloride product. For an 8 molar solution of CuCl₂, the energy input into the evaporator must be at least 2 times the energy required to decompose water. It is essential that a major portion of this energy input be recovered

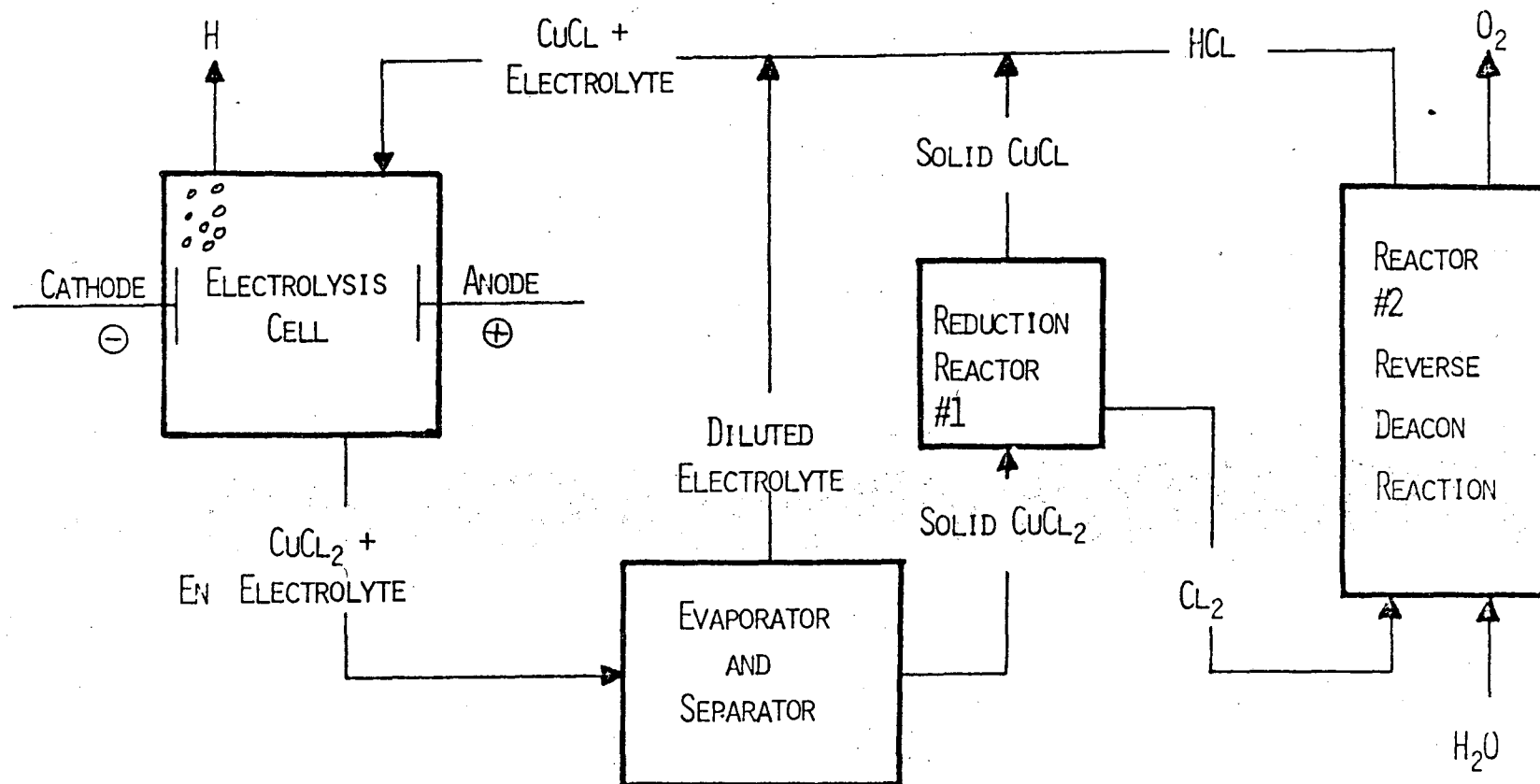


Fig. 11. Schematic for the Cuprous/Cupric Redox Hybrid Cycle.

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elsewhere in the hybrid cycle.

Historically, however, evaporative processes have suffered extremely low efficiencies. Desalination of water,⁸⁷⁻⁸⁹ for instance, is accomplished only at efficiencies much less than 10%. It is recognized, of course, that the desalination process serves only to concentrate the salt and not to crystallize the NaCl. Thus it is assumed that the crystallization of cupric chloride could only be accomplished at comparable efficiencies to the desalination process despite the differing operating conditions. If the process is indeed as inefficient as typical desalination processes, the redox cycles should not deserve further consideration.

A second problem with the redox cycles is that the solids will require heat exchange to facilitate the reduction reaction in reactor #1. The heat transfer process is subject to all of the limitations presented earlier in this chapter. An additional problem is the corrosiveness of the chlorine product.

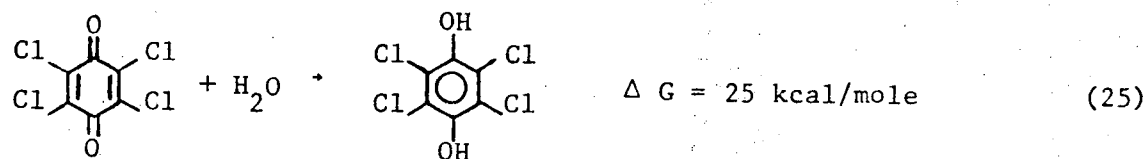
A third area of troubles can be recognized if one considers that redox cycles involve the reverse Deacon reaction. The negative characteristics of the reverse Deacon reaction have been discussed by several authors.^{69,72,127} The general conclusion is that the reaction will proceed, but the irreversibilities, high capital costs, and corrosion problems will prove to be too serious for practical application.

On the basis of these considerations, redox hybrid cycles are not considered promising for the large scale generation of hydrogen from water.

4. Organic Redox Cycles

The high reversibility of the quinone/hydroquinone couple¹²⁸⁻¹³⁰ forms the basis for the consideration of organic redox systems for hybrid cycles. Sandstedt, et al.¹³¹ have demonstrated the reversible characteristics of the chloranil electrode (an insoluble derivative of quinone, Table 8) in 2 molar sulphuric acid electrolyte. They reported a reaction that was carried out at a current density of 120 mA/cm² with an overpotential of < 100 mV. The use of an electrode with this degree of reversibility could prove to be very attractive.

Unfortunately, little is known about the thermal regeneration step (Fig. 12) to reduce the oxidized chloranil. There is no indication in the literature that the reaction:



will actually occur.

However, there is experimental evidence that the reverse of reaction 25 is the preferred reaction. Sandstede et al., demonstrated that the reduced forms of duroquinone and chloranil (Table 8) can be used as oxygen absorbers. The large, positive Gibbs free energy change¹³⁰ of reaction 25 seems to indicate that the reaction may not occur below a temperature level at which further decomposition of the quinones is possible.

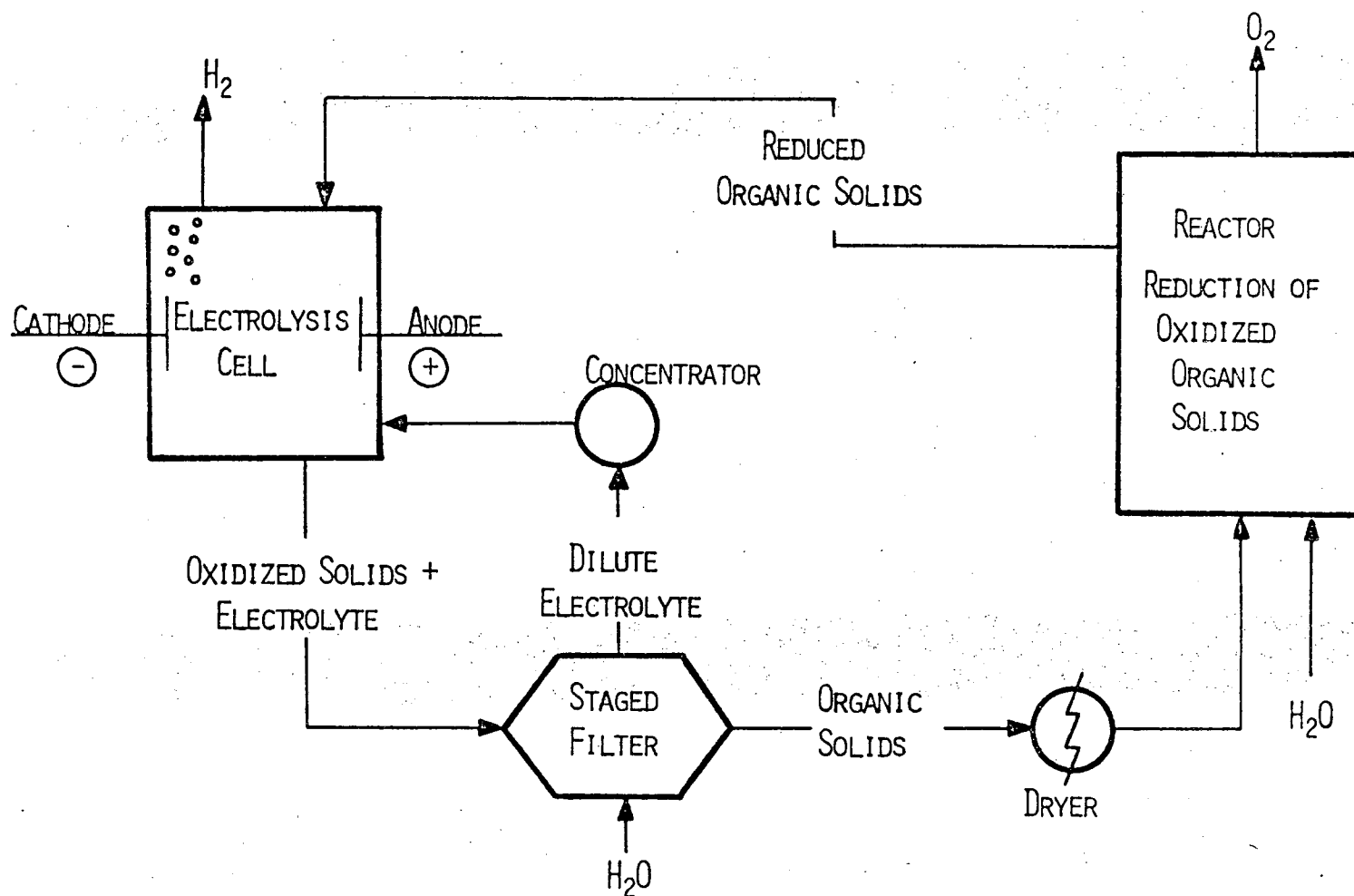
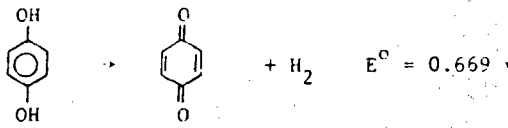
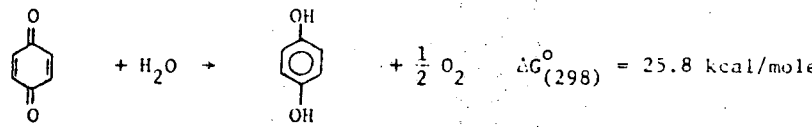
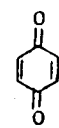
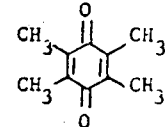
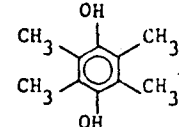
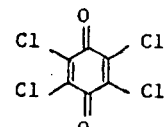
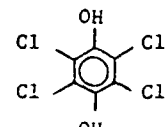
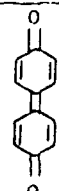
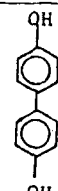


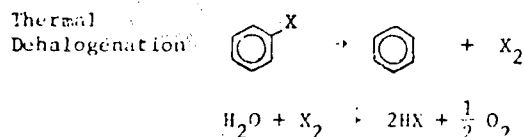
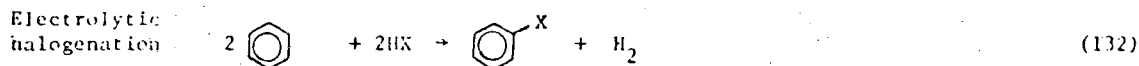
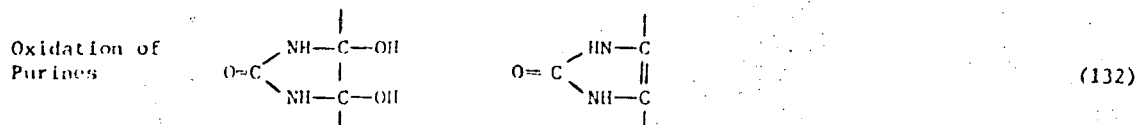
Fig. 12. Schematic of the Organic Redox Hybrid Cycles.

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Table 8. List of organic redox couples that are the basis of the organic hybrid cycles (Fig. 13)
All organic cycles follow the general scheme:

Electrochemical Reaction:				
	hydroquinone Quinone			
Thermochemical Reaction:				
Name	Oxidized Form	Reduced Form	E° and $\Delta G^{\circ}_{(298)}$	Comments
Quinone			0.699 v 25.8 kcal	High solubility (131)
Duroquinone			0.43 v 34.6 kcal	Low solubility (131)
Chloranil			0.664 v 25.8 kcal	Low solubility (131)
Diphenylquinone			0.95 v 12.9 kcal/mole	

The following organic system do not involve the Quinones.



Listed in Table 8 are the basic redox couples involved in the hybrid cycles employing derivatives of the quinones as well as cycles which involve other organic structures. Since little is known about the electrochemical and thermochemical behavior of these organic systems, it would appear that further investigation into their characteristics is necessary before their potential usefulness in hybrid schemes can be evaluated.

IV. CONCLUSIONS

The realization of a hydrogen economy is dependent upon the development of a feasible process for large-scale production of hydrogen from water. Conventional water electrolysis and thermochemical water decomposition cycles are the two most discussed methods for achieving this end. This study deals with a merger of the two processes into a hybrid electrochemical-thermochemical cycle that exhibits the positive characteristics of both the electrolysis and thermochemical cycles.

Theoretically, a hybrid cycle would be capable of bypassing many of the problems that plague conventional water electrolysis processes. First, the electrical energy requirements could be reduced by proposing electrolysis reactions that have lower reversible cell potentials than that for conventional water electrolysis. Second, the sources of irreversibilities in the electrolysis cell could be eliminated or reduced in magnitude.

The two most serious sources of inefficiencies in a water electrolysis cell are the irreversibility of the oxygen electrode, and the voltage loss due to the ohmic drop across the electrolysis cell. The hybrid processes are proposed to alleviate these problems by replacing the oxygen electrode with a more reversible oxide electrode, one which allows oxidation to occur without gas evolution. The ohmic voltage loss could be correspondingly reduced by design improvements made possible by the replacement electrode. These improvements include the elimination of the gas-separation diaphragm, closer electrode spacing, and fewer nonconducting gas bubbles.

Hybrid cycles can also, in principle, offer improvements over the use of the thermochemical water decomposition cycles. The most obvious advantage of a hybrid cycle would be that reactions that could not ordinarily be accomplished by thermal means could be driven electrochemically. The use of two distinct phases in the thermochemical reactor of the hybrid scheme would allow for much simpler separations than most thermochemical water decomposition cycles. Also, the corrosion problem common to many thermochemical cycles would be reduced since the hybrid cycles do not involve extremely reactive intermediates.

The thermodynamic work efficiencies for the proposed hybrid cycles are estimated as being substantially higher than the efficiency of conventional water electrolysis. The hybrid schemes exhibit comparable efficiencies to the proposed thermochemical cycles found in the literature.

On the basis of these conclusions, the hybrid cycle would appear to be an attractive alternative to electrolysis or to thermochemical cycles for the production of hydrogen from water.

However, if one considers the limitations placed on the hybrid processes by physical and economic criteria, the hybrid cycles of the type described in this study do not seem to offer worthwhile alternatives for large-scale production of hydrogen from water.

Some of the major problems characteristic of the electrolysis portion of the hybrid process include high solubility of the anode reaction material, thin layers of oxide that prevent high degrees of conversion, and difficulties in transferring the reactants into and out of the electrolysis cell.

Problems associated with the thermal phase of the hybrid cycles include solids material handling, poor heat exchange between solids streams, and difficult filtration due to degradation of the particular solids.

The foregoing preliminary evaluation pertains to a special set of hybrid cycles conceived in this laboratory. The negative conclusions regarding their technological feasibility and their economic promise should not be interpreted to be valid for all possible hybrid cycles. The various thermochemical cycles proposed so far each have their own particular combination of inefficiencies and uncertainties, and there seems to be no obvious basis for regarding the latter as being of higher promise than the hybrid cycles.

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