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TITLE: THERMOCHEMICAL PRODUCTION OF HYDROGEN FROM WATER, A CRITICAL REVIEW

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THERMOCHEMICAL PRODUCTION OF HYDROGEN FROM WATER, A CRITICAL REVIEW

EXECUTIVE SUMMARY

This report has assessed the current status of thermochemical hydrogen technology as regards process chemistry, preliminary chemical engineering design and techno-economics for a number of cycles undergoing active research and development efforts throughout the world at this time.

Three cycles are receiving the bulk of the total effort and most of the funding:

- In the USA, the cycles are:
  1. The Hybrid Sulfuric Acid cycle - Westinghouse.
  2. The Sulfuric Acid-Hydrogen Iodide cycle - General Atomic.
- In Europe:
  3. The Hybrid Sulfuric Acid-Hydrogen Bromide Cycle - Euratom (Mark 13).

All three cycles are at the stage where a laboratory scale continuous plant can be or is in operation. The only plant (100 liters of hydrogen per hour) in operation is one at Ispra, Italy on the Mark 13 cycle. Both Westinghouse and General Atomic have been funded and expect operation of their closed-circuit laboratory units by the end of 1978 or early 1979. These plants will develop data to assess:

- reference design conversions and concentrations,
- control problems for operating equipment,
- materials problems, especially corrosion in sulfuric acid service, and
- possible by-product formation and their elimination.

At the design level of these plants, no accurate evaluation of plant capital cost or overall thermal efficiency of the cycle is possible, however, data for the design of the next (larger) scale-up should be obtained that will aid in determining these quantities.

Two other cycles were noted:

4. The Hybrid Bismuth Sulfate cycle - Los Alamos Scientific Laboratory, and
5. The Magnesium-Iodine cycle - NCLI, Japan.

The LASL cycle, in principle, offers an improvement over the earlier-mentioned cycles in two areas. By avoiding the handling of sulfuric acid other than at reasonable temperature, pressure and concentration (5-50%), the corrosion and heat penalty problems are minimized; in addition, the electrochemical voltage for the hydrogen generation reaction may be lowered as a result of operating at low acid strengths. The Japanese cycle is included to illustrate efforts in other countries. Serious difficulties exist in this cycle as a result of low conversion, mutual solubility of intermediate compounds and large quantities of water that require evaporation.

Materials problems are endemic to all cycles. In most cases reference materials for the sulfuric acid vaporization stages and the sulfuric acid or sulfur trioxide decomposition vessels have not yet been defined. A prime difficulty is the need for the vessel walls to transmit heat to interior fluids as well as withstand their corrosive effects. Serious efforts must be undertaken in the materials area prior to demonstration of any of the sulfuric acid-based cycles on a pilot plant scale under realistic pressure (30 atm) and temperature conditions.

In the area of techno-economics, several studies have been done mainly under assumed conditions. The most studied cycle has been the hybrid sulfuric acid cycle (Westinghouse and Ispra Mark 11). Values of efficiency and cost were developed in early reports by Westinghouse on the basis of "overly optimistic" operating conditions. These gave efficiencies in the 50%+ range at costs for product hydrogen at around $\$5/10^6$ BTU. Since that time, Euratom (Ispra) and further Westinghouse studies have shown values in the 35 to 45% range for the efficiency, and costs from \$7 to $\$10/10^{16}$ BTU for the hydrogen produced.

Heat penalty analysis has been applied by Funk and Knoche to determine the irreversibilities in the different steps of a thermochemical cycle. These heat penalties can be directly related to the capital cost and the hydrogen production cost for a thermochemical cycle. The method has been applied with success to the hybrid sulfuric acid cycle (however, under assumed operating conditions) to obtain cost and efficiency similar to the latter ones quoted above. Part of the problem of using this method is the lack of reliable thermodynamic data. These are gradually being accumulated for key substances such as sulfuric acid, etc.

In the comparison of electrolysis of water with thermochemical cycles for producing hydrogen, exponents of both technologies have emerged.

Techno-economic assessments of these competing processes to produce hydrogen have been performed at both Euratom and at Westinghouse recently. These have shown small differences in efficiency and cost between thermochemical cycles and electrolysis. The values obtained are as follows:

Process	Efficiency (%)	Cost ($/$10^6$/BTU)
Thermochemical		
Ispra Mark 11	41.2	8.02
Ispra Mark 13	37.2	8.88
ouse HSA	47.0	7.30
Electrolysis		
(Ispr	32.7	8.54
Westinghouse	40.9	7.80

It appears reasonable to state that at this point in thermochemical cycle development, the differences shown above are not truly significant in view of the uncertainty in the estimation procedure. Both the thermochemical and the water electrolysis systems require further development to substantiate the assumptions used in flowsheet definition, performance capability, component design, and process economics. In view of this point, continued efforts in both technologies should be strongly supported by vigorous funding designed to obtain factual information to make a clear-cut case favoring either one or the other options for hydrogen production from water. This will probably take a 10 to 15 year developmental time period and, in view of the elasticity afforded by the price of synthetic hydrogen, it will allow adequate time to fully explore options before choosing a single thermochemical cycle or water electrolysis process for commercialization.

INTRODUCTION

Currently there is widespread interest in the development of a "hydrogen economy" as an eventual solution to many of the problems associated with the energy crisis. Hydrogen deserves serious consideration in ensuring a continuing gaseous fuel supply as it can be manufactured from a variety of thermal energy sources, and water - a relatively inexhaustible resource. Many studies have been published that discuss the advantages and disadvantages associated with the use of hydrogen as an energy carrier or "medium" for energy storage, energy transmission, and indeed for large-scale use as a non-polluting fuel. Technologies that produce hydrogen at high energy efficiencies are being developed and improved to provide a usable technology base for the future.

In addition to the potential for a "hydrogen economy", it is important to emphasize that hydrogen is a very valuable chemical commodity that is used in large volume for the production of ammonia, methanol, and in chemical processing. Requirements for these applications are increasing rapidly and it is clear that expanded production of hydrogen is necessary. It is equally clear that fossil fuel supplies are becoming inadequate to satisfy the demand for hydrogen, and that coal, a major fossil resource, not only is finite, but its use involves placing severe burdens on the environment such as the increasing level of carbon dioxide in the earth's atmosphere. Large-scale hydrogen production must, therefore, utilize "renewable" primary energy sources such as nuclear fission, fusion, and/or solar energy for the decomposition of water by thermochemical cycles, electrolysis, or perhaps, by hybrid combinations of these methods.

Hydrogen is attractive as an alternative fuel for several reasons, some of which are listed: (a) It provides a high energy density storable chemical form of energy; (b) It can be synthesized from "renewable" energy supplies and water; (c) On combustion, water is essentially the only product, thus completely compatible with the environment. After substitute natural gas (SNG), hydrogen has the best prospects for supplementing natural gas supplies (to 45 million US customers) without major changes to existing equipment for delivery and use of fuel gas.[1]

In regard to producing hydrogen by water-splitting, the potential higher efficiency and lower cost for thermochemical cycles, versus the overall electrolysis path (involving large losses due to mechanical irreversibilities in power generation) has been rather widely recognized. As a consequence, several laboratories throughout the world are conducting programs to develop thermochemical processes for water decomposition. A large number of thermochemical cycles have been conceived. Unfortunately, many of these have been published without experimental verification of the reactions in the cycle.

As a result of this, most evaluations and/or comparisons of thermochemical processes for process efficiency and cost have been on assumed data or on reaction conditions that have not been actually achieved. Nevertheless, several cycles have now been published where all of the reactions in the cycle have been proven experimentally. As a consequence, the development of methodology for the engineering and cost analysis for this new technology can now be based with some firmness on the actual chemistry involved in the demonstrated cycles.

There are three important and inter-related parameters which characterize a thermochemical hydrogen production process:

- Thermal efficiency,
- Capital cost, and
- Operating cost.

The meaning of capital cost and operating cost is clear, however, it is necessary to carefully identify all of the assumptions that enter into deriving these values. The thermal efficiency of a thermochemical cycle is defined as the ratio of the higher heating value of hydrogen (325 BTU/SCF, 12,100 kJ/m^3, 286 kJ/mol) to the thermal equivalent of the total energy entering the hydrogen production process.

Figure 1 illustrates an electrolysis process for hydrogen production and a thermochemical process. The efficiency of the conventional electrolysis process--from the primary energy source to hydrogen output--is approximately 28%. Increases in the efficiencies of the power generation step as well as in the electrolytic cell might increase the overall efficiency to about 40%. Indeed, a number of electrolyzer manufacturers are projecting efficiencies of the order of 90-100%. The single most attractive feature of the thermochemical process is that it offers the potential of a high thermal efficiency by elimination of the power generation step. There are thermodynamic restrictions and irreversibilities in the thermochemical process arising from incomplete reactions and separations that have to be overcome. These are somewhat more obscure and have not been formalized to nearly the same extent as those in power generation. While it is possible to derive theoretical efficiency limitations from thermodynamic constraints, the practicalities and the resulting cost of the product hydrogen can only be determined fron engineering design work. It is probable that such engineering assessment will reveal serious flaws in most cycles, but in many cases changes in process flow sheets will be possible that will minimize the flaws. It is anticipated that this process of iteration will not only yield improvements in existing cycles, but also lead to the development of criteria to guide the search for and evaluation of newer and possibly better (in terms of efficiency) thermochemical cycles.

THERMOCHEMICAL WATER DECOMPOSITION

In its most general sense, thermal water decomposition implies the splitting of water into its elements, hydrogen and oxygen, by the use of heat. Water (liquid state) has an extremely high enthalpy and free energy of formation (-286 and -237 kJ/mol) that decrease slowly as the temperature increases. For this reason, direct or one-step processes to decompose water are impractical. Temperatures in excess of 3000 K are required to obtain a reasonable yield of hydrogen and one is faced additionally with separating this hydrogen from oxygen and the unreacted water before the products recombine. The reaction is also favored by low pressure which is detrimental if the final product is hydrogen at pipeline pressure.[2]

To improve on direct water-splitting, researchers have tried methods that deompose water in a number of steps. These processes, by which water is decomposed by a set of chemical reactions at various temperatures with complete recycling of the intermediate reactants, are known as thermochemical cycles.

Thermochemical Efficiency

The definition of efficiency, η, adopted by the International Energy Agency,[3] is the ratio of the theoretical energy required, ΔH^o, (286 kJ) to the total heat input required, Q_T, for the decomposition process, based on one mol of water. Thus,

$$\eta = \frac{\Delta H^o}{Q_T} = \frac{286}{Q_T} \quad . \tag{1}$$

The efficiency is sometimes defined on the basis of the free energy of formation of liquid water rather than on the enthalpy:[4]

$$\eta' = \frac{\Delta G^o}{Q_T} = \frac{237}{Q_T} \quad . \tag{2}$$

This definition takes into account the pressures at which the gases are produced. Under standard conditions, the ratio of the two efficiencies is 1.2:

$$\eta/\eta' = \Delta H^o/\Delta G^o = 286/237 = 1.2 \ . \qquad (3)$$

The upper limit on thermochemical cycle thermal efficiency, η, was first defined by Funk and Reinstrom[5] as:

$$\eta = \frac{\Delta H^o}{\Delta G^o} \ \frac{T_h - T_c}{T_h} \ , \qquad (4)$$

where T_h and T_c represent the maximum and minimum temperatures in the cycle.

The cycle efficiency has an upper limit of 1.2 multiplied by the efficiency of a Carnot engine operating between the same temperatures in the cycle. For temperatures of 1000 K and 400 K, a 72% cycle efficiency is theoretically attainable.

The Step-Wise Decomposition of Water

The basic thermochemistry involved in the step-wise decomposition of water was published in 1966.[5] A large ΔS value is required so that the $T\Delta S$ term equals the ΔH term for the high temperature reaction of a two-step cycle. It was concluded that simple two-step cycles would not be feasible for the 1150 K maximum temperature available from a nuclear high-temperature reactor at that time. Recently, other workers have considered the thermochemistry of water decomposition cycles and essentially confirmed the conclusions of Funk and Reinstrom. Bowman[6] has repeated the analysis in order to point out that specific values for the sum of the ΔS^o and the ΔH^o terms are required for the endothermic reactions if maximum heat efficiencies are to be realized. These values depend on the maximum temperature at which heat is available and the ΔG_f^o of H_2O at the low temperature. Thus, for a general two-step decomposition cycle:

1. $R + AB \rightarrow RA + B$ at T_1,
2. $RA \rightarrow R + A$ at T_2.

The "ideal" ΔS^o and ΔH^o values are given by,

$$\text{ideal } \Delta S^o = \frac{-\Delta G^o(AB)}{(T_2 - T_1)} , \qquad (5)$$

$$\text{ideal } \Delta H^o = \Delta S^o \times T_2 . \qquad (6)$$

For decomposition of water with T_1 = 400 K and T_2 = 1100 K, i.e.,

3. $R + H_2O \rightarrow RO + H_2$ at 400 K,
4. $RO \rightarrow R + 1/2\ O_2$ at 1100 K.

For reaction 4, $\Delta S^o \sim 320$ J/K, and $\Delta H^o \sim 350$ kJ.

The striking feature of the above analysis is the large ΔS^o value required for the decomposition reactions. Typically, reactions such as 4 above exhibit ΔS^o changes of about 100 J/K. Thus, it is quite clear that simple two-step cycles for H_2O decomposition will not be found unless temperatures much higher than 1100 K are used.

Examination of the ideal ΔS^o values emphasizes the value of reactions with large entropy changes in water splitting cycles in order to minimize the number of reactions required. This, of course, suggests gaseous reactants and/or products to provide for large entropy change.

Practical considerations that have to be met before conceptual cycles become reality include the following criteria:

Process:
- Availability of accurate thermodynamic and equilibrium data
- Kinetic data
- Effect of losses of intermediate compounds
- Effect of competing reactions and side products

Engineering:
- Development of separation methods to allow for reactant recycle and product separation
- Minimization of heat exchange area

- Materials to withstand high temperature and hostile environments

These are the primary reasons why cycles have not yet been developed commercially although three 'laboratory-scale' models have been set up at this time. Mention has already been made of the large amount of scientific activity in this field; much of it is devoted to laboratory testing of the key reactions and to engineering evaluation of the cycles undergoing examination.

THERMOCHEMICAL CYCLES UNDER ACTIVE RESEARCH AND DEVELOPMENT

Research programs in the United States and abroad (Europe, Japan) have identified large numbers of prospective thermochemical cycles since the inception of this technology in 1972. These cycles have been screened through a series of laboratory and preliminary engineering/economic tests to determine their potential for further effort.

Support for cycle development has been granted by both government agencies (DOE, in particular) and by private industry. At present, cycles must show economic competitiveness with other cycles under development as well as with conventional and future electrolysis schemes in order to obtain funding. The economic analysis that ultimately determines product cost starts with a detailed engineering flow sheet based on (reliable) laboratory data. Workable separation schemes for process and product streams are required for product recycle and recovery. Kinetics and reaction yield obtained in the laboratory define the sizes and configuration of the needed chemical reactors as well as the amount of chemical inventory on hand. Heat exchange, an important factor in determining cycle efficiency, must be optimized both for heat recovery and minimization of heat exchange surface area. The cycle process efficiency is an important parameter that may be used, with due care, to monitor the effect of changes in process conditions and of other variables, such as alternate separation processes.

Three cycles, not necessarily the "best" ones, have survived the screening process and are presently being tested in continuous-circuit bench-scale units. Typically, these units are designed to produce hydrogen at a rate of 2 liters/min (4.25 SCF/hr) and use recycle chemicals. The basic purpose of the bench-scale tests is to demonstrate "operability" rather than to obtain serious information on cycle efficiency and cost.

The cycles are:

- o Hybrid sulfuric acid cycle - (Westinghouse/Euratom Mark 11)
- o Sulfuric acid - hydrogen iodide cycle - (General Atomic/Euratom Mark 16)
- o Hybrid sulfuric acid - hydrogen bromide cycle - (Euratom Mark 13)

The Hybrid Sulfuric-Acid (HSA) Cycle

Hybrid cycles are those in which some of the reactions are thermally driven and others are effected by electrolysis at a lower voltage than that employed in the electrolysis of water (1.6-2.0 V). This is one of the hybrid cycles studied at an early stage in the LASL Thermochemical Hydrogen Program.[7] The two step cycle is written as:

1. $SO_2(g) + 2H_2O(l) \xrightarrow{350\ K} H_2(g) + H_2SO_4(sol)$ elec.

2. $H_2SO_4(g) \xrightarrow{1100\ K} H_2O(g) + SO_2(g) + 1/2\ O_2(g)$.

In the United States, active development of this cycle has been pursued by the Westinghouse Electric Corporation.[8] The cycle has also received attention in Europe, primarily at the Euratom J.R.C. laboratory at Ispra, Italy. The latter have termed the HSA cycle - Mark 11. Fundamental work on the electrochemical step 5 above has recently been disclosed at the 2nd World Hydrogen Energy Conference by Appleby[9] and by Struck.[10] Due to the basic simplicity of the reaction sequence, this cycle has had detailed design studies done on it by Westinghouse,[7] Funk under contract to the Electric Power Research Institute,[8] and by Euratom.[9]

The cycle has many features which make it attractive for hydrogen production, including:

- o The cycle consists of only two chemical reactions,
- o The hydrogen is produced in a pure state, and

- All reactants and products are either in the liquid or in the gas phase.

A simplified flowsheet of the process is given in Fig. 2. The cycle can be divided into four major sections: the electrolyzer, the acid concentrator, the acid decomposer, and the separation system.

In the electrolyzer system, sulfur dioxide is mixed with makeup and recycle water. This solution is transferred to the anode side of the electrolyzer in which approximately 50% of the sulfur dioxide is oxidized to sulfuric acid, while hydrogen (99.9%) is evolved at the cathode. Sulfur will be produced at the cathode if sulfurous acid migrates from the anode to the cathode compartment. This will result in a loss of faradaic efficiency for hydrogen generation for the cell. To prevent migration of sulfurous acid, a membrane is placed between the two electrode compartments and a slight electrolyte overpressure is maintained in the cathode compartment. The membrane and overpressure cause an increase in the cell internal resistance and a net flow of slufuric acid from the cathode to the anode compartment. Subsequently, the sulfuric acid stream is purged of sulfur dioxide and sent to the acid concentrator.

In the earlier Westinghouse designs,[11] an acid concentrator section was not included as the electrolyzer effluent was at 75 or 80% acid (by weight). Serious doubts as to whether electrolysis can be performed at these high concentrations have been raised by both Appleby[9] and Struck.[10] In their opinion, 55% acid is the highest concentration practical in this application. In all likelihood, therefore, an acid concentrator section, possibly a multiple-effect evaporator, will be required to concentrate the acid from 55% to the 75-80% design basis or further to the 98% azeotrope.

The decomposition system consists of the equipment required to decompose the acid into sulfur trioxide and water, and thermally reduce the sulfur trioxide to sulfur dioxide and oxygen. The acid from the concentrator is preheated and further concentrated to greater than 98% (azeotropic composition) by contact with the hot effluent of the acid decomposer and vaporized in the acid vaporizer section. The gas mixture enters a convectively heated catalytic reactor where the decomposition products, water, undecomposed sulfur trioxide, sulfur dioxide and oxygen result. On removal of the undecomposed sulfur trioxide and part of the water, this gas mixture is sent to the sulfur dioxide-oxygen separation system.

Water and the remaining sulfur dioxide can be removed by several conventional separation schemes. Compression and cooling is the scheme adopted in the Westinghouse design. Ispra is testing a gas adsorption scheme using activated charcoal as the adsorbent species. The purified oxygen is vented to the atmosphere and sulfur dioxide is returned to the electrolyzer portion of the process.

A complete description of the Westinghouse design may be found in recent reports[8,36] with efficiency and economics. In their Case 3, utilizing a Very High Temperature Nuclear Reactor (VHTR) rated at 2790 MW(t) producing 380 x 10^6 SCFD of hydrogen, an efficiency of 54.1% overall was obtained. An earlier study, published as NASA CR-134976,[11] arrived at an efficiency of 45.2%. An EPRI report authored by Funk quotes an efficiency of 44% using the same design bases (compare to 45.2%).[12] The 44% efficiency was obtained by the Lummus Company. The Euratom Laboratory using a different design basis than Westinghouse, i.e., 100,000 m^3/hr of hydrogen (roughly 1/4 the Westinghouse size) arrived at an overall thermal efficiency of 41.4%. In this author's opinion, the design bases were somewhat "over-optimistic" as regards the performance of key plant facilities, especially the electrolyzer unit. In reality, with the use of actual laboratory data for design, the plant efficiency would be below 40%. The efficiency/cost values will be reviewed in a later section of this report.

Funding for the development of this cycle is being obtained from DOE primarily, DOE-Solar is supporting some work in the sulfur trioxide decomposition area. Corporate funding is also being applied to the laboratory-scale facility that will illustrate the "proof-of-concept" for this cycle.

Construction of a continuous closed-cycle bench-scale unit is ongoing with a scheduled start of operation by November 1978 at the Westinghouse Advanced Energy Systems Division's laboratory in Pittsburgh, Pennsylvania.

Key Problem Areas - Hybrid Sulfuric Acid Cycle

Electrolyzer - Operating voltage, current density and effluent acid concentration. These parameters will bear heavily on the cycle efficiency/cost.

- Electrode materials, should be inexpensive and long-lasting. Presently, carbon electrodes with platinum loading.
- Cell construction, to withstand 30 atm operating pressure and temperature in the 50-80 C range.

Acid concentrator and vaporizer - No reference materials for these units have been identified. Duriron and Durichlor have been suggested, but both are difficult to form and expensive.

Capital cost estimate - This is deemed inaccurate for two reasons. One, the design basis was predicated on a highly idealized conceptual design of the process (using overly optimistic assumptions as to operating data), and two, materials are as yet unidentified and thus costs are difficult to determine. Using typical chemical engineering estimating methods, based on the cost-factor approach, it is approximated that the total installed cost may be 1.5 to 3 times that presented.

In a positive light, one might add that this cycle is one of the "best" of those under present-day development and that there is sufficient evidence to state with considerable confidence that this process can be made workable technically. The process design is acceptable from the point of view of feasibility. The various steps in the cycle have been demonstrated in the laboratory or are well known in the chemical industry. However, if the proposed plant were to be built with current technology, the system could be made operable but the cost of hydrogen would be higher than that derived from the optimistic economics given by Westinghouse.

The Sulfuric Acid Hydrogen Iodide Cycle

This cycle differs from the others under development in that it is a "pure" thermochemical cycle. No electrolytic steps are included. A cycle with the same chemical steps is undergoing evaluation at the Euratom Laboratory, Ispra, Italy, and has been named the Mark 16 thermochemical cycle there. In the United States, its development is being conducted by the General Atomic Company (GA).[13]

This water-splitting process consists of the three following chemical reactions:

1. $2\ H_2O(l) + SO_2(g) + xI_2 \xrightarrow{300\ K} H_2SO_4(sol) + 2\ HI_x(sol)$

2. $2HI_x(g) \xrightarrow{600\ K} H_2(g) + xI_2(g)$

3. $H_2SO_4(g) \xrightarrow{1100\ K} H_2O(g) + SO_2(g) + 1/2\ O_2(g)$

The first reaction is conducted at around room temperature in aqueous solution. Use of excess iodine by GA, or of excess sulfur dioxide by Euratom, causes the formation of two distinct liquid phases which can be separated by decantation. The lighter phase is predominantly sulfuric acid and the heavier (lower) phase contains the HI_x.

By itself, the second reaction is relatively straightforward, however, conversions are low (roughly 20%) at the temperatures indicated, 600-700 K, for rapid reaction kinetics. The separation of HI_x from the aqueous heavy phase of the first reaction is complicated by the formation of a HI-water azeotrope. Phosphoric acid, H_3PO_4, is used as an azeotrope breaker forming a preferential aqueous solution that must be evaporated.

The final reaction in this cycle is the decomposition of sulfuric acid that is common to this and the previous cycle under discussion. Concentration of the acid is done by multiple-effect flash evaporation in order to improve the thermal efficiency and matchup with the heat source.

A schematic diagram of the process is given in Fig. 3. The water, iodine, and sulfur dioxide enter the low-temperature (368 K) reactor where the two liquid phases are formed. The lower phase of this reaction, containing the HI_x aqueous solution, is sent to a vacuum still and desulfurizer to remove trace sulfur dioxide and sulfur. After concentration and recovery from aqueous solution, the hydrogen iodide is thermally cracked to give hydrogen and iodine vapors. The iodine is condensed from this stream and recycled to the first reactor leaving a pure hydrogen product. The sulfuric acid is concentrated and then vaporized at about 98% acid. The sulfur trioxide in this stream is thermally decomposed in a catalytic reactor to produce sulfur dioxide and oxygen. General Atomic has discovered that this gas mixture can be passed directly into the first reactor to effect the separation. The sulfur dioxide takes place in the reaction and oxygen passes through without effect and is vented to the atmosphere. This obviates the need for a separate sulfur dioxide-oxygen separation step.

The overall process efficiency, as determined from an early flowsheet prepared by the Lummus Company, was 36.2%.[12] A later flowsheet, prepared and analyzed by GA, and quoted in the EPRI report, indicates an efficiency of 41.4%. In late 1978, with 60% of the latest flowsheet optimized, GA expects an efficiency in the neighborhood of 45% or higher for their cycle.[13] This in turn contrasts with the Euratom estimate for the Mark 16 flowsheet of approximately 40%. An independent estimate of the Mark 16 flowsheet made by the Chemical Engineering section of the Belgian SCK/CEN Laboratory gives a value of 31% for the efficiency.[14] Energy consumption due to the product separation steps, for example HI decomposition,[4] leads to this value.

As with Westinghouse, GA hopes to have in operation a continuous, closed-circuit laboratory-scale unit of their process in operation by the end of 1978. GA is receiving funds from the Gas Research Institute (GRI), DOE, and corporate sources to develop this cycle.

Key Problem Areas - Sulfuric-Acid Hydrogen Iodide Cycle

Main solution reaction - Degassing of the sulfur dioxide from the solutions. Elimination of the oxygen effluent without loss of intermediate species, sulfur dioxide or iodine. Handling and recovery of large quantities of iodine are required.

Acid concentration - Tradeoff between amount of heat recovery and capital cost. In the GA flowsheet, six flash evaporation stages are called for to concentrate sulfuric acid from 55% to 98%. These are highly capital-intensive. Materials are a major consideration here as boiling sulfuric acid is being handled.

Hydrogen iodide recovery and decomposition - Phosphoric acid is used to separate the HI-H_2O azeotrope. The resulting phosphoric acid solution must be distilled resulting in a heat penalty for the process. HI decomposition may be improved by use of a catalyst that allows iodine to be recovered in the liquid state.

GA concludes that this cycle appears to be a promising approach to producing hydrogen from non-fossil sources matching the thermal output capability of the High Temperature Gas-Cooled Reactor (HTGR) rather well.[13] The all-liquid and gas phase characteristics of the cycle are claimed to give this cycle a considerable advantage over cycles requiring solids handling. This last point has not been verified, however.

The Sulfuric-Acid Hydrogen Bromide Cycle

This cycle is another example in the class of "hybrid" cycles, one of the chemical reactions being carried out in an electrochemical cell, obviously at a lower voltage than that of water electrolysis. The Mark 13 cycle under development by the Euratom Laboratory, Ispra, Italy, consists of the following three reactions:[15]

1. $SO_2(g) + Br_2(l) + 2\ H_2O(l) \xrightarrow{350\ K} 2\ HBr(g) + H_2SO_4(sol)$

2. $2\ HBr(sol) \xrightarrow{350\ K} H_2(g) + Br_2(l)$ elec.

3. $H_2SO_4(g) \xrightarrow{1100\ K} H_2O(g) + SO_2(g) + 1/2\ O_2(g)$.

A flowsheet of this cycle is shown in Fig. 4. Reaction 1 is performed with an excess of bromine to produce a sulfur dioxide-free gas stream containing only hydrogen bromide and bromine as well as a concentrated sulfuric acid solution at 70-80% concentration. The HBr/Br_2 gas stream is fed together with the recycle fluid from the HBr electrolysis cell, reaction 2, to a Br_2 distillation-HBr absorption tower to separate bromine for recycle to the first reaction step. The concentrated sulfuric acid is decomposed, reaction 3, in a manner similar to that already described in the previous cycles. The gaseous product containing water, sulfur trioxide, which are recycled, and sulfur dioxide and oxygen is then separated to recover sulfur dioxide. The oxygen, as before, is vented to the atmosphere. In the electrolytic cell, the entering fluid consists mainly of HBr solution practically free of bromine. The effluent contains approximately 4% bromine. The inlet HBr concentration to the cell is 45% and at the outlet decreases to 41%.

Designs on this cycle have been performed at Euratom to obtain efficiency and hydrogen cost. The cell voltage for the electrolytic step, reaction 2, is a key parameter in the process. Laboratory work has indicated a cell voltage in the range of 0.8-1.0 V at a current density of 2000 Am^{-2} at the HBr concentrations indicated above.[16] Using a value of 0.8 V for the electrolyzer voltage, an efficiency of 37.2% was obtained for this cycle.[17]

A complete, continuous, closed-cycle laboratory-scale unit operating at 100 liters/hour (4 mol H_2/hr) is now in operation at the Ispra facility of Euratom. This unit is the first working model of a hybrid thermochemical process in the world and, as such, represents a new frontier in hydrogen energy technology. The aims of this plant are to study the following:

- Whether the reference design conversions and reactant concentrations can be achieved and maintained.
- Testing of control and analytical equipment under actual, corrosive conditions.
- Determination of possible by-product formation and developing suitable remedies.
- Obtaining data for plant scale-up.

Observation of the plant in operation during a visit to Ispra in August 1978 indicated that most of the above objectives were being met. Hydrogen was being produced in the unit and the HBr/Br_2 streams were being recycled and reused without significant loss or by-product formation. A novel feature of the plant was the use of a membraneless electrolyzer to cut down on losses due to internal cell resistance. At the time of the visit, this electrolyzer was operating at a voltage higher than the 0.8 V design specification, however this was to be remedied by the use of an electrolyzer of newer and better design (as regards electrode materials, configuration, flow passages, etc.).

Key Problem Areas - Sulfuric-Acid Hydrogen Bromide Cycle (Mark 13)

Electrolyzer - Operability at design conditions of 0.8 V or less. The electrical requirements of this cycle are rather severe as 0.8 V is approximately half the voltage requirement for water electrolyzers using advanced technology, such as the GE SPE electrolyzer. This problem may be very difficult to overcome; it also has a large effect on the efficiency.

Materials - for containment of the HBr and Br_2 species.

ALTERNATIVE CYCLES UNDERGOING ACTIVE RESEARCH

A selection of two of the cycles under experimental research was made. The cycles chosen were the Los Alamos Scientific Laboratory (LASL) Bismuth Sulfate Cycle and a Japanese cycle known as the Magnesium-Iodine Cycle. There are many other cycles being actively pursued at other laboratories such as the Institute of Gas Technology,[18,33] Argonne National Laboratory,[19] Oak Ridge National Laboratory,[20] and the Lawrence Livermore Laboratory[21] in the USA alone. The cycles are shown in Table IA and B. However, it was felt that preliminary data on these cycles indicated either a low efficiency or a low promise of commercialization.

The LASL Bismuth Sulfate Cycle[24,25]

We have seen in previous sections that sulfuric acid is a common denominator to the hybrid cycles as well as to the GA cycle. Sulfuric acid poses serious problems, both in its handling which requires materials resistant to corrosion as well as in its concentration to the azeotropic composition, 98%. The latter step involves evaporation of sulfuric acid solutions. This operation incurrs a large heat penalty unless the latent heat in the vapor is recovered. Multiple effect evaporation may accomplish this recovery but, in doing so, adds largely to the capital cost of the plant.

Avoidance of these problems can be achieved by the use of an insoluble metal sulfate that is precipitated from the sulfuric acid solution. To be most efficient, the metal sulfate should additionally not possess water of hydration. Bismuth sulfate was found to have the desired properties and the cycle thus formed is shown below:

1. $SO_2 + 2\ H_2O(l) \overset{350\ K}{\quad} H_2SO_4(sol) + H_2(g)$ elec.

2. $H_2SO_4(sol) + 1/3\ Bi_2O_3(s) \xrightarrow{350\ K} 1/3Bi_2O_3 \cdot 3SO_3 + H_2O(l)$

3. $1/3Bi_2O_3 \cdot 3SO_3(s) \xrightarrow{900-1100\ K} 1/3Bi_2O_3(s) + SO_2(g) + 1/2\ O_2(g)$.

A flowsheet of the cycle is seen in Fig. 5. The bismuth sulfate precipitates on adding bismuth oxide to the sulfuric acid produced in the electrochemical step, reaction 1. In this manner, sulfur trioxide is recovered from the sulfuric acid without the need for a costly and corrosive acid drying step. In addition, use of the bismuth sulfate or a bismuth oxysulfate may allow the electrochemical reaction to proceed at a lower acid concentration than 55% or higher required in the hybrid sulfuric acid cycle, possibly lowering the voltage requirements and therefore improving the efficiency of this cycle.

Preliminary calculations based on these effects shows a potential 10-12% efficiency improvement when solid sulfate processing is substituted for sulfuric acid in these cycles. The major challenge is to devise the means of handling large quantities of solids and process them at high temperatures (1000-1500 K).

Bismuth sulfate, $Bi_2O_3\ 3SO_3$ or $Bi_2(SO_4)_3$, decomposes with increasing temperature to a series of bismuth oxysulfates and sulfur trioxide. The latter in turn decomposes to sulfur dioxide and oxygen as shown:

4. $Bi_2O_3 \cdot 3SO_3(s) = Bi_2O_3 \cdot 2SO_3(s) + SO_3(g)$

5. $Bi_2O_3 \cdot 2SO_3(s) \quad Bi_2O_3 \cdot SO_3(s) + SO_3(g)$

6. $Bi_2O_3 \cdot SO_3(s) = Bi_2O_3(s) + SO_3(g)$

7. $SO_3(g) = SO_2(g) + 1/2\ O_2(g)$.

As a result, the options for generating SO_3 over a temperature range that includes intermediate temperatures, in addition to higher temperatures for SO_3 decomposition exist, and should be useful in achieving efficient extraction of heat from a HTGR, a fusion reactor or a solar heat source.

A laboratory-scale unit to test the decomposition of bismuth sulfate is being designed at LASL with operation contemplated for later in 1979. Initially electrical heating will be used with plans to implement the heating with a solar source later. To avoid the circulation of large quantities of bismuth sulfate, it is proposed to heat and decompose sulfur trioxide. The product sulfur dioxide and oxygen will recombine in another section of the chemical reactor giving up its thermal energy in the form of exothermic heat of reaction. We hope to try this new concept of a "chemical heat pipe" as an efficient method for heat transfer in the unit to be built later this year. The unit will be sized at approximately 100 liters/hr to be comparable in size and output with the other bench-scale units under construction, presently.

Key Problem Areas - LASL Bismuth Sulfate Cycle

Decomposer - In general, the major unknown in this cycle is solids handling. The bismuth sulfate must be decomposed to yield bismuth oxide and sulfur trioxide. Reaction rate and heat transfer to the solid phase must be rapid. The mechanism of heat transfer by use of a "chemical heat pipe" to avoid the circulation of large amounts of gases must be proven. The configuration of the solids decomposer, i.e., fixed bed, moving bed, or fluidized bed must also be selected and verified.

Electrolyzer - Electrolysis at significantly lower voltages (in dilute acid solution) must be demonstrated; the electrochemical reaction must also be tested to determine the effect of the low concentration of bismuth ion present in the solution.

The Magnesium-Iodine Cycle (Japan)

This cycle comprising four thermal steps may be carried out at temperatures around 900 K or below. It is being investigated by the National Chemical Laboratory for Industry in Tokyo, Japan. The chemical reactions included in the present cycle are represented as follows:[26]

1. $6/5\ MgO(s) + 6/5\ I_2(s) \xrightarrow{450\ K} 1/5\ Mg(IO_3)_2(s) + MgI_2(sol)$

2. $1/5\ Mg(IO_3)_2(s) \xrightarrow{900\ K} 1/5\ MgO(s) + 1/5\ I_2(g) + 1/2\ O_2(g)$

3. $MgI_2 \cdot 6\ H_2O(s) \xrightarrow{700\ K} MgO(s) + 2\ HI(g) + 5\ H_2O(g)$

4. $2\,HI(g) \xrightarrow{600-700\ K} H_2(g) + I_2(g)$.

The cycle is similar in many respects to a calcium-iodine cycle that was reported earlier by the authors.[27] The cycle flowsheet is shown on Fig. 6.

In this cycle, redox reaction 1 of iodine with magnesium oxide in aqueous solution forms magnesium iodide in the aqueous phase and the iodate as a precipitate. Thermal decomposition of the magnesium iodate results in magnesium oxide, iodine and oxygen in reaction 2. Hydrolytic decomposition of magnesium iodide into more magnesium iodide and hydrogen iodide follows with the final reaction 4 being the thermal dissociation of hydrogen iodide into product hydrogen and recycle iodine. Experiments have proven the validity of this cycle in good agreement with thermodynamic estimates. Disadvantages in the cycle with calcium showed an excess of water used to obtain a high degree of reaction 3 as well as melts of calcium oxide forming in reaction 2. These difficulties were partly remedied by the substitution of magnesium for calcium in the cycle. In addition, the temperature for reaction 2 is lowered from 1100 K to 900 K with the rates of reactions 2 and 3 being speeded up.

Cycle efficiencies for this type of cycle are not expected to be high largely as a result of having to handle chemical species in solution which involves the use of large amounts of low-temperature thermal energy for drying. In addition, the final reaction 4, decomposition of HI is energy-inefficient due to the separation problems involved and low conversion. An estimate of the efficiency for this cycle is in the 20-30% range, based on results for the similar calcium-iodine cycle.[20]

Key Problems in the Magnesium-Iodine Cycle

Reaction 1 - Both magnesium iodide and magnesium iodate are formed in this reaction with the latter precipitating. Practical problems are the degree of completion of the reaction, the solubility of the iodate, and evaporation of the solution to recover the hydrated magnesium iodide species.

Reaction 2 - Although not shown, the magnesium iodate is actually a magnesium iodate tetrahydrate, this involves driving off the water of hydration and more importantly, recovering their latent heat of vaporization in an energy-efficient cycle.

Reaction 3 - The problem is similar, six waters of hydration have to be removed in addition to supplying the endothermic heat for decomposition of magnesium iodide.

Reaction 4 - Separation of hydrogen from iodine and undecomposed hydrogen iodide must be effected.

With these difficulties and the need to evaporate large amounts of water in this cycle, it is doubtful if this cycle will be competitive with the previously mentioned cycles. The chemical studies being done will, no doubt, contribute to a greater understanding of cycles involving solution chemistry.

The Japanese have also proposed a cycle in which a mixture of barium and magnesium oxides are reacted with iodine in the first reaction. The barium/magnesium-iodine cycle may offer some interesting possibilities that have not yet been determined.

HEAT PENALTY ANALYSIS OF THERMOCHEMICAL CYCLE

A key parameter associated with any thermochemical process is the efficiency, η, that is redefined below.

$$\text{Process Thermal Efficiency, } \eta = \frac{\Delta H}{Q_T},$$

where ΔH = total enthalpy associated with hydrogen produced, and Q_T = total thermal energy required from primary energy source to produce the hydrogen.

The value of ΔH is 68.3 kcal/mol (286 kJ/mol) for all cycles and Q_T includes all the heat and work energy required by the process. Since ΔH is constant, the value of the efficiency clearly depends on the method used to compute Q_T.

It appears obvious that the most accurate method of obtaining the cycle efficiency is that of conventional chemical engineering. A complete flowsheet is drawn up based on the chemical reactions in the cycle and the separations required. Heat and mass balances are then used to calculate the process efficiency. This method is not amenable to a quick determination and thus early efforts in thermochemical hydrogen were spent in obtaining a rough estimate of this parameter for the purpose of cycle selection.

A computer program, HYDRGN, was written at the University of Kentucky under the direction of Funk to estimate the efficiency in a quick and rather simple manner.[28] The HYDRGN program used thermodynamic data for the pure components involved in each chemical reaction to calculate enthalpy, entropy, and free energy changes for each reaction step as well as for the heating and cooling steps in the cycle. A heat exchange routine determines the net heat by balancing the endothermic requirements against the exothermic heat liberated in the process. Finally, the program calculates the efficiency estimates which are used in evaluating the process.

The estimate used is shown in the equation below, and is obtained after heat matching. The heat needed by the cycle, Q', is the sum of the endothermic heats remaining after the matching process. The work of separation, calculated from the ideal work of separation, is reduced by the work that can be generated by unmatched exothermic heat and it is further assumed that the separation processes are only 50% efficient.

$$2. \quad \eta = \frac{\Delta H}{Q' + \dfrac{W_{sep}/0.5 - W_{gen}}{0.3}} \quad .$$

The 0.3 figure in the denominator is the value assumed for the conversion from heat to work (30%).

Since then, Funk and Knoche have devised a more sophisticated and accurate means of determining the process efficiency and relating this parameter to capital and operating costs, as well as to the final production cost of hydrogen.[29,30] The method, known as heat penalty analysis, is based on the result that the hydrogen production cost is linear with the product of the heat penalty and direct capital cost of each component or collection of components (battery) of the thermochemical plant. The heat penalties are the result of irreversibilities, or entropy production, associated with the process equipment and they are an indication of the quality, from a basic thermodynamic viewpoint, of a particular flowsheet or process design. The sum of all the heat penalties, plus an ideal heat requirement, is the total amount of energy, Q_T, required of the primary heat source. The formalism of this methodology is indicated in the equations below (process thermal efficiency expressed in terms of second law effects on "heat penalties"):

3. $$\frac{1}{\eta} = \frac{1}{\eta_{id}} + \frac{1}{\Delta H} \sum_j Q_{pj} \text{ ,}$$

where η_{id} = ideal efficiency - a function of the temperature of primary heat source and properties of material input and output, and Q_{pj} = heat penalty associated with the j^{th} battery.

The heat penalty, Q_p, can be related to the entropy production by 4 (heat penalty Q_p, and entropy production, s):

4. $$Q_p = \frac{T_m}{T_m - T_0} \cdot T_0 \cdot s$$

where T_0 = sink temperature; where T_m is a characteristic of the primary energy source,

5. $$T_m = \frac{T_{out} - T_{in}}{\ln \frac{T_{out}}{T_{in}} + \frac{R}{C_p} \ln \frac{p_{in}}{p_{out}}} \text{ .}$$

Combining these expressions, we get,

6. $$\frac{1}{\eta} = \frac{T_m}{T_m - T_o} \left(\frac{\Delta G}{\Delta H}\right) + \frac{T_m}{T_m - T_o} \frac{T_o}{\Delta H} \sum_j s_j r_j \text{ ,}$$

where ΔH and ΔG are kcal/kg H_2, s is kcal/kgX-°K, and r is kgX/kg H_2.

Table II shows a heat penalty analysis as performed by Funk for the hybrid sulfuric acid cycle using highly optimistic values for the electrochemical reaction parameters (80% H_2SO_4, 0.45 V).

A battery in the chemical plant is usually the collection of process equipment required to accomplish a necessary step in the process. The total plant is the collection of batteries required to accomplish the overall process. There are two important characteristics associated with each battery - the capital cost and the heat penalty - and trade-offs may be made among these to minimize the production cost.

For a fixed primary energy source output:

7. $$P_c = \frac{1}{\eta} [K_1 + K_2 \sum_j (DCC)_j] ,$$

where P_c = production cost, \$/10^6 BTU or \$/GJ; η = process thermal efficiency, $(DCC)_j$ = direct capital cost of the j^{th} battery; K_1 = constant related to the cost of primary energy; and K_2 = constant related to capital recovery and operating costs for chemical plant.

Combining the expressions for the production cost and heat penalties:

8. $$P_c = [\frac{1}{\eta_{id}} + \frac{1}{\Delta H} \sum_j Q_{pj}] \cdot [K_1 + K_2 \sum_j (DCC)_j] .$$

Note the important characteristics of each battery, (1) heat penalty, Q_p, and (2) direct capital cost, DCC. The tradeoff is between capital cost and heat penalties.

The procedure is applied to the hybrid sulfuric acid process and the results are shown in Table III and plotted on a production cost, capital cost, thermal efficiency diagram, Fig. 7.

Under conditions approaching reality (point X, 0.8 V), the efficiency of the hybrid sulfuric acid process is 40% rather than 51%, with the hydrogen production cost reaching \$10.55/10^6 BTU (\$10.55/GJ).

MATERIALS

Key questions arise concerning the materials requirements of any thermochemical process involving sulfuric acid. The first concerns technical feasibility: i.e., whether materials can be found to effect the vaporization and decomposition of sulfuric acid at the relatively high temperatures needed for the endothermic stage of these cycles. The second question is unique to hybrid cycles, and is one of economics: can materials be found that are inexpensive enough to offset by the energy savings due to the hybrid electrochemical step relative to that of water electrolysis?

The unique materials requirements for sulfuric acid processing occur in the acid vaporizer and SO_3 reduction reactor. Candidate materials for the vaporizer that have been selected are:[11] previous metals, ceramics, superalloys, and cast high-silicon irons (duriron). Conventional experience with these materials do not match process requirements in three important areas: temperature, pressure, and acid concentration. In industrial practice with sulfuric acid, the flow is normally from the acid to the containment wall; thus, the vessel walls can be kept cooler than the acid itself. In sulfuric acid decomposition, heat must be transferred to the acid, so that wall temperatures in the heat exchanger necessarily must be higher than in the bulk acid. Current data on sulfuric acid corrosion are limited to approximately 150 C and most have been obtained only at atmospheric pressure.

In addition, the changing composition of the acid solution, the conversion to a two-phase vapor-liquid mixture, and finally the superheating to a vapor in the vaporizer section represent a diversity of chemical environments that may require more than one containment material. The problem is further exacerbated by the requirement that the containment material conform to a geometry which provides efficient heat flow to the acid. It is difficult to accomodate materials such as duriron and silicon nitride in conventional heat exchanger designs.

In summary, the feasibility and economic aspects of materials for thermochemical cycles are open questions at the present state of development. The feasibility question hinges strongly on the degree to which process operating parameters (particularly temperature and pressure) can be adjusted to accomodate materials capabilities. Experimental data on the corrosion and mechanical behavior of materials must also be provided to answer this problem.

HYDROGEN PRODUCTION - THERMOCHEMICAL CYCLES OR WATER ELECTROLYSIS

Two competing methods are available for the production of massive quantities of hydrogen for the future. These methods, thermochemical cycles and water electrolysis, both employ water as the starting raw material and are coupled to a high-temperature heat source. Water electrolysis is a well-known technology with present, relative poor characteristics which may offer improvement through some amount of research. Most hydrogen produced in the industrial countries of the world today is derived from hydrocarbons, indeed, the abundance of cheap hydrocarbons until recently, slowed efforts in the development of efficient electrolyzers. Less than 1% of the world's hydrogen supply derives from electrolysis which is used only where electricity generation is favorable or where product purity is needed for some specific application. With estimated increases in both the efficiency of power generation and of the electrolysis process forecast, thermochemical or hybrid cycles must achieve higher levels of performance and cost to be competitive.

Attempts to estimate costs have been made recently at Euratom, Ispra[31] and those at Westinghouse.[32] The Ispra efforts have attempted to estimate the costs of advanced electrolytic systems on par with hybrid thermochemical cycles. As an example, using the OPTIMO code, they have calculated the hydrogen production cost and efficiency of Mark 11, Mark 13, and Advanced water electrolysis. Their data are shown in Table IV.

Interestingly enough on the "bottom line," the hydrogen production cost is remarkably similar despite differences in the three processes. Mark 11 has a cost of \$8.02/10^6 BTU, Mark 13: \$8.88 and advanced electrolysis: \$8.54. Westinghouse has recently concluded a study for the Electric Power Research Institute (EPRI) that indicates much the same thing.[32] In their work, a comparison was made on the economics and efficiency for the hybrid sulfuric acid cycle and a water electrolysis process using sulfuric acid (rather than potassium hydroxide) solution as the electrolyte. The two processes were based on the same assumptions as much as possible, i.e., the same VHTR supplying thermal energy, etc. Their results show for the thermochemical cycle a 47% efficiency (at a voltage of 0.6 V in the electrochemical cell and 80% sulfuric acid) resulting in a hydrogen cost of \$7.30/10^6 BTU. (Note: It may be optimistic to expect hydrogen generation at 80% sulfuric acid at 0.6 V). The water electrolysis process indicated that at a cell voltage of 1.68 V, an efficiency of 41% and a cost of \$7.80 for the product hydrogen would be obtained.

As all values are based on future technology, which has not yet been developed, it is "safe" to say that thermochemical hydrogen costs are in the same range as those for electrolytic hydrogen and hence continued R&D efforts in both the thermochemical (pure or hybrid) and the water electrolysis areas should proceed in parallel until one technology <u>clearly</u> demonstrates superiority over the other on factual, rather than on assumed, grounds.

ECONOMICS AND EFFICIENCY

Clearly the best method to determine the economics of a particular process for hydrogen manufacture is to base the determination on a realistic flowsheet of the process that in turn is based on a design supported by laboratory evidence. In the case of thermochemical hydrogen, the technology has not yet progressed to this stage of refinement, thus cost estimates are often made based on flowsheets put together on the basis of assumed design information. These assumptions are made on the hope that continued research and development will yield the desired results. This approach has the effect of yielding results that are somewhat over-optimistic when viewed in the light of actuality.

Better estimates of the efficiency and production cost of hydrogen have been made with the use of the Funk-Knoche heat penalty analysis and the OPTIMO computer code developed at the Euratom Laboratory, Ispra, Italy.[29] The heat penalty method has been described in the previous section and the Euratom methods are shown here.

The OPTIMO code uses a modular cost estimating technique based on the process flowsheet. The flowsheet must include all the unit operations necessary for the technical feasibility of the cycle and show the principal recycle streams. The operating conditions should be fixed as a result of experimental data or estimated carefully from thermodynamic considerations. A detailed plant cost estimation then can be performed after definition of the process units from the flowsheet knowing the mass flows through each unit. Knowing the mass flow and the necessary outlet conditions, the dimensions of the individual units can be calculated. As an example of this procedure, the mass flow indicates the diameter of a separation tower while the outlet conditions determine the number of plates. Once these dimensions are found, the process unit costs may be evaluated after materials considerations.

The key to obtaining the thermal efficiency of a thermochemical cycle is the heat exchange network. Heat recovery largely affects this parameter. However, there is always a compromise between the amount of heat recovered and the cost of the heat exchange surface required. It should also be evident that the heat exchanger capital cost plays a large role in determining the total plant investment. In OPTIMO, a heat recovery routine was developed to calculate the cost of each chemical process heat exchanger, in order to optimize the total heat exchange network. The calculation employs the following equation:[30]

$$\text{Installed Cost} = \text{Basic Cost } \$/m^2 \times \text{Size Factor} \times \text{Pressure Factor} \times \text{Heat Transfer Area, } m^2 \times 4.57+1.42x \text{ Materials Factor}$$

All costs are based on the cost per unit area of carbon steel corrected by size, pressure, and materials factors to give the final installed cost. 4.57 is a constant relating basic to installed cost for equipment. The materials factor used is shown in Table V.

Application to the Hybrid Sulfuric Acid Cycle

The OPTIMO code was applied to a flowsheet, Fig. 8, derived at Euratom, Ispra for the hybrid sulfuric acid cycle. It must be emphasized that the results shown in the tables only refer to the flowsheet presented. A different flowsheet as developed in the US for this cycle would have different process conditions, etc., giving a completely different picture of the estimates in these tables. One distinct advantage of computer estimation such as OPTIMO is that it allows one to perform parametric analyses on key variables in the process. Parametric analysis will show the influence of these variables and indicate where more work is necessary to better define values. As an example, in the electrochemical step of this cycle, the cell voltage is closely linked to the investment cost through the current density. Parametric analysis shows that the cell voltage has a strong influence on the hydrogen production cost thus necessitating a major research effort to reduce it.

Table VI indicates the main characteristics assumed in the Euratom design of the Mark 11-V6 (hybrid sulfuric acid) process. The cell voltage was chosen at 0.62 V at an acid concentration in the cell of 75% H_2SO_4. (Author's note: These conditions may be somewhat optimistic in practice). The end result of the estimation is to obtain the thermal efficiency of the process, the total capital investment and the hydrogen production cost. The Euratom design is based on a hydrogen production rate of 100,000 m^3/hr of hydrogen. The values obtained are shown in Table IV. The thermal efficiency is 41.4%, the investment cost \$119.8 million resulting in a product hydrogen cost of \$8.85/10^6 BTU (7.62/GJ).

The parametric analysis for this process flowsheet is shown in Fig. 9. As the cell voltage rises to a value of 0.8 V, the thermal efficiency decreases to under 37% and the hydrogen cost increases to \$10/10^6 BTU. Other important variables influencing these values are the primary energy cost (cost of thermal energy from the primary heat source), and the minimum ΔT that is used in the design of the heat exchangers. Increases in ΔT lead to a reduced area, hence a decreased overall capital cost, however, the process ΔS is increased leading to a lowered efficiency and greater energy requirements (for the same net amount of hydrogen produced). These competing effects lead to a trade-off situation; optimization of this position gives a minimum production cost, the position of which depends on the relative importance of the cost of capital and energy.

Other investigators have made estimates of the energy efficiency and hydrogen production cost for thermochemical hydrogen. Funk detailed costs for the hybrid sulfuric acid cycle and a methanol cycle (Author's comment: technically unworkable), in an earlier EPRI report.[12] Another appraisal of these variables was done in a similar study by Westinghouse for the same cycle.[8] In addition the Euratom Laboratory has performed an analysis using the OPTIMO code on their Mark 13 cycle.[30] These data have been collected in Table VII and are plotted on Fig. 10. The data from the table and plot show a minimum cost of $4.90/10^6 BTU at 45% efficiency from an early Westinghouse report,[11] a later report gives the cost as $5.56 at an efficiency of 54%.[8] These costs and efficiencies were obtained for certain assumed conditions in the electrochemical reaction that have not been, and are not likely to be achieved in the near future (as a result of fundamental chemical mechanisms in the reaction). A recent Westinghouse report[32] comparing the techno-economics of the hybrid sulfuric acid cycle with that of sulfuric acid (water) electrolysis using a more realistic voltage of 0.6 V arrives with an efficiency of 47% at a hydrogen cost of $7.30/10^{6}BTU. In comparison, their assessment of the water electrolysis, of which more will be added in the next section, comes to a 41% efficiency at a cost of $7.80.

The maximum cost is for the Lawrence Livermore Laboratory Zinc-Selenium cycle indicating a $13.50 cost at 42% efficiency.[21] Part of the reason for the high cost for this cycle is a result of a large amount of material circulation, mainly water, hence capital intensive. The design was also based on laboratory data rather than on assumed conditions, which affects the flowsheet design and ultimately the hydrogen cost.

From the data presented, it appears likely that a successful thermochemical hydrogen process will have a thermal efficiency in the 40-45% range with the cost of product hydrogen being in the \$8.00 to \$10.00/10^6 BTU bracket. Costs lower than this will result if there is a drop in the cost of the primary heat source and/or capital equipment, both of which are very unlikely to happen.

CONCLUSIONS

- Three thermochemical processes are under active development today with efforts being made to produce hydrogen in laboratory-scale units in a continuous mode at 100 liters per hour. Design data for a larger unit will result, but data on efficiency and cost estimates will not be much furthered.
- Lesser efforts in researching other cycles are being done at laboratories both in the USA and abroad. Many seek to avoid materials and heat penalty problems caused by the use of sulfuric acid in the three leading contenders. The LASL option uses an insoluble metal sulfate to transfer sulfur values in the cycle.
- Materials problems are endemic to all cycles. A healthy effort is needed to develop high-temperature, corrosion-resistant materials for thermochemical cycle usage.
- Improvements are being made in estimating the cost and efficiency of hydrogen produced from water and a thermal energy source either by thermochemical cycle technology or by water electrolysis. These include the heat penalty analysis (Funk) and the OPTIMO computer code (Euratom). Costs of thermochemical hydrogen have been found to fall in the \$7 to \$10/10^6 BTU range with efficiencies in the 35 to 45% bracket.
- A 10 to 15 year developmental effort with increased funding of both options (thermochemical and water electrolysis) should find a clear-cut solution and resolve the situation of the "best" option to use for producing synthetic hydrogen from water.

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TABLE IA

COMPILATION OF OTHER THERMOCHEMICAL CYCLES UNDER DEVELOPMENT

1. Institute of Gas Technology (USA)[18]

   Cycle H-5

   1. $CuO + 6H_2O + SO_2 \rightarrow CuSO_4\ 5H_2O + H_2$
   2. $CuSO_4\ 5H_2O \rightarrow CuSO_4 + 5H_2O$
   3. $CuSO_4 \rightarrow CuO + SO_3$
   4. $SO_3 \rightarrow SO_2 + 1/2\ O_2$

2. Argonne National Laboratory (USA)[19]

   Cycle ANL-4

   1. $2NH_3 + 2KI + 2CO_2 + 2H_2O \rightarrow 2NH_4I + 2KHCO_3$
   2. $2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$
   3. $Hg + 2NH_4I \rightarrow 2NH_3 + HgI_2 + H_2$
   4. $HgI_2 + K_2CO_3 \rightarrow 2KI + Hg + CO_2 + 1/2O_2$

3. Hitachi (Japan)[23]

   Na_2CO_3-I_2 Cycle

   1. $2NaI + 2NH_3 + 2CO_2 + 2H_2O \rightarrow 2NaHCO_3 + 2NH_4I$
   2. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
   3. $2NH_4I + Ni \rightarrow NiI_2 + 2NH_3 + H_2$
   4. $NiI_2 \rightarrow Ni + I_2$

4. Lawrence Livermore Laboratory (USA)[21]

L^3 Zinc-Selenium Cycle

1. $2\ ZnO(s) + Se(l) + SO_2(g) \rightarrow ZnSe(s) + ZnSO_4(s)$
2. $ZnSe(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2Se(g)$
3. $ZnCl_2(l) + H_2O(g) \rightarrow ZnO(s) + 2HCl(g)$
4. $ZnSO_4(s) \rightarrow ZnO(s) + SO_2(g) + 1/2\ O_2(g)$
5. $H_2Se(g) \rightarrow Se(l) + H_2(g)$

TABLE IB

CYCLES WITH DEMONSTRATED REACTIONS

1. <u>Institute of Gas Technology (USA)</u>[33]

   <u>Cycle B-1</u>

   1. $3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2$
   2. $Fe_3O_4 + 8HCl \rightarrow 2FeCl_3 + FeCl_2 + 4H_2O$
   3. $2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$
   4. $Cl_2 + H_2O \rightarrow 2HCl + 1/2O_2$

2. <u>Oak Ridge National Laboratory (USA)</u>[20]

   <u>Cu/Cu (Ba, F) Cycle</u>

   1. $2Cu^o + Ba(OH)_2 \rightarrow BaCu_2O_2 + H_2$
   2. $BaCu_2O_2 + H_2O \rightarrow Ba(OH)_2 + CU_2O$
   3. $2Cu_2O + 4HF \rightarrow 2CuF_2 + 2CU^O + 2H_2O$
   4. $2CuF_2 + 2H_2O \rightarrow 2CuO + 4HF$
   5. $2CuO \rightarrow Cu_2O + 1/2\ O_2$

3. <u>Los Alamos Scientific Laboratory (USA)</u>[22]

   <u>LASL Cerium-Chlorine Cycle</u>

   1. $2CeO_2 + 8HCl = 2CeCl_3 + 4H_2O + Cl_2$
   2. $2\ CeCl_3 + 2H_2O = 2CeOCl + 4\ HCl$
   3. $2ceOCl + 2H_2O = 2CeO_2 + 2HCl + H_2$
   4. $Cl_2 + H_2O = 2HCl + 1/2O_2$

TABLE II (Ref. 12)

HEAT PENALTY ANALYSIS
HYBRID SULFURIC ACID CYCLE

$T_m = 962^{o}$ K

$\frac{\Delta H}{\Delta G} = 1.2$ $\Delta H = 33{,}900$ kcal/kgH_2

$T_o = 300^{o}$ K

		X	$\dot{s}, \frac{\text{kcal}}{\text{kgX} - {}^{o}\text{K}}$	r	$\dot{s}r$	$\frac{T_m}{T_m - T_o} \frac{T_o}{\Delta h} \dot{s}r$
IHX		H_2	8.2	1	8.2	0.015
Battery						
F + G	Elec.	H_2	7.7	1	7.7	0.099
H	H_2SO_4 Decomp.	H_2SO_4	0.35	49	17.1	0.220
I	SO_2 Sep.	SO_2	0.058	32	1.8	0.023
J	Power Gen.	H_2	21	1	21	0.270
	Misc.	H_2	3	1	3	0.038
						0.755

$$\frac{T_m}{T_m - T_o}\left(\frac{\Delta g}{\Delta h}\right) = 1.206$$

$$\eta^{-1} = 1.961$$

$$\eta = 51\%$$

TABLE III (Ref. 12)

HEAT PENALTY AND CAPITAL COST ANALYSIS
HYBRID SULFURIC ACID CYCLE

1510 MW H_2	0.48V* @ 2000 A/m2
T_m = 962°C	80% H_2SO_4 *
T_o = 300°C	No O_2 credit

			MW	DCC, 10^6\$
A.	Theoretical (ideal) Heat Requirement		1820	
B.	Heat Penalties			
		IHX	155	83.4
	Battery			
	F + G	Electrolyzer and Power Cond.	145	200.6
	H	H_2SO_4 Decomposition	323	167.6
	I	SO_2 Separation	35	23.6
	J	Power Generation	396	57.1
	Miscellaneous		88	
			2962	532.3
			η = 51%	

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*Overly-Optimistic assumed conditions, actual conditions are 0.6V at 50% H_2SO_4, @ 2000 A/m^2.

TABLE IV

COSTS FOR THERMOCHEMICAL AND ELECTROLYTIC HYDROGEN - 10-15 YEAR FUTURE TECHNOLOGY (Ref. 35)

	Mark 11 - V6					Mark 13 - V2					Electrolysis				
		Unit. Cost ($/kW)	Green Field (M$)	Fix. Cost (%)	Ann. Char (M$)		Unit. Cost ($/kW)	Green Field (M$)	Fix. Cost (%)	Ann. Char (M$)		Unit. Cost ($/kW)	Green Field (M$)	Fix. Cost (%)	Ann. Char (M$)
Chemical Installations			10.5	25	4.6			23.1	25	5.7					
Process Heat Exchangers			24.7	25	6.1			23.3	25	5.8					
Interest During Construction (%)	13.0		5.6	11	0.6	13.0		6.0	11	0.6					
Electrolyzers Output (MWTH)	354.4	118.8	42.1	15	6.3	354.4	118.8	42.1	15	6.3	354.4	118.8	42.1	15	6.3
Electrolytic Cell Voltage (V)	0.62					0.80					1.64				
Required Electricity, DC (MWe)	148.3					191.3					400.0				
Compressors Power (MWe)	5.5		0.2	15	0.0	4.8		0.2	15	0.0					
Transformers and Rectifiers (MWe)	152.8	77.1	11.1	15	1.6	197.2	77.1	14.4	15	2.1	412.3	77.1	31.7	15	4.7
Required Electricity, AC (MWe)	158.4					202.1					412.3				

TABLE IV (continued)

COSTS FOR THERMOCHEMICAL AND ELECTROLYTIC HYDROGEN - 10-15 YEAR FUTURE TECHNOLOGY (Ref. 35)

	Mark 11 - V6					Mark 13 - V2					Electrolysis				
		Unit. Cost ($/kW)	Green Field (M$)	Fix. Cost (%)	Ann. Char (M$)		Unit. Cost ($/kW)	Green Field (M$)	Fix. Cost (%)	Ann. Char (M$)		Unit. Cost ($/kW)	Green Field (M$)	Fix. Cost (%)	Ann. Char (M$)
Recovered Electricity (MWe)	48.3	476.7	23.0	15	3.4	48.5	476.7	23.1	15	3.4					
Interest During Construction (%)	8.0		6.1	11	0.6	8.0		6.3	11	0.7	8.0		5.9	11	0.6
Hydrogen Plant Investment			119.8		23.6			126.3		25.0			73.9		11.7
H_2 Capacity $(M3/H)*10^3$	100.0					100.0					100.0				
Capacity Factor (%)	80.0					80.0					80.0				
Annual Production, $(GJ/yr)*10^6$	8.92					8.92					8.92				
Overall Thermal Efficiency (%)	41.4					37.2					32.7				
Nuclear Heat Cost ($/GJ)	1.7					1.7									
Process Heat Required, $(GJ/yr)1^6$	14.2				24.9	13.8				24.1					

TABLE IV (continued)

COSTS FOR THERMOCHEMICAL AND ELECTROLYTIC HYDROGEN - 10-15 YEAR FUTURE TECHNOLOGY (Ref. 35)

	Mark 11 - V6					Mark 13 - V2					Electrolysis				
		Unit. Cost ($/kW)	Green Field (M$)	Fix. Cost (%)	Ann. Char (M$)		Unit. Cost ($/kW)	Green Field (M$)	Fix. Cost (%)	Ann. Char (M$)		Unit. Cost ($/kW)	Green Field (M$)	Fix. Cost (%)	Ann. Char (M$)
Electricity Cost (Mills/kWh)	20.0					20.0					20.0				
Electric Generating Efficiency (%)	38.0					38.0					38.0				
Electricity Required, (kWh/yr)*1^6	771.8				15.4	1076.				21.5	2889.				57.7
Non-energy Utilization (% of energy)	10.0				4.0	10.0				4.5	5.0				2.8
Total Annual Charges					67.9					75.2					72.4
Hydrogen Production Cost ($C/M3)	9.70					10.74					10.33				
Hydrogen Production Cost ($/GJ)	7.62					8.43					8.11				
Hydrogen Production Cost ($/MBTU)	8.02					8.88					8.54				

TABLE V

MATERIALS FACTOR (Ref. 25)

Carbon Steel	1	Incoloy 6F	10
Stainless Steel	2	Hastelloy C4	11
Incoloy 800	6.5	Titanium	12
Graphite	8		

TABLE VI

MAIN CHARACTERISTICS OF THE HYBRID SULFURIC ACID, MARK 11-V6 CYCLE (Ref. 30)

Plant Capacity	100,000 $Nm^3 H_2/h$
Electrolytic Cell Voltage	0.62 V
H_2SO_4 Concentration in Electrolytic Cell	75 wt%
Electrolytic Cell Temperature	363 K
Electrolytic Cell Pressure	30 bar
H_2SO_4 Train Pressure	10 bar
SO_3 Decomposition Temperature	1083 K
SO_3 Conversion	52%
Hydrogen Delivery Pressure	30 bar
Electricity Generation Efficiency	38%
Overall Thermal Efficiency	41.4%

TABLE VII

EFFICIENCY AND HYDROGEN PRODUCTION COST - THERMOCHEMICAL CYCLES
- ELECTROLYSIS -

Cycle	Efficiency (%)	Cost $\$/10^6$BTU	Done By	Reference	Point, Fig. E1
1. Hybrid Sulfuric Acid					
	54.1	5.56	Westinghouse	8	A
	45.18	4.90	Westinghouse	8	B
	47.0	7.80	Westinghouse	32	I
	44.0	7.40	Funk-Lummus	12	C
	41.3	8.85	Euratom	25	D
	51 (0.48 V)	8.20	Funk-DOE Panel	26	E
	40 (0.8 V)	10.00	Funk-DOE Panel	26	F
2. Hybrid Sulfuric Acid-Hydrogen Bromide (Ispra Mark 13)					
	36.9	9.70	Euratom	25	G
3. Zinc-Selenium					
	42.0	13.50	LLL	27	H
4. Sulfuric Acid-Hydrogen Iodide (6.A Ispra Mark 16)					
	45+	NA	General Atomic	13	
	31	NA	SCK/CEN, Belgium	14	
	41.4	NA	Funk-Lummus	12	
	36.2	NA	Funk-Lummus	12	
5. Hybrid Bismuth Sulfate					
	41	NA	LASL	24,25	
6. Hybrid Copper Sulfate					
	37.1	NA	IGT	18	
7. Sulfuric Acid (Water) Electrolysis					
	41	7.80	Westinghouse	32	J
8. Water Electrolysis (Advanced)					
	32.7	8.54	Euratom	31	K

FIGURE CAPTIONS

Fig. 1. Hydrogen from a thermal energy source.

Fig. 2. Hybrid sulfuric acid cycle, schematic diagram.

Fig. 3. Sulfuric acid-hydrogen iodide cycle, schematic diagram.

Fig. 4. Hybrid sulfuric acid-hydrogen bromide cycle, schematic diagram.

Fig. 5. Hybrid bismuth sulfate cycle, LASL, schematic diagram.

Fig. 6. Magnesium-iodine cycle, NCLI, Japan, schematic diagram.

Fig. 7. Production cost, capital cost, and efficiency; hybrid sulfuric acid cycle.

Fig. 8. Hybrid sulfuric acid cycle, Ispra Mark 11-V6 flowsheet (Ref. 30).

Fig. 9. Parametric analysis of hydrogen production cost and efficiency vs. electrochemical cell voltage (Ref. 30).

Fig. 10. Hydrogen production cost vs. efficiency for thermochemical cycles.

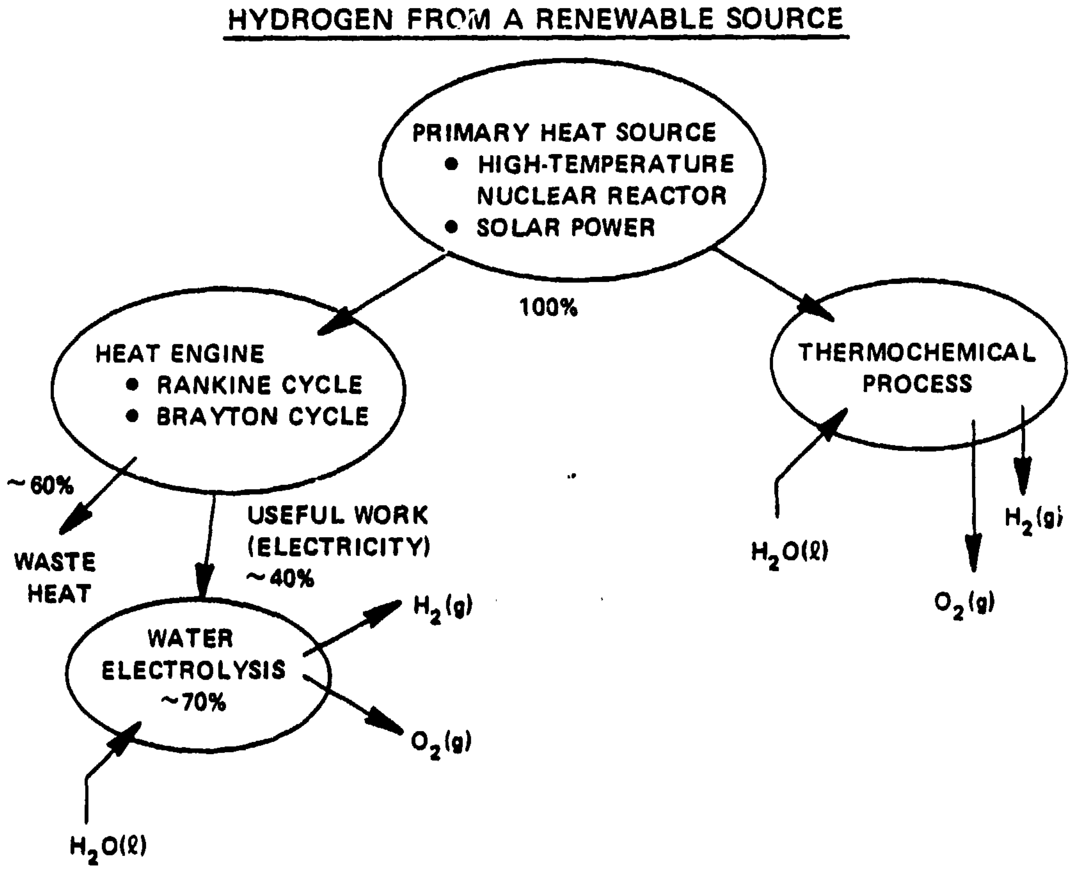


Fig. 1. Hydrogen from a thermal energy source.

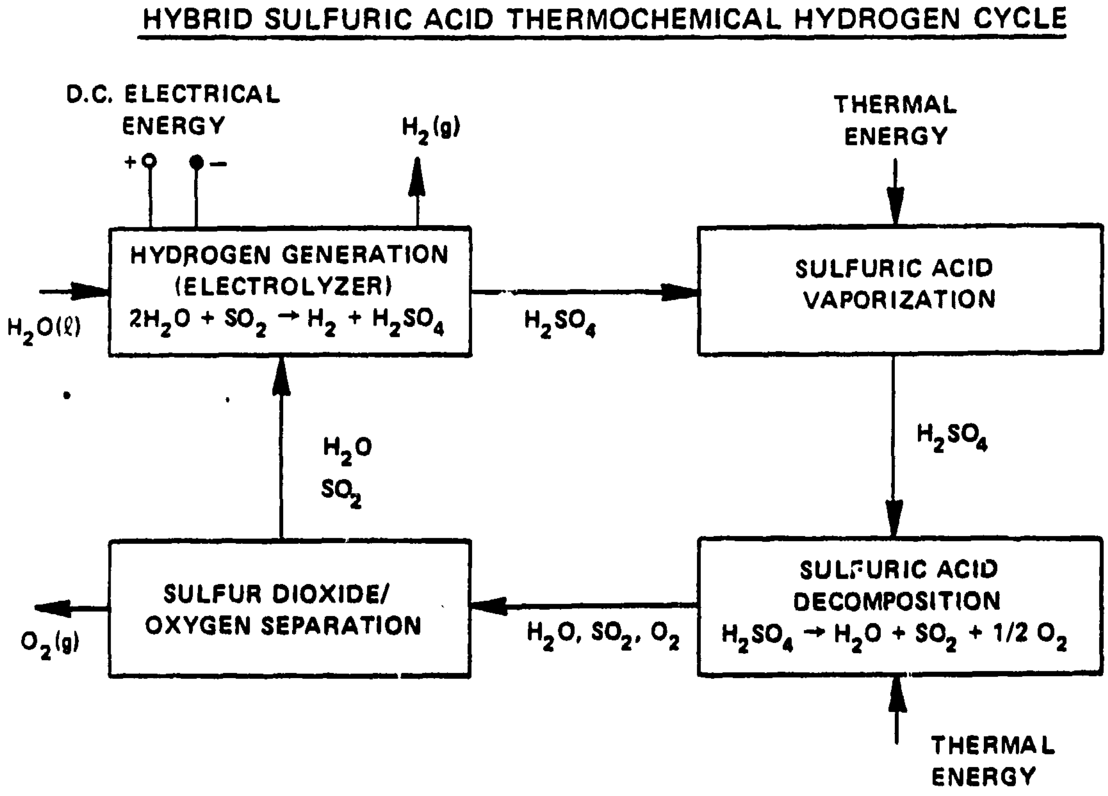
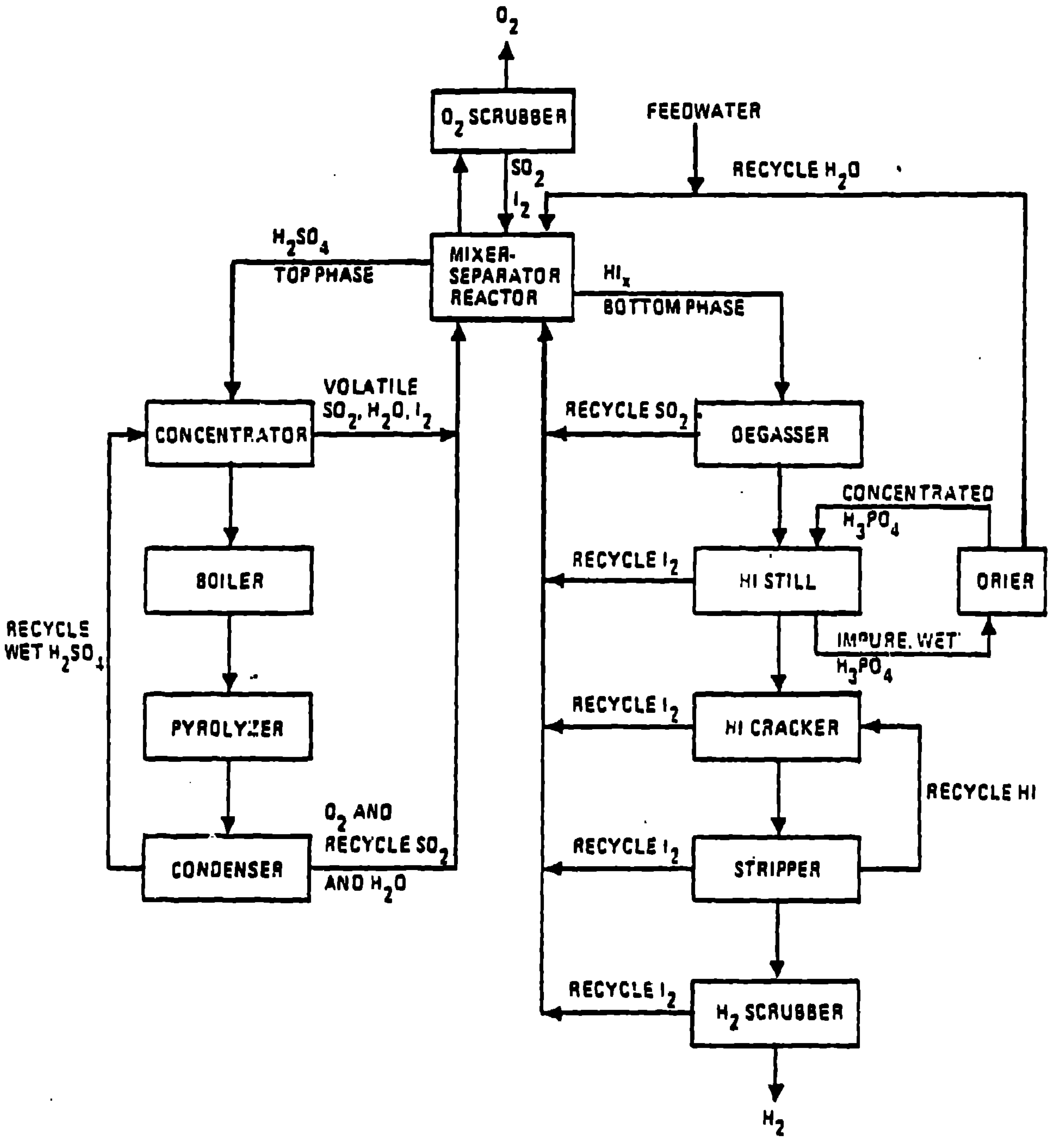


Fig. 2. Hybrid sulfuric acid cycle, schematic diagram.



SULFUR-IODINE THERMOCHEMICAL HYDROGEN CYCLE

Fig. 3. Sulfuric acid-hydrogen iodide cycle, schematic diagram.

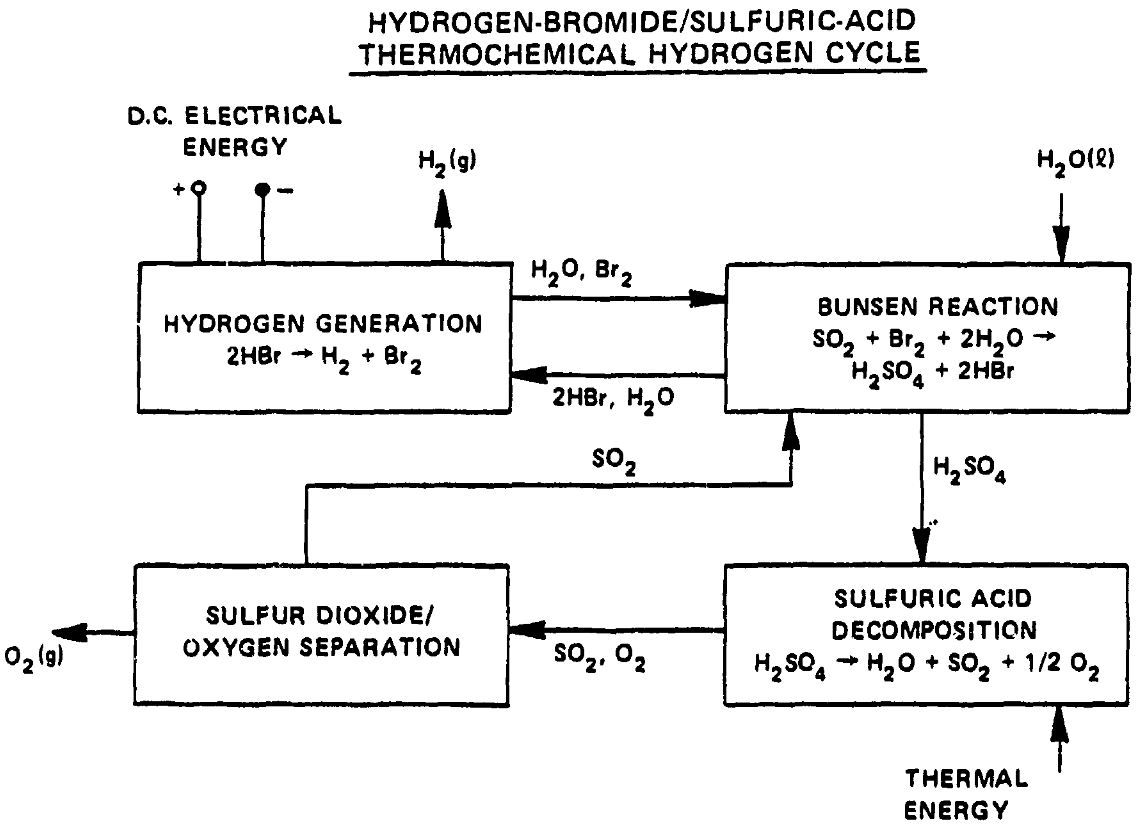


Fig. 4. Hybrid sulfuric acid-hydrogen bromide cycle, schematic diagram.

BISMUTH-SULFATE/SULFURIC-ACID HYBRID THERMOCHEMICAL HYDROGEN CYCLE

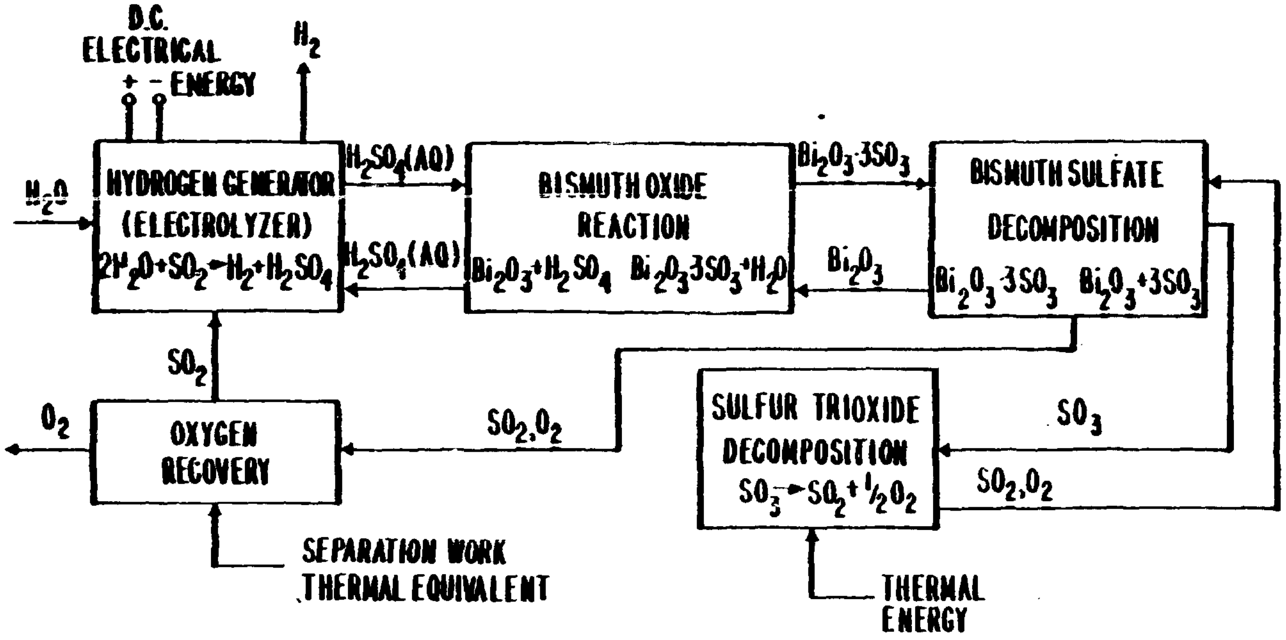


Fig. 5. Hybrid bismuth sulfate cycle, LASL, schematic diagram.

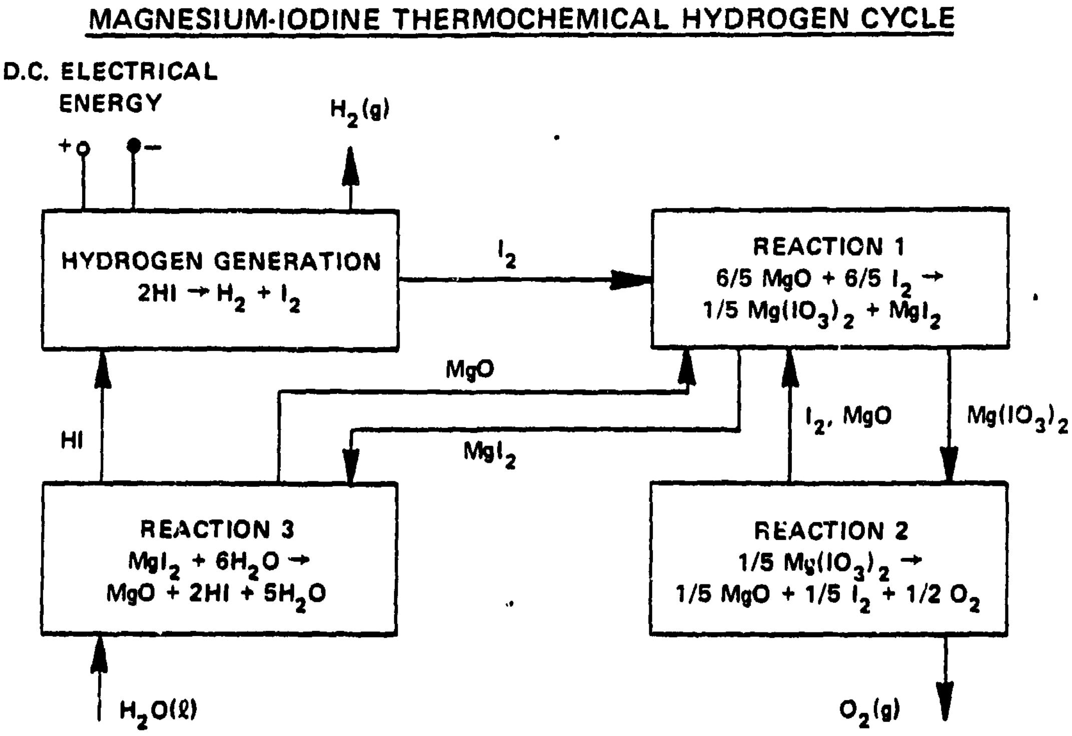


Fig. 6. Magnesium-iodine cycle, NCLI, Japan, schematic diagram.

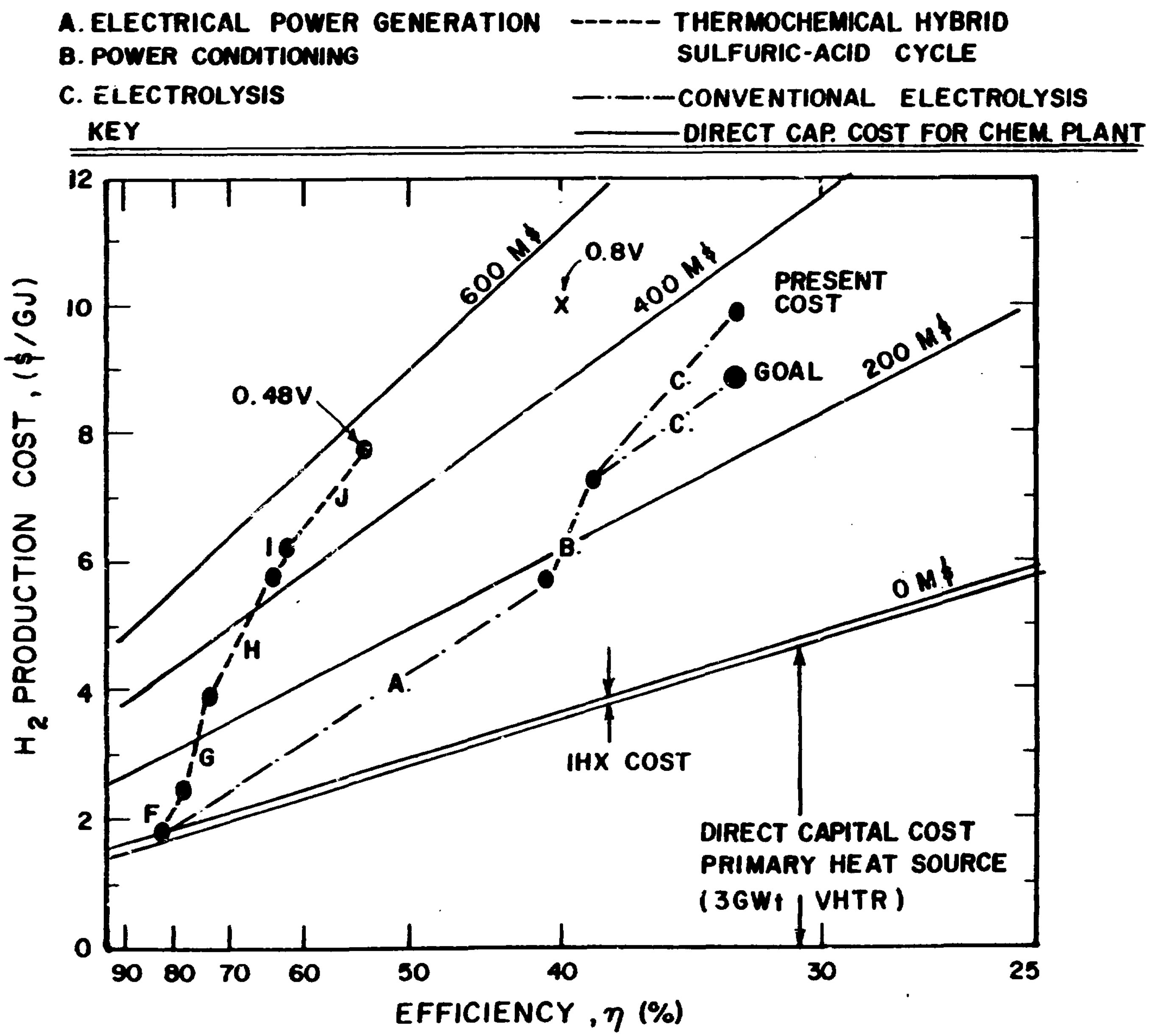
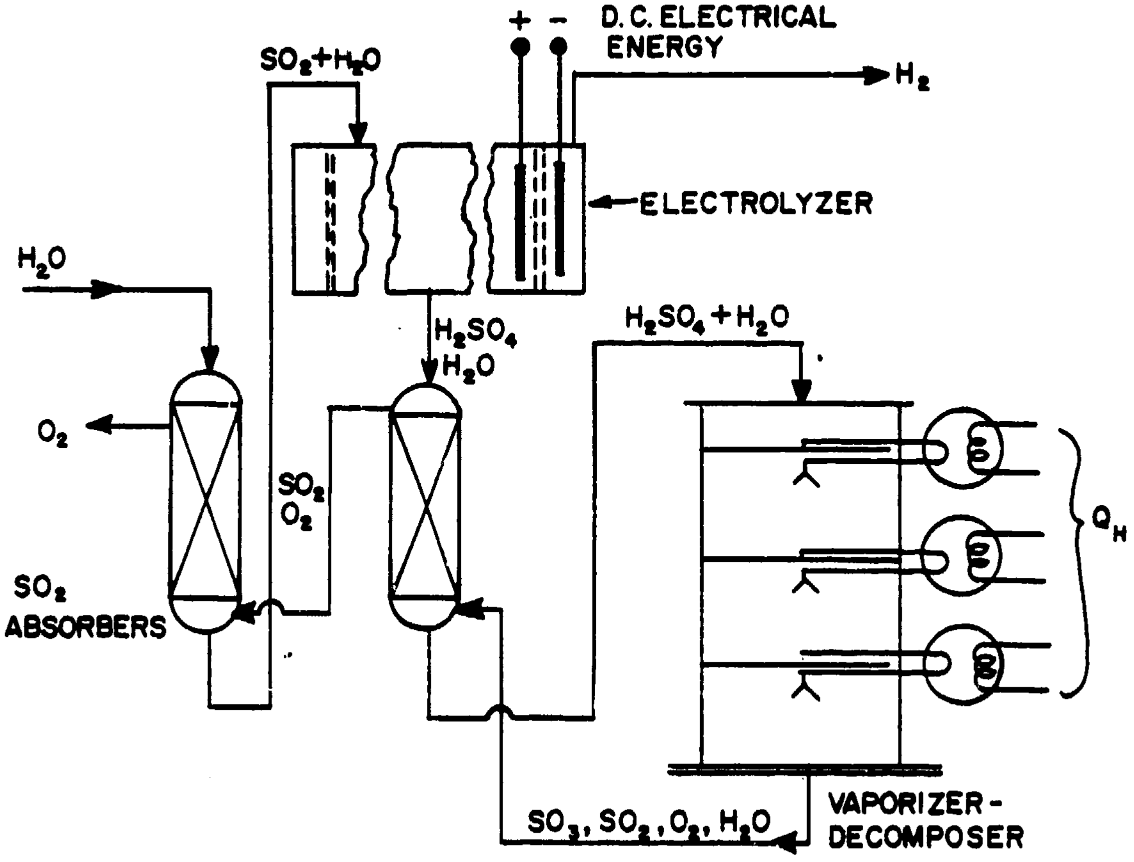


Fig. 7. Production cost, capital cost, and efficiency; hybrid sulfuric acid cycle.



MARK 11 FLOWSHEET HYBRID SULFURIC ACID CYCLE

Fig. 8. Hybrid sulfuric acid cycle, Ispra Mark 11-V6 flowsheet (Ref. 30).

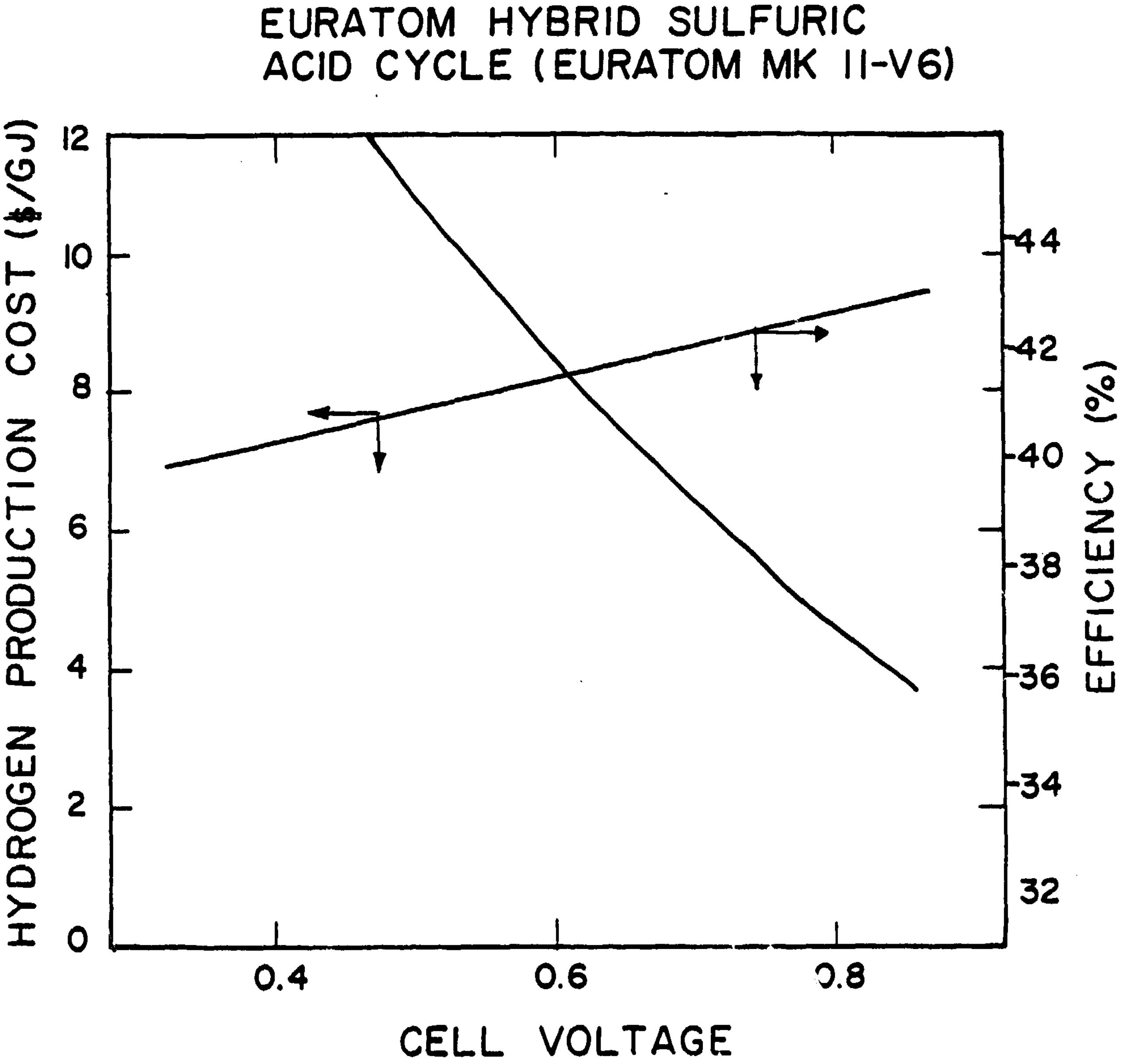


Fig. 9. Parametric analysis of hydrogen production cost and efficiency vs. electrochemical cell voltage (Ref. 30).

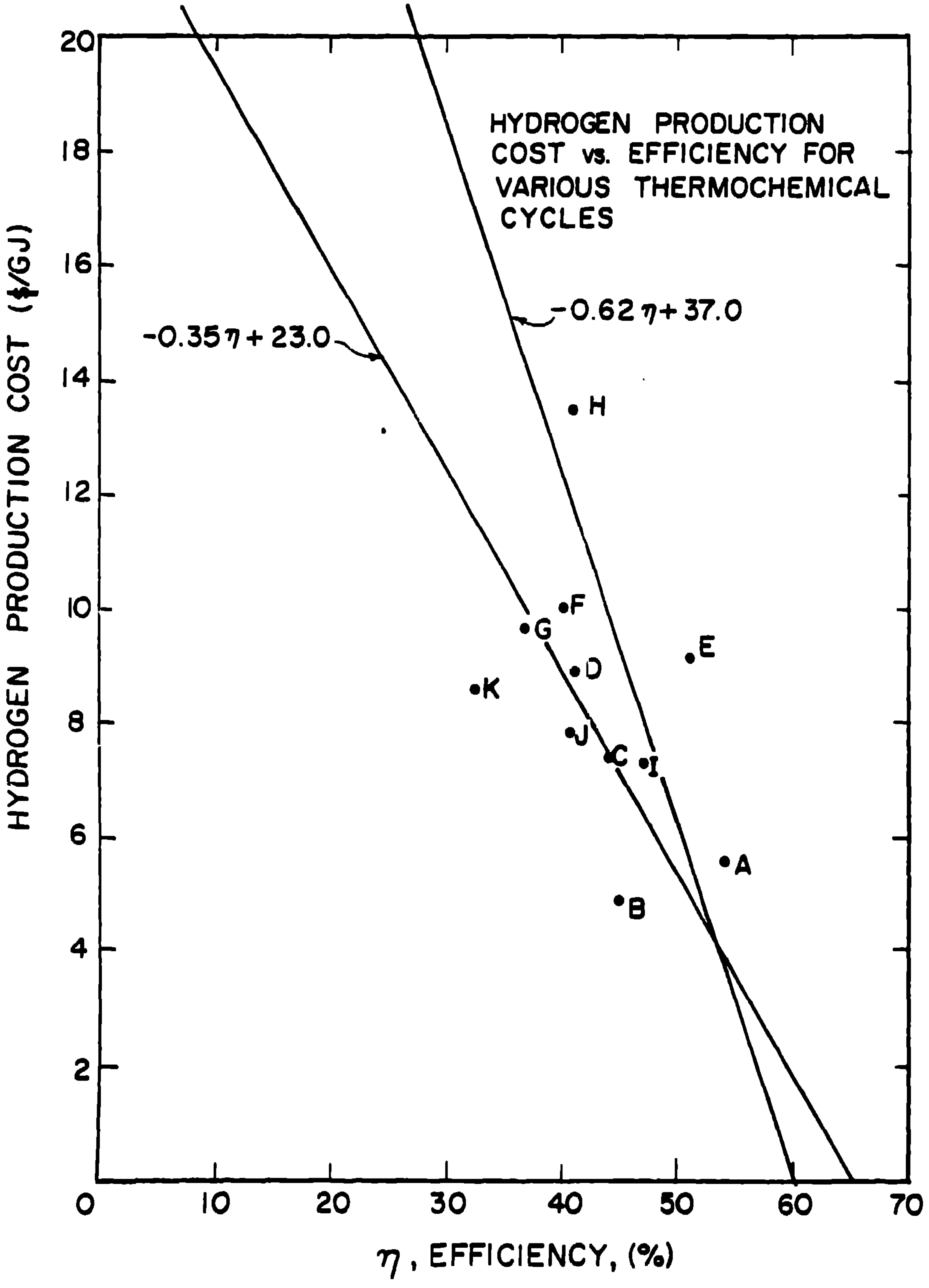


Fig. 10. Hydrogen production cost vs. efficiency for thermochemical cycles.

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