

# Thermochemical and Hybrid Cycles for Hydrogen Production. A Differential Economic Comparison with Electrolysis

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A method for economic evaluation of new processes is presented. The method is especially suitable for evaluating new technology at a stage where much of the detailed process information is still missing. It is based on differential comparison of the new process with available technology for focusing on evaluating its advantages in dealing with stoichiometric, thermodynamic, and process constraints and the interactions between them. The method is demonstrated by performing thorough evaluation of a class of processes that has been proposed for generation of hydrogen from nuclear reaction. The paper shows that one can conclude that the processes that have been proposed in the literature are inferior to electrolysis of water and that this conclusion can be obtained without any detailed process information using only available thermodynamic properties of the components involved.

## I. Introduction

In recent years hydrogen has received increased attention as a potential fuel source that could be produced from nonfossil fuel sources (ERDA, 1977; Marchetti, 1974; Gregory, 1973). It has also been suggested as a storage medium for off-peak energy (ERDA, 1977), or even as the main energy medium for the future, to take the place of natural gas and oil. This attention generated a secondary interest in new methods for producing hydrogen, especially from nuclear reactors, which are often lumped together under the generic name of "thermochemical cycles for hydrogen production" (Chao, 1974; Wentoff, 1974; Funk, 1972, 1976).

Although the interest in thermochemical cycles has diminished and other authors have shown them to be unattractive (Shinnar, 1975; Donat et al., 1977), they still present an interesting example of our method of economic evaluation. We will try to show how a sound economic process analysis can be performed on a process that has not yet been developed and for which important parts of the relevant information are missing. Very often in research, economic evaluation is postponed till the process is at least well defined in the laboratory stage. It is the experience of one of the authors (R.S.) that if such an analysis turns out to be unattractive, that often could have been seen at the conceptual stage, when kinetic and other data were still missing. Hydrogen production by thermochemical cycles is illuminating, as it can be shown that all the processes proposed till now are economically unattractive, even if they were to work close to their thermodynamic limits. We will therefore in the following emphasize the problem of screening new processes or ideas for which the process information is incomplete. Although there have been engineering evaluations for some of these processes (Funk, 1976; Farbman, 1976, 1978), we will try to derive results based solely on a knowledge of the competing existing technology, namely, electrolysis of water as well as of the thermodynamic properties of the proposed processes that can be computed without development work. Where possible, we will compare the results with more detailed published studies. The main purpose of the paper is the exposition of the method of evaluation and we will begin with a general discussion of the problem of evaluating processes at an early stage of development.

## II. Method of Process Evaluation

Technical and economic evaluation of new processes is an important part of research and process development.

The standard approach is to prepare a flowsheet of the proposed process and estimate the cost. If data are not available, one might make some optimistic assumptions based on the stoichiometry and the thermodynamic properties of the process. One can then compare these costs with published costs of other competitive routes or preferably an engineering group can prepare consistent estimates of several competing processes. Recently, a large number of such estimates have been published by various engineering companies, and they provide a valuable source of information for the researcher. There are, however, some inherent problems with this approach, as illustrated in Figure 1, where various published cost estimates for SNG from Western coal are compared. Although all estimates deal with commercially available technology and have similar flowsheets using the same process, the investment costs vary by a factor of 8 between 1972 and 1977. During these years construction costs increased by a factor of 2, but whatever the explanation might be, the fact of the factor of 8 over a 5-year period indicates the problem faced when comparing processes solely on the basis of cost estimates.

An accuracy of a factor of 2 is sufficient if we consider products with novel properties or future energy processes that can utilize totally new resources. It is much more problematic for evaluating competitive routes with the same raw material and similar products. There, a cost reduction of 25% would be a worthwhile goal. In this case, the inherent inaccuracy of engineering cost estimates causes severe problems, since even with detailed process information it is seldom better than  $\pm 20\%$ , even if it is prepared by the same company. Even achieving such accuracy often involves a very large engineering effort.

Since the results of such evaluation are dependent strongly on the judgment and the competence of the evaluator, it is therefore important that the results are presented in a way which allows the tester to judge the assumptions underlying the conclusions and provides feedback to the process developer as to what the critical parameters are and what is the chance of modifying the process to make it more competitive. If the results are presented mainly in dollars and cents, they put the decision-making processes solely into the hands of the process evaluator where they do not necessarily belong.

It is also natural that in preparing flowsheets for new processes, the assumptions are often optimistic. There is nothing wrong with that as long as the optimism is still on realistic grounds, consistent with the state of the art

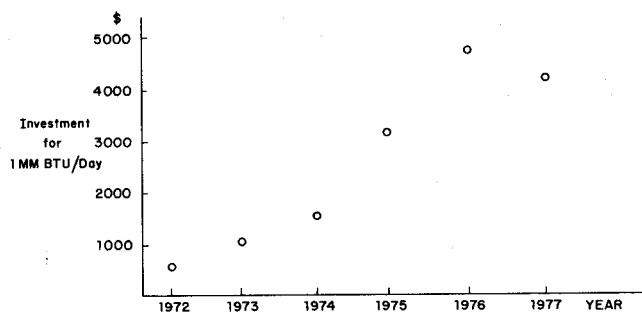


Figure 1. Investment estimates for producing SNG using a Lurgi process.

and consistent with thermodynamic limitations. It is important that the optimism relates to the innovation itself and not to the design of the total plant, which may contain many elements common to both processes. Otherwise, the improvement will not be due to the innovation itself, but rather due to a more optimistic design of the total plant that, if achievable, would lead to the same benefits in the existing process. Existing processes may be designed conservatively to allow for reliable plant operation and should not be directly compared with a flowsheet that is based on very tight design.

In no way do we want to sound overly critical of engineering evaluations or detailed cost estimates. In many cases the conventional detailed flowsheet and the cost estimate will still be needed. What we want to do is to set forward a methodology that will help the evaluator to present his results in a more transparent and meaningful way. In the process of screening new ideas, we can often reach reliable conclusions without detailed flowsheets and cost estimates. Here, where detailed data are not available, we are only interested in eliminating processes which are a priori noncompetitive with existing technology. In this case differential economic comparison is a powerful tool.

The approach presented can be summarized as follows.

(1) In comparing the difference between two uncertain numbers or quantities, it is preferable to get a direct estimate for the difference, as opposed to estimating the difference from independent estimates of the two numbers. Therefore, if we think that one process has an advantage over another, we should be able to explain the technological reasons for this advantage and try to quantify directly the effect of any advantage on cost.

(2) In evaluating new processes vs. available technology, it is important to look at both the similarities and the differences of the processes at three levels: (a) stoichiometric and thermodynamic constraints, (b) kinetic and process constraints, and (c) equipment and material constraints. Since b and c are often strongly related to each other, they will be treated together. Only by understanding how these constraints affect the costs of the different processes can we really understand the potential advantage of a new process.

(3) It is important to thoroughly understand the available technology with which the new process competes. The designs of existing processes are based on compromises among investment and process costs, thermal efficiencies, and raw material. In order to see whether the new process has any inherent advantage, we must understand the nature not only of the constraints, but also of the cost performance tradeoffs of existing and proposed processes. It is important to check if the main improvements that would lead to cheaper cost in a new technology would not benefit the existing technology in a similar way with lower risks of development.

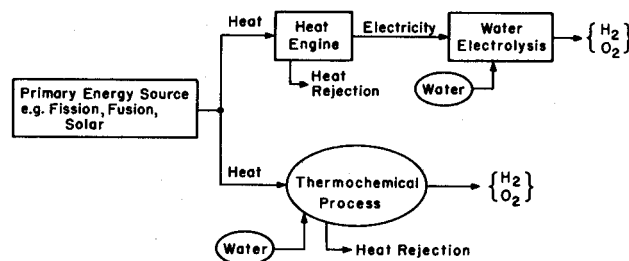
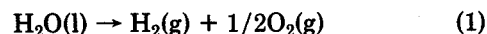


Figure 2. Hydrogen production processes (Funk, 1976).

(4) It is important to crystallize from the preceding points what are the real advantages of the new process and how much they would be worth if they can be fully realized. In a previous paper (Shinnar, 1975) the method was applied to a comparison of two processes for which detailed process information exists. Here, we want to concentrate on showing how to apply it in the screening stage when much of the process information is still missing.

### III. Outline of Problem

**Thermochemical Routes to Hydrogen.** One way of converting nuclear energy (or solar heat (Eisenstadt, 1975)) (see Figure 2) available today is to generate steam, drive an electric generator, and split water electrolytically into hydrogen and oxygen by the reaction



$$\Delta H^\circ_{298} = 68.3 \text{ kcal/g-mol}; \quad \Delta G^\circ_{298} = 56.7 \text{ kcal/g-mol}$$

The reaction involves an increase in free energy or available work.

It has been proposed that instead of using the heat to generate electricity, we would use the heat directly to drive reaction 1. The splitting of water by heat requires high temperature, but it can be achieved by carrying out the reaction in several intermediate steps, which result in the net reaction 1.

Examples of such reaction sets are given in Table I. We can write them in a general form

$$\sum \alpha_{ij} A_i = 0 \quad (2)$$

where  $A_i$  are the compounds involved and  $\alpha_{ij}$  is the stoichiometric coefficient of compound  $A_i$  in reaction  $j$ . The reasoning behind developing such cycles is that they would lead to higher thermal efficiencies in utilizing the heat of the nuclear reactor and in substantial savings of the overall investment required.

In the beginning the cycles proposed were totally uncompetitive (Shinnar, 1975) as they involved very large recycles and separation processes. Their potential cost was bigger by at least ten times or more than that of electrolysis. Recently, researchers learned to avoid the worst mistakes, and proposals have emerged for cycles that would be very reasonable if electrolysis did not exist.

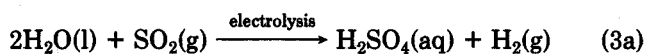
For our purposes it is not important if the processes can be realized or not, since the fact that some cycles are actually operable is of minor interest if they are not economically superior to existing technology. We therefore included in Table I the Schulten cycle, despite the fact that one of its steps (conversion of methanol to methane with  $\text{SO}_2$ ) has never been demonstrated.

A proposal also has been made that eq 2 might be improved by including an electrolytic step with a low voltage that could improve the overall thermal efficiency (Farbman, 1976, Warde and Brecher, 1976). An example of such

Table I. Thermochemical Cycles for Hydrogen Production

	$T_R$ , K	$\Delta H^\circ_{298}$ , kcal/ g-mol	$\Delta G^\circ_{298}$ , kcal/ g-mol
Mark 9			
$3\text{FeCl}_2(\text{c}) + 4\text{H}_2\text{O}(\text{g}) = \text{Fe}_3\text{O}_4(\text{c}) + 6\text{HCl}(\text{g}) + \text{H}_2(\text{g})$	1127	76.3	56.12
$3\text{FeCl}_2(\text{l}) = 3\text{FeCl}_2(\text{c}) + 1.5\text{Cl}_2(\text{g})$	775	15	9.23
$3\text{FeCl}_3(\text{c}) = 3\text{FeCl}_3(\text{l})$	579	30.9	~0
$\text{Fe}_3\text{O}_4(\text{c}) + 6\text{HCl}(\text{g}) + 1.5\text{Cl}_2(\text{g}) = 3\text{FeCl}_3(\text{c}) + 3\text{H}_2\text{O}(\text{g}) + 0.5\text{O}_2(\text{g})$	358	-64.4	-10.72
$\text{H}_2\text{O}(\text{l}) = \text{H}_2\text{O}(\text{g})$	373	10.5	2.07
Agnes			
$3\text{FeCl}_2(\text{c}) + 4\text{H}_2\text{O}(\text{g}) = \text{Fe}_3\text{O}_4(\text{c}) + 6\text{HCl}(\text{g}) + \text{H}_2(\text{g})$	1127	76.3	56.12
$\text{MgCl}_2(\text{c}) + \text{H}_2\text{O}(\text{g}) = \text{MgO}(\text{c}) + 2\text{HCl}(\text{g})$	796	23.23	14.53
$2\text{FeCl}_3(\text{l}) = 2\text{FeCl}_2(\text{c}) + \text{Cl}_2(\text{g})$	774	10	6.15
$2\text{FeCl}_3(\text{c}) + 2\text{FeCl}_2(\text{l})$	579	20.6	~0
$\text{MgO}(\text{c}) + \text{Cl}_2(\text{g}) = \text{MgCl}_2(\text{c}) + 0.5\text{O}_2(\text{g})$	696	-9.53	-5.45
$\text{Fe}_3\text{O}_4(\text{c}) + 8\text{HCl}(\text{g}) = \text{FeCl}_2(\text{c}) + 2\text{FeCl}_3(\text{c}) + 4\text{H}_2\text{O}(\text{g})$	406	-62.8	-16.72
$\text{H}_2\text{O}(\text{l}) = \text{H}_2\text{O}(\text{g})$	373	10.5	2.07
Schulten			
$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 3\text{H}_2(\text{g}) + \text{CO}(\text{g})$	751	59.8	36.1
$2\text{H}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$	350	-30.6	-4.5
$\text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}_2\text{SO}_4(\text{l})$	1006	-16.2	-11.4
$\text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g}) + 0.5\text{O}_2(\text{g})$	876	55.3	36.5

a hybrid cycle is the cycle proposed by Westinghouse (Farbman, 1978, 1976).



$$\Delta G^\circ_{298} = 7.8 \text{ kcal/g-mol}$$



$$\Delta G^\circ_{298} = 12.4 \text{ kcal/g-mol}$$



$$\Delta G^\circ_{298} = 36.5 \text{ kcal/g-mol}$$

For concentrated solution (3a) + (3b) can be written as



$$\Delta G^\circ_{298} = 20.2 \text{ kcal/g-mol}$$

The possibility of higher thermal efficiency has been stressed as the main advantage of both thermochemical and hybrid cycles. If we believe that a new process will allow us to achieve higher thermal efficiencies, we must understand whether this hope is based on any inherent stoichiometric or thermodynamic advantage, or it is due to process and design considerations that lead to lower process losses. In the next section we will show that the proposed new technology has no inherent thermodynamic advantage; therefore in screening we have to focus on potential process advantages.

#### IV. Stoichiometric and Thermodynamic Constraints

Our first concern is stoichiometry. We limit ourselves here to closed cycles and disregard coproduction of hydrogen with other products. Obviously, in a closed cycle

the overall stoichiometry is the same as eq 1:  $\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2$ . In reality it would be hard to find a complex system for which the net reaction is exactly eq 1. There will always be some side reaction and we seldom have 100% selectivity and recovery. Here, electrolysis has an inherent advantage. Its selectivity is very high, and chemical consumption (for electrolytes) is very low. All other cycles use large amounts of chemicals in a closed cycle to make them competitive with electrolysis.

Let us now look at the thermodynamic constraints that determine thermal efficiency. If the heat source is used to generate electricity and we use the electricity to split water, the only thermodynamic constraint is the Carnot cycle limitation. This limitation, obviously, applies to all processes. Theoretically, we cannot improve on an idealized electrolysis process. Its real efficiency is, however, limited by design considerations. A real nuclear power plant does not operate with an ideal Carnot cycle but on a steam cycle that operates rather far from the conditions desirable for maximum thermal efficiency. One of the main limitations, namely, the top steam temperature, is solely dictated by material and cost constraints. If we exceed 1100–1200 °F, steam dissociates and in order to prevent corrosion, expensive high-quality alloy steels are required. There is no inherent technical difficulty in designing a topping cycle that operates between the available top temperature of the heat source and the steam cycle. It is only difficult to design such a cycle at an acceptable cost. In fact, present nuclear power plants are designed at lower pressures and top temperatures than some of the advanced coal power plants.

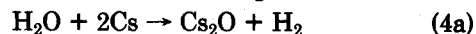
Design decisions, due to cost or safety considerations, have thermodynamic consequences and the thermodynamics is a powerful tool to analyze different design options. But this is different from an inherent constraint.

This immediately raises a question about the new technology. It requires higher temperatures and more expensive design materials than present nuclear or power plants. We therefore later will have to ask ourselves in what way electricity generation would benefit from the development of materials and technology which the new technology would require.

The same argument applies to electrolysis. It has no inherent constraints like the Carnot law. There is really no chemical process that can be run as close to reversible conditions as an electrolytic process. The reader may here ask a question: What about the fact that  $\Delta G^\circ_{298}$  for splitting of water is less than  $\Delta H^\circ_{298}$ ? Most electrolytic processes are carried out such that the current supplies not only the free energy required but also the heat of reaction. This is again a design constraint. Theoretically we could supply the heat of reaction by condensing the steam of the turbine in the electrolytic cell at no penalty in thermal efficiency. In reality we probably would not do that since the losses associated with achieving a reasonable current density are sufficient to supply the heat required.

It is important to note that rate considerations limit efficiency in real electrolytic processes, and not thermodynamic constraints. On the other hand, all thermochemical and hybrid cycles have additional inherent constraints. They result from two factors: (1) chemical reactions have inherent irreversibilities; (2) we cannot fit chemical reactions to get the maximum available efficiency from a given heat source.

Consider for instance the following reactions.



$$\Delta H^\circ_{298} = -13.8 \text{ kcal/g-mol}; \quad \Delta G^\circ_{298} = -11.7 \text{ kcal/g-mol}$$



$$\Delta H^\circ_{298} = 82.1 \text{ kcal/g-mol}; \quad \Delta G^\circ_{298} = 68.4 \text{ kcal/g-mol}$$

Reaction 4b is endothermic and requires a temperature of above 1500 °C to get a reasonable conversion into oxygen, whereas reaction 4a gives high conversion at room temperature.

To get a good conversion from step 4a, it must be operated at a temperature at which  $\Delta G(T) = 0$ . This temperature is far lower than the temperature required for step 4b and the only way to transfer the heat (or the free energy) released in this step to reaction 4b would be by a heat pump. At high temperatures such a pump is neither practical nor efficient. Without such a pump the minimum heat that has to be supplied from the nuclear reactor to the process is 82.1 kcal. If we just look at the Carnot law we only require 68.4 kcal.

Therefore the decision not to use a heat pump imposes a constraint that has thermodynamic consequences just as the choice of a top temperature in a power cycle. Here the consequences of this decision strongly depend on the nature of each cycle. We should immediately point out that this constraint does not make the process unattractive. If it would be realized it might have a much lower process loss than electrolysis.

Therefore we have to be careful what we mean by a thermodynamic constraint. Often we mean the thermodynamic consequences of process constraints. In a pure thermochemical cycle the free energy should be generated by supplying heat to chemical reactions. If we do not allow heat pumps, the maximum efficiency  $\eta_G$  (available work generated divided by the total heat input from the reaction) is given by

$$\eta_G = \frac{\Delta G_0(\text{H}_2\text{O}(l))}{\sum q_i} \quad (5)$$

In reaction 4  $\sum q_i = 82.1 \text{ kcal/g-mol}$ , which is the heat of reaction of reaction 4b. In estimating  $\sum q_i$  from  $\Delta H$ , we assume that the heat requirements of heating the reactants can be met by heat exchange with the products, or that  $\Delta C_p$  for the reaction is zero. This assumption is not true for reaction 4b, since cesium boils at 690 °C and is a gas at reaction temperature. If we cool the products (Cs and  $\text{O}_2$ ), Cs condenses at a temperature where we cannot use the heat in our process. This heat has to be supplied to the reactant and further decreases our efficiency significantly. We have no exact data for this process, but the example illustrates the additional limitations that a thermochemical cycle imposes on thermal efficiency.

The process is hypothetical as we could not transfer heat at 1500 °C from a nuclear reactor with available materials. There are no two-step processes operating at acceptable temperatures (below 900 °C or preferably 800 °C) (see Glandt and Myers, 1976). We need at least three or four steps. That puts some further limitations on the efficiency, since it is hard to find several steps all occurring at optimum conditions. We can consider any proposed scheme and derive a limiting thermal efficiency by just looking at the heat balance. We can construct a hypothetical flow-sheet in which all steps are carried out at a temperature  $T_R$  at which  $\Delta G(T_R)$  is less than or equal to zero. We can then try to match all heat inputs and outputs and supply the part that we cannot match from the heat source. For a first screening we can use just  $\Delta H^\circ(298 \text{ K})$  to compute the heat requirements. For the accurate screening we can estimate all heat capacities and phase changes and estimate the limiting efficiency from eq 5.

Table II. Limiting Thermal Efficiencies for the Cycles in Table I

	sum of pos. free energy, $\Sigma + \Delta G^\circ_{298}$ , kcal/g-mol	limiting thermal efficiency, $\eta$ , %	sum of mol wt, $\Sigma M_w$
Mark 9	65.35	42.7	2000
Agnes	76.8	47	1866
Schulten	72.6	57.3	288

Some estimates for the limiting efficiency of the cycles are given in Table II. These are based on  $\Delta H^\circ_{298}$  only and do not contain the phase changes and the lack of match in  $C_p$ . The accurate theoretical limiting efficiency would be lower.

We assumed that we can carry out the processes at optimal temperatures  $T_R$  at a reasonable rate, but that is not necessarily true. Furthermore, we neglected the possibility of other reactions between the same reactants. Pure thermodynamics does not allow us to estimate the products of such reaction systems, as there are often too many reactions that are thermodynamically possible. Thus, in addition to reaction 4a the reaction



might also occur.

All we can get from thermodynamics is a limiting efficiency. As said before, any advantage in thermal efficiency such a process might have would have to come from lower process losses, but for many published cycles the limiting theoretical efficiency imposed by the constraint that no heat pumps are allowed is lower than the efficiency of electrolysis with available technology. We can therefore use the criterion in cycle 5 as a screening criterion. A high efficiency in this screening step does not by itself promise a high real efficiency, but a low efficiency eliminates the process from further consideration.

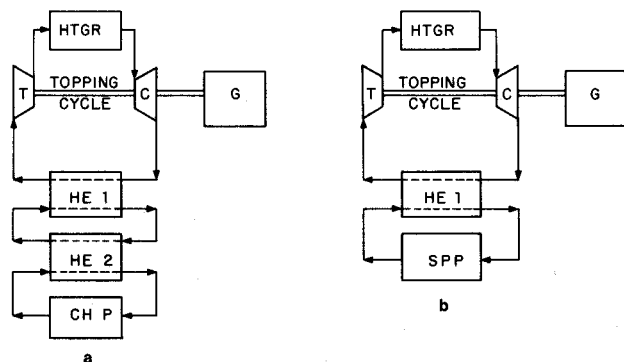
We can summarize that, compared with electrolysis, thermochemical cycles have much more severe inherent restrictions on their thermal efficiency. The difficulty due to the requirements of matching a large number of steps can be reduced by choosing a hybrid cycle. By introducing a low-voltage electrolytic step, we can find a cycle with only one high-temperature chemical step, therefore improving the efficiency given by eq 5. We should note, however, that such a cycle does not lead to any theoretical advantage over electrolysis; it only removes part of the inherent disadvantages of thermochemical cycles.

The fact that the thermodynamic constraints do not favor the new processes does not mean that they cannot be attractive, both in cost and in thermal efficiency. There are quite a number of cases where process constraints are more important than thermodynamic limitations. We must therefore look how these translate into real efficiencies dominated by process and cost considerations, to see if such processes have any potential advantage.

## V. Process Constraints of Electrolysis

(a) **Efficiency with Available Technology.** The first item we should consider in any comparison is the process on which we want to improve. We must thoroughly understand its process constraints and its design considerations.

We ask ourselves what is the real efficiency of electrolysis and how does it relate to the Carnot constraints? In the electrolysis of water we can express efficiency in two ways. One is to compare the theoretical electric energy requirement with the actual one, which is an efficiency in terms of  $\Delta G$ . The other way is to express it in terms of the higher heating value of hydrogen divided by the heat



**Figure 3.** (a) Helium cycle in thermochemical plant with high-temperature gas-cooled reactor. (topping cycle for process power requirements only). (b) Helium cycle in water electrolysis with high-temperature gas-cooled reactor. HTGR = high temperature gas-cooled nuclear reactor; HE = heat exchanger; T = turbine; C = compressor; G = generator; CHP = chemical plant; SPP = steam power plant.

equivalent of the electric energy. The latter is larger by a factor of 1.2, which is the ratio of  $\Delta H^\circ/\Delta G^\circ$  of reaction 1. The first way is more logical as it is related to a thermodynamic constraint, but we will use both since most of the literature uses the second way. We designate the first efficiency expression as  $\eta_G$  and the second as  $\eta_H$ .

Present nuclear reactors such as a light water reactor have an overall efficiency (Btu of electric power divided by Btu generated by fission) of approximately 33%. Presently available commercial electrolytic plants require a voltage of 1.80–2.0 V as compared with a theoretical voltage of 1.23 V, which leads to an overall efficiency  $\eta_H$  of 27% and  $\eta_G = 22.5\%$ . Often this figure is used as a yardstick for comparison with proposed processes, but the comparison is questionable for two reasons.

First, the efficiency of 68% for electrolysis corresponding to a voltage of 1.8 V is not a real process limitation. A loss of 0.6 V is common to many electrolytic processes, but it has been significantly reduced in pilot plant work (Appleby et al., 1978; Nuttel, 1977) and a voltage of 1.45 V or efficiency of 85% equivalent to  $\eta_H = 100\%$  for the electrolytic step has been achieved in space applications (Chalmers, 1968). General Electric (Nuttel, 1977) has developed a new electrolytic process using a polymer film as a solid electrolyte and has achieved efficiencies in terms of  $\eta_H$  above 100% in practical cells. This all would lead to an overall process efficiency  $\eta_H = 33\%$ , or  $\eta_G = 27\%$ .

Second, the current reactors were built to minimize the cost of electricity and not to maximize efficiency. Their efficiency has very little meaning for our comparison. The only efficiency of real interest is the total system efficiency based on available fission energy in the uranium, which depends not only on reactor efficiency but also on the total fuel cycle, including fuel enrichment, fuel utilization, and waste disposal. Thermal efficiency is therefore here regrettably a meaningless criterion, unless we again compare it with cost. That seems like a difficult hurdle, but for our case we can overcome this problem. Any reactor that supplies heat at a high temperature could also be used to generate electricity. This fact allows us a reasonable process comparison, as we can use the same reactor in both cases.

If the comparison shows a strong advantage for the new technology using the same reactor, we can come back to this point and evaluate the potential advantage of electrolysis resulting from its ability to use a low temperature reactor. Efficient process evaluation should always be iterative in this sense.

**Table III.** Investment for Hydrogen by Electrolysis using Current Nuclear Reactor (In 1977 Dollars/MMBTU of  $H_2$ /day)<sup>a</sup>

electrolysis plant	\$3 000– \$4 500
nuclear reactor, 12–15 kW installed capacity at \$800/kW	\$9 600–\$12 000
total investment	\$12 600 \$16 500
breakdown of nuclear reactor cost per kW installed (approximate)	
reactor itself (installed)	\$250
investment associated with electricity generation (steam turbine, generator, condenser, cooling water system)	\$200
shielding, construction, offsite	\$350
total	\$800

<sup>a</sup> Note: Erected plant cost includes engineering but no contingencies or interest during construction.

**(b) Efficiency of Electricity Generation in High-Temperature Nuclear Reactors.** We will therefore consider the differential efficiency of electricity generation in a high-temperature nuclear reactor used for a hybrid or a thermochemical cycle. A general representation of such a scheme is given in Figure 3. A primary helium cycle cools the reactor and transfers the high-temperature heat to a secondary helium cycle that in turn transfers heat to the process. Instead of a chemical cycle and the heat exchanger of the second cycle, we can substitute a steam generator and a steam power plant. One would probably prefer to use the primary helium cycle as a topping cycle and the steam as a bottoming cycle. In fact, some of the high temperature reactors mentioned in connection with thermochemical cycles were originally developed to generate electric power using topping cycles. An efficiency of 47% for electricity generation is therefore a reasonable base case for our comparison, since it is based on the same reactor and on the same design principles.

There is a reasonable possibility that electricity from such high-temperature reactors is going to be more expensive compared with electricity from present reactors. Topping cycles coupled with high-temperature reactors have been promoted for years, but have never caught on in nuclear reactors because of their cost and other associated problems. Thermochemical cycles are more expensive and more complex than helium topping cycles, having additional corrosion and safety problems, and have very similar cost tradeoffs between temperature and thermal efficiency.

**(c) Cost Considerations.** To understand the importance of different elements of the electrolysis process, let us look at the investment breakdown for such a plant, which is given in Table III, both for available technology and future technology. Costs for electrolysis are taken from Nuttel (1977) Cornell et al. (1977). This investment depends on cell voltage. We can increase efficiency in available cells by reducing current density and thereby increasing investment cost.

The total nuclear reactor investment is estimated as \$800/kW installed. The part associated directly with electricity generation, containing the turbine, the condenser, the heat exchangers in the steam generator, the cooling water, and so on, costs about \$150–\$200/kW installed. The reactor itself is cheap, and its installed costs would be about \$200–\$250/kW. The rest is for the containment, construction cost, safety features, and so forth. The actual capital requirement in a nuclear plant is considerably higher, as there is a large interest charge during the long delays required for licensing. We do not include

Table IV. Cost of Hydrogen by Electrolysis (Utility Financing)

	\$/MMBTU product
capital charges + operating charges and maintenance ( $8 \times 10^{-4} \times$ investment per daily MMBTU)	10.70-13.35
fuel charges	1.50
	\$12.20-14.85

this factor in the calculations, which deal with erected plant costs only.

The capital related cost of hydrogen from such a plant would be far larger than present costs of oil or gas. For utility financing, a reasonable approximation is given by multiplying the investment, which here is for one MMBTU of  $H_2$  per day by a factor of  $8 \times 10^{-4}$  to  $10^{-3}$ . The experience factor was derived by looking at a large number of published cost estimates for utility plants and computing the cost of a delivered unit of product from the investment required to produce one unit per day. The computation is complex but the results fall into this narrow range. This factor is based on current finance charges and includes depreciation, profit, taxes, interest on debts, and operating and maintenance expenses estimated on the basis of investment per unit of daily production. (It does not include the large charge for interest during construction that is typical for nuclear reactors.)

If we use a factor of  $8 \times 10^{-4}$  (\$/unit/\$ investment for producing one unit per day) the investment-related cost of hydrogen on a 1977 basis would be about \$10.70/MMBTU, whereas the fuel cost would be about \$1.50/MMBTU (Table IV). The total cost is \$12.20-\$14.85/MMBTU, far too high for present use. But we deal here with the far future, and we can therefore look at the cost of hydrogen generation from a nuclear reactor by the proposed new technology in comparison with the estimated cost for available technology using nuclear reactors. The numbers in Table III are not very accurate. However, in differential analysis the accuracy is less crucial than in straightforward cost estimates.

We must now ask what is minimum potential advantage that would make a new route attractive for development. That is an important management judgment that should be specified as it affects the required accuracy of the analysis. We ourselves would consider the minimum advantage required to be at least 20% of total investment, but the reader can adjust it according to his judgment. Our reason is as follows: electrolysis is a readily available technology with significant potential for further development. Furthermore, it has significant safety advantages since it is easier to separate the nuclear reactor geographically, from the hydrogen plant. A large hydrogen plant or any refinery has a small finite chance for occurrence of fires or explosions and therefore should not be close to a nuclear reactor. Furthermore, in electrolysis there is no possibility of contamination by radiation. Considerations of safety, potential raw material prices, or availability should be a part of any new process evaluation.

## VI. General Process Constraints of Thermochemical and Hybrid Cycles

The requirement of two intermediate helium loops introduces an additional inherent disadvantage to thermochemical cycles. To get a high theoretical efficiency, we want a process with all the net heat input occurring at a high temperature. Assume now that we can find a process that requires all its heat inputs at 1700 °F (927 °C). We are restricted, at present, in the maximum temperature

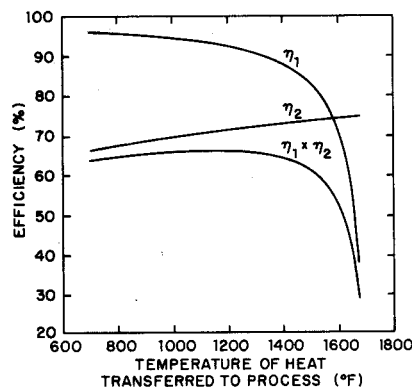


Figure 4. Theoretical process efficiencies.  $\eta_1 = Q/(Q + P_a) =$  efficiency of transferring heat to the process;  $\eta_2 = 1 - (T_L/T_m) =$  Carnot efficiency for a process operating with ramp heat input;  $P_a =$  energy needed to pump helium to enable heat transfer;  $Q =$  heat transferred to process, 3345 MW;  $T_L = 80$  °F;  $T_m =$  mean temperature of ramp =  $[(1700 + 460) - (T + 460)]/\ln [(1700 + 460)/(T + 460)]$ ; pressure drop in helium cycle = 30 psi; compressor efficiency = 85%; heat to power efficiency = 45%.

for the reactor and the helium loops by the availability of suitable materials to about 1800 °F. The design of such a system would be difficult. As helium is a gas and, unlike steam, does not condense, the amount of heat transferred per pound of helium is a function of the temperature drop,  $\Delta T$ , in each helium loop. We must allocate the 100 °F drop to provide the heat-transfer driving force between the primary and the secondary cycles, the secondary cycle and the process, and the required temperature drop of the helium in each loop. To fit all these with a 100 °F temperature drop would require a very large helium circulation, a small  $\Delta T$  between streams, and therefore large heat exchangers. Power is required to pump the helium in the two loops and power requirements are inversely proportional to the  $\Delta T$  in the loop. Therefore, we must find a process with heat requirements that allow a reasonable  $\Delta T$  for the helium cycle. The best we can hope for is a ramp input with constant slope. We can then compute the Carnot efficiency of such a ramp process, taking into account the energy needed to overcome the friction losses in two heat exchangers. A preliminary estimate and breakdown of these efficiencies is given in Figure 4. (Also given are the assumptions underlining the calculations.)

Note that the overall efficiency has a maximum of 66% for a  $\Delta T$  of approximately 600 °F. Despite the fact that the top temperature is higher by 600 °F, we start with a lower theoretical Carnot efficiency than a steam cycle due to the penalties of indirect heat transfer. We can overcome part of this limitation by using the primary helium cycle for power generation at the same time. But then we are departing from a pure thermochemical process. We will have to include this penalty in estimates for a maximum efficiency of a thermochemical cycle, since the penalties incurred in the cycle itself are additive to it.

## VII. Process Constraints of Hybrid Cycles

We consider first the hybrid cycles, which at present are considered the most promising cycles and are also easier to evaluate. Hybrid cycles gain their advantage over thermochemical cycles by incorporating a low-voltage electrolytic step, therefore allowing a two-step cycle. The electrolytic step makes the comparison easier, as all electrolytic processes have some similarities with respect to both efficiencies and cost.

Let us look at what determines the efficiency of an electrolytic process. There are three main types of energy losses: (1) losses associated with solution and electrode

Table V. Performance Data of Various Existing Electrochemical Processes<sup>a</sup>

process	over voltage, V	working voltage, V	theoretical voltage, V	voltage efficiency, %	current efficiency, %
chlorine-diaphragm	0.6-2	2.9-4.3	2.3	63-79	95
chlorine mercury	0.85-1.6	3.95-4.70	3.1	72-85	95-98
chlorine-Downs	3.15	6.60	3.4	52	80
fluorine-diaphragm	6.1-10.1	8-12	1.90	16-24	90-95
chlorate	0.82	3.4	2.58	76	9.4
water	0.33-0.81	1.56-2.04	1.23	60-79	99

<sup>a</sup> Chalmers (1968); Hardie (1976); Stuart (1972).

Table VI. Estimated Efficiency for the Sulfuric Acid Cycle (Theoretical). Basis: 10<sup>6</sup> Btu of H<sub>2</sub>

step	T <sub>m</sub> , K	$\eta_G$ (Carnot)	$\Delta G \times 10^{-3}$ (kcal)	$\Delta G \times 10^{-3}$ (Btu)	heat required to process (theoret), Q $\times 10^3$ Btu	heat from nuclear reactor, Q/0.9 $\times$ 10 <sup>3</sup> Btu	efficiency, $\Delta G/0$ , %
Case 1: Sulfuric Acid Solution 80%							
concentration	550	45.4	25.66	101.8	329.3	365.8	27.8
evaporation and dissociation	700-900	66.6	72.86	289.1	542.3	602.5	48
decomposition	950	68.4	61.49	244	335	372.2	65.5
separation			1.4	5.5	55.5	55.5	10
total			161.41	640.4	1262.1	1396	45.8
Case 2: Sulfuric Acid Solution 50%							
concentration	550	45.4	45.96	182.4	1044	1160	15.7
evaporation and dissociation	700-900	66.6	72.86	289.1	542.3	602.5	48
decomposition	950	68.4	61.49	244	335	372.2	65.5
separation			1.4	5.5	55.5	55.5	10
total			181.71	721	1976.8	2190.2	32.9

resistance, (2) losses due to selectivity of the reaction, and (3) losses due to excess voltage due to polarization of the electrode.

Item 2 is negligible in electrolysis of water. Items 1 and 3 are independent of theoretical voltage and mainly a function of current density and electrode properties. The fact that these losses are not correlated with process voltage can be seen from Table V, which lists  $V$  and  $\Delta V$  for different commercial processes. The dependence of excess voltage on current density is well known, and actually, water electrolysis has the best performance achieved by any electrolytic process. There is no reason to expect that any proposed process, such as the cycle in eq 3, should have any advantage over the electrolysis of water. We must be careful in formulating this conclusion. We do not say that one cannot build a cell for the hybrid process with a lower excess voltage than for the electrolysis of water, but rather that the cost benefit relations that determine the excess voltage are very similar for the two cases. We note here, suddenly, an unexpected penalty. The low voltage of the electrolytic cell makes the theoretical overall cycle efficient, but it reduces the practical efficiency of the electrolytic step. In fact, the losses associated with that step are at least the same as those associated with the electrolysis of water, if not larger. If we hope to get a better efficiency, it has to come from the thermochemical step. It must generate the positive  $\Delta G$  associated with it more efficiently than electricity generation, which has an estimated efficiency of 45-47%.

The  $\Delta G$  that the chemical step must generate is equivalent to 1.23 V minus the voltage of the electrolytic step in the hybrid process. Even if there is a 20% advantage here, the overall advantage is going to be much smaller, as we deal a priori only with 50-65% of the electricity requirement for electrolysis.

Let us now consider the proposed Westinghouse process as an example for hybrid cycle (Farbman, 1976). A sim-

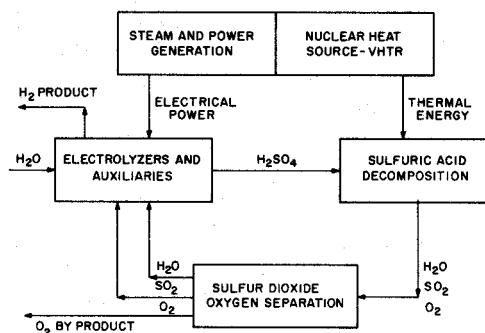


Figure 5. Schematic flow sheet of the hybrid sulfuric acid cycle (Farbman, 1976).

plified flowsheet of this process is given in Figure 5. The electrolytic reaction, step 3, has a theoretical voltage between 0.2 and 0.45 V depending on the concentration of the solution. For 100% (wt) sulfuric acid the theoretical voltage will be 0.45 V and our real voltage based on experience with other processes about 1.1 V. However, operating in 100% (wt) sulfuric acid is not practical. The use of a more dilute solution calls for a lower voltage but also requires larger amounts of heat to concentrate the solution. Creating  $\Delta G$  by concentrating a solution is inherently inefficient.

In the Westinghouse process, about 16-36% of the free energy is generated in the electrolytic cell. The rest is generated in the thermochemical step. However, the generation of  $\Delta G$  in the cell has a low efficiency since it has the same total loss as electrolysis of water and a much smaller  $\Delta G$ .

Let us now look at the efficiency of the decomposition of sulfuric acid. We can estimate the theoretical efficiency of steps 3b to 3d simply by considering the thermodynamic requirements of each step. Table VI gives two cases. The first deals with a cell producing a concentrated sulfuric acid

(80% (wt)  $H_2SO_4$ ). Such a cell has not been demonstrated, but is included as an optimistic limiting case. The second deals with a more dilute solution (50% (wt)) similar to the one in the experiments published in Warde (1976). The efficiency given is equivalent to eq 5, which is appropriate, since we are interested in evaluating an upper limit on the efficiency of the thermochemical step.

The only exception is the separation of  $SO_2$  for which we used a practical estimate, since efficiencies of separation processes are normally less than 10% of theoretical. The overall penalty due to the separation is small, since the contribution to the overall increase in  $\Delta G$  is small.

The most efficient step is the catalytic decomposition (step 3). It occurs at the highest temperature and is therefore expected to be more efficient (65%). Regrettably, it generates only half the required increase in  $\Delta G$ . The concentration and evaporation of the sulfuric acid occur at lower temperatures, which generate about half the  $\Delta G$ , and are less efficient. It is therefore a priori clear the case 2 will be less efficient than case 1, since case 2 generates a significant  $\Delta G$  at low temperature by concentrating a solution of sulfuric acid.

The overall efficiency of case 1 (46%) is about the same as generating electricity from a high-temperature nuclear reactor. In case 2 the efficiency is lower (33%). The impact of the high heat requirement at low temperature can be reduced by incorporating the thermochemical step into the electricity generation and operating it partly as a bottoming cycle. It would still be difficult to exceed the overall efficiency of electricity generation in a plant with a combined helium-steam cycle.

The above efficiencies were based on theoretical requirements assuming 100% conversion. In practice, conversion will be less than 90%, which will affect all heat requirements but that of the reaction. Furthermore, we neglected losses due to finite driving forces which are at least 100 Btu per pound of sulfuric acid decomposed or at least 90 000 Btu.

This loss increases the minimum total heat requirements of case 1 to  $1.61 \times 10^6$  Btu/ $10^6$  Btu  $H_2$  and of case 2 to  $2.49 \times 10^6$  Btu/ $10^6$  Btu  $H_2$ . The corresponding efficiencies  $\eta_G$  will be 40% and 29%. These efficiencies are not estimates of real process efficiencies but optimistic bounds. We see that this step is not competitive with electricity generation in a high-temperature nuclear reactor, even under the most optimistic assumptions. The overall thermal efficiency of the hybrid process will therefore be lower than for the electrolysis of water.

We conclude that the Westinghouse cycle offers no potential advantage with respect to thermal efficiency and would probably have a lower efficiency than an electrolytic process designed on the same basis. With the present state of technology, this would apply to all hybrid processes proposed.

### VIII. Differential Process Comparison of Hybrid Cycles vs. Electrolysis

Table VII summarizes the process requirements of two routes. The first route is electrolytic decomposition of water and the second route is the Westinghouse process, but our arguments can be generalized to any hybrid cycle.

The next step is evaluating the similarities and differences between the two processes. If we find sections of the plant that are similar, we can compare them and evaluate any cost difference due to size, and then focus our comparison on the relative costs of those sections which are different. Such a comparison is given in Table VIII. We assume here that the basic nuclear reactors are identical, as explained before. Electrolysis has an advantage

Table VII. Process Requirements for Electrolysis and Westinghouse Process

	electrolysis	Westinghouse hybrid cycle	$\Delta$
efficiency			
$\eta_G$	30.6%–38.3%	28.7%–35.4%	
$\eta_H$	36.7%–46%	34.4%–42.5%	
size of nuclear reactor	same or smaller	same or larger	
primary helium cycle	same	same	
secondary helium cycle	not required	required	+
electrolytic cell	same	same	+
voltage required	1.23 V + losses	0.29 V + losses	-
electricity generation			
installed capacity required	12.0–15 kw/ $10^6$ Btu of $H_2$ /day	4.2–7.2Kw/ $10^6$ BTU of $H_2$ /day	-
steam generation	larger	smaller	
sulfur cycle	not required	required	
		(a) concentrate 1100 lb of sulfuric acid	
		(b) evaporate 900 lb of sulfuric acid	
		(c) decompose catalytically 900 lb of sulfuric acid	
		(d) separate 520 lb of $SO_2$ from 130 lb of $O_2$ to very high purity in both streams	

Table VIII. Differential Investment Cost (\$/Daily MMBTU of  $H_2$ )

	electrolysis	hybrid Westinghouse cycle
steam electricity generator (incremental 7.7 kW)	\$1150–\$1550	
chemical plant (based on mass flows and comparison with sulfuric acid plants)		>\$3000
total	\$1150–\$1550	>\$3000

in the primary helium cycle, which has less constraints. We will neglect this advantage and lump the primary helium cycle together with the basic reactor, plus all costs associated with the reactor itself, such as structure, containment, and so on.

If the thermal efficiency is approximately the same, the cost of the nuclear reactor itself can be assumed to be equal for both processes. Let us look first at other features common to both routes. There is no reason to assume that the electrolytic cell of the hybrid process should be significantly cheaper than an equivalent electrolytic cell for water. The tradeoff between cell cost and energy losses in the cell are similar, since losses are a function of current density. The only savings are in the lower transformer and distributor costs, which are less than 20% of the total cell cost. Estimating a potential savings does not always require accurate process data. If we understand the cost factors involved in designing electrolytic cells, we can evaluate the basis for any hope to reduce those costs. GE looks to reduce all costs by increasing current density without increasing the losses due to resistance, and by reducing the distance between electrodes using a polymer fiber as the electrolyte. In contrast none of the proposed

hybrid processes uses any principles that should make their cell design potentially cheaper than a conventional electrolytic cell. We have focused here on a critical parameter that the researcher must evaluate. If he does not agree with the opinion presented here, he can put forward his counter-arguments. In accepting the fact that there is little potential for savings in the cell cost, we are left with only one item in each route that cannot be matched. The electrolytic route will have a larger electricity requirement, whereas the hybrid cycle here substitutes a thermochemical step. The cost of increased electric requirement that we must include here is only the cost of the incremental electricity generation excluding the nuclear reactor. As both routes share the primary helium cycle and the hybrid process must also generate electricity, we can assume that the incremental electricity is made by steam in the steam bottoming cycle. We can break this cost into two parts: the steam generation itself and the turbine generator section, including the condenser and the cooling water requirements. The steam generation section can again be matched with an equivalent item in the hybrid cycle. The secondary helium cycle has a thermal load as big as the load of the steam generator. However, the heat transfer coefficients are lower and compression is required. The steam generator should therefore cost less.

The cost comparison is reduced to comparing the cost of the turbine generator, the condenser, and the cooling water system in the electrolytic route vs. the cost of the thermochemical step in the hybrid cycle, which in the Westinghouse cycle is decomposition of sulfuric acid.

The incremental electricity requirements are equivalent to the voltage of  $(1.23V_{\text{hybrid}})$ . If  $V_{\text{hybrid}}$  is 0.29 V, it is equivalent to an installed capacity of 7.7 kW/MMBtu  $H_2$ /day. Let us look at the investment cost of this section. The electricity generating section of a standard nuclear reactor (or of a coal power plant) costs about \$150–\$200 per kW installed. Thus, the total investment for this item is \$1150–\$1550. We have to compare this total cost with the cost of concentrating and evaporating 0.5 ton of sulfuric acid per day, catalytically decomposing it, and then separating the  $SO_2$  from  $O_2$ . We need no analysis to show that the thermochemical step is more expensive than a steam power cycle. A sulfuric acid plant, which is far simpler, requires an investment of \$3000 for the same production rate per day.

We can go a little further. The amount of material that must be dealt with, in the thermochemical step, is extremely large. One MMBtu of hydrogen is 16.4 lb. If the molecular weight of the material in the thermochemical step is 50, we need to treat 410 lb of sulfuric acid per day. There are very few processes that can do that for an investment of less than \$1150. A compilation of investment costs per unit product was made for 46 chemical processes of varying complexity. (See Table IX.) The only one with an investment of less than \$1/lb per day is a naphtha pretreater in a refinery or a crude tower. Catalytic reforming of naphtha, which is far simpler, is already \$3/lb. There is therefore practically no chance that the thermochemical step of a hybrid cycle could compete with the cost of electricity generation. The operating and maintenance costs would also be far higher for a chemical process. Here, we come to one important point that should always be checked in preliminary evaluation, namely, that costs are based on the same design criteria. Power plants are designed for lower maintenance costs than chemical plants. If we computed, as is common in preliminary estimates, maintenance and investment costs as a percentage of an investment, we precluded any benefit from incremental

investments that are made to reduce operating and maintenance costs.

We can finish our evaluation at this point and conclude that hybrid cycles have inherent disadvantages, compared with electrolysis, that are not compensated for by any significant advantage. Their cost should be intrinsically higher if properly computed on the same basis. This conclusion applies to all hybrid cycles proposed till now, since the disadvantage has fundamental causes that can be seen by considering the process constraints of both processes.

Till now we have performed all the evaluations without taking into account any detailed engineering evaluation. We were able to achieve our results just by looking in detail at the similarities of the processes. We can now compare our results with actual detailed evaluations of the Westinghouse process. The first evaluation (Farbman, 1976) projected a totally unrealistic potential advantage: half the cost and a much better thermal efficiency. This illustrates what can happen in straight cost evaluations when no attempt is made to put both processes on the same basis; there, the two cases compared had different nuclear reactors with different cost basis. In Farbman (1978) an attempt was made to make the comparison on a consistent basis. Farbman (1978) still claims the potential of a small advantage in cost and thermal efficiency. Its analysis shows that this could only occur if the energy losses in the Westinghouse electrolytic cell are all much smaller than in the electrolysis of water, at no penalty in cost, which is highly unlikely.

## IX. Limitations of Thermochemical Cycles

We discussed in section IV the general stoichiometric and thermodynamic constraints of the thermochemical cycles. Since at present there is really no thermochemical cycle that is considered attractive, we will try to look at the problem in a more general way. How can we estimate in advance, in a simple way, whether such a process looks attractive, and how can we efficiently screen for new processes?

In section IV we gave a relation for thermal efficiency that yields an approximate estimate for the upper limit that could be achieved by a pure thermochemical cycle. For processes that survive the first screening, we can refine that estimate by actual calculations of  $\Delta G$  and  $\Delta H$  and the entropy changes due to heating, cooling, and phase changes of each step at the projected operating conditions. That will give us a refined upper bound, one that is lower than the first.

In power cycles there are reasonable experience factors between the theoretical efficiency and the practical efficiency of a proposed cycle. There are no equivalent relations between the theoretical and real efficiencies of chemical process (Linhoff, 1978). That can be seen immediately from the fact that many mildly exothermic processes, those with a negative free energy, such as a hydrotreater for fuel oil, often require outside net energy input to operate. However, a reasonable estimate for an upper bound for efficiency is useful for screening new processes as it provides a tool to eliminate those processes that are a priori inferior to existing technology. We can now go to step 2 of our screening process. We can look at a simplified flowsheet in somewhat more detail and evaluate the inevitable thermal losses associated with the process steps. A specific flowsheet can yield a preliminary estimate of thermal efficiency of each step without detailed engineering.

**1. Losses Due to Heating and Cooling.** Equation 5 assumed perfect heat exchange between the feed and the

Table IX. Investment Cost for Various Chemical Processes (1978)<sup>a</sup>

	investment cost		
	\$/ (ton day)	\$/ (lb day)	\$/ (lb-mol day)
acetic acid: via exothermic conversion of methanol and carbon monoxide in presence of catalytic agents; PU and SF	130 000	65	3900
acetone: from propylene, using copper, chloride; PU and SF	32 000	16	928
acrylonitrile: via catalytic reaction from acetylene and hydrogen cyanide PU and SF	160 000	80	4240
alkylation: PU	20 000-25 000	10-12.5	
ammonia: via steam reforming to convert light hydrocarbon gases or naphtha into 99.9% pure anhydrous ammonia; PU and SF	83 000	41.5	705
ammonium sulfate: reaction of ammonium hydroxide and sulfuric acid, with evaporative process resulting in solid nitrogenous fertilizer	8000	4	460
butadiene: from butane, via dehydrogenation and catalytic reaction butylene are byproducts; PU and SF	51 000	25.5	1379
butanol: from propylene, carbon monoxide and water, via catalytic reaction to produce high-purity 1-butanol and 2-butanol; PU and SF	66 000	33	2446
chlorine: via electrolysis of sodium chloride; byproduct: caustic soda; PU	51 000	25.5	1808
crude oil distillation: PU	1500-2000	0.75-1	
cyclohexane: from benzene, via catalytic hydrogenation (99.9% pure) PU, hydrogen plant and SF	15 000	7.5	631
ethanol: from ethylene gas and condensate, via catalytic reaction and purification; PU and SF	950 000	475	21 883
ethylene (high-purity): from ethane via steam pyrolysis and low-temperature distillation	180 000	90	2520
ethylene oxide (high-purity): from commercial ethylene, via catalytic oxidation and isothermal process; PU and SF	290 000	145	6387
formaldehyde (aqueous): via catalytic oxidation and absorption; PU and SF	260 000	130	3903
fluid bed cracking: PU	6000-8000	3-4	
glycol (high-purity): from ethylene and chlorine; PU	660 000	330	20 483
hydrochloric acid: from HCl and water via dissolution; PU and SF	130 000	65	2370
hydrofluoric acid: from HF and water via dissolution; PU and SF	220 000	110	2201
hydrogen (high-purity): via separation from petroleum and petrochemical off-gas; PU	80 000	40	80
hydrogen from steam reforming of methane	250 000	125	250
isoprene: via a catalytic reaction and distillation, using propylene, methanol, and oxygen as feedstock; byproducts: isobutylene and off-gas; PU and SF	88 000	44	2996
methanol: from natural gas, via a reforming and synthesis process; PU and SF	30 000-40 000	15-20	480-640
naphtha pretreater: PU	2100	1.05	
nitric acid: (high-strength, high-purity): from anhydrous or gaseous ammonia, via catalysis and absorption; PU and SF	12 000	6	378
p-xylene: from xylene-rich hydrocarbon streams and hydrogen, via a crystallizing and catalytic recycle process; byproducts: light ends, aromatics; PU and SF	360 000	180	
phenol (high-purity): from toluene, via oxidation and catalytic conversion; PU and SF	130 000	65	6117
phosphoric acid: from calcium phosphate and sulfuric acid; PU and SF	73 000	36.5	2919
phthalic anhydride (high-purity): from naphthalene and air, via an exothermic reaction and distillation process; PU and SF	66 000	33	
polyethylene (high-density): from pure ethylene, via a catalytic reaction and high-pressure separation; PU and SF	510 000	25.5	
polyvinyl chloride: from vinyl chloride; PU only	440 000	220	
reforming of naphtha	7000-8000	3.5-4	
styrene: from benzene, ethylene, steam, via a catalytic reaction, with alkylation, and distillation to recover styrene monomer; PU only	80 000	40	4165
sulfur: via an oxidation reaction to recover basic sulfur from hydrogen sulfide gas; PU only	66 000	33	1058
sulfuric acid: from sulfur, via a catalytic reaction; PU and SF	6600	3.3	323
total refinery cost	30 000-35 000	15.0-17.5	
urea (prills or crystals): from ammonia and carbon dioxide, via exothermic reaction, decomposition and prilling; PU and SF	28 000	14	840
vinyl acetate: from ethylene and oxygen, via a catalytic reaction and distillation; PU	13 000	6.5	559
vinyl chloride: from ethylene, chlorine, and air, via thermal cracking, high-pressure compression and distillation; PU	80 000	40	2500

<sup>a</sup> The investments' costs are taken from Guthrie (1970) and *Hydrocarbon Process*. (1978) and are updated by the following method: The numbers in Guthrie (1970) were chosen for the largest plant multiplied by a factor of 4 which includes an inflation adjustment by a factor of 3 and another 33% for incremental offsite. PU = Process Units. SF = Storage Facilities.

product streams. In reality the driving force needed leads to an irreversible energy loss. A good minimum estimate is about 50-100 Btu per pound of material processed. Here, we must also take into account the amount of recycle processed: thus the 50-100 Btu refers to the total feed and

not simply to the fresh feed.

**2. Pumping and Compression Requirements.** Moving materials through reactors in any process requires energy. Again, a reasonable estimate for minimum requirements is about 50 Btu per pound of total feed han-

dled.

**3. Energy Degradation in Phase Changes.** Most of the cycles proposed contain steps where either the feed or the product undergoes a phase change. In most cases there is another loss: the phase changes in feed and product occur at different temperatures and the heat invested in feed preparation cannot be recovered. The penalty increases with incomplete conversion. An example was already noted in the sulfuric acid decomposition step. Another example can be seen in step 1 of the Schulten cycle. To achieve the conversion excess steam is used. We supply high-grade steam to the process but recover it from a gas as low quality heat. This is the main process loss for steam reforming of methane. If we look only at theoretical requirements, the loss is small. We could recover the steam by separating it from the gas in an ideal membrane. In reality the heat of condensation is recovered at a low temperature which leads to a large energy penalty for incomplete conversion.

**4. Separation Processes.** Separation processes, such as distillation and crystallization, are very inefficient and have energy requirements between ten and one hundred times that of theoretical. They therefore must be minimized. A factor of 10 gives a reasonable lower estimate for screening.

We can use these experience factors to derive some additional constraints for thermochemical cycles. Let us look at the hypothetical case where our theoretical efficiency is 60% in terms of  $\Delta G$ . If we are ready to accept  $\eta_G = 40\%$  or  $\eta_H = 48\%$ , we can allow a total of 2 MMBtu/1 MMBtu of  $H_2$  produced to be used in the plant. Assuming the energy losses in the helium cycles are 10%, that leaves us with 1.8 MMBtu for the plant; 1.39 MMBtu of this are required for the theoretical heat requirement of the process, which leaves 0.41 MMBtu for the total process losses.

What limitations does this impose on the choice of potential processes? Let us look at the unavoidable losses related to heating and cooling. If we assign 250 000 Btu of our total allotment for losses to these demands, and assume loss of 100 Btu/lb processed, then we can process at best 2500 lb of total feed to all process steps per MMBtu  $H_2$  produced per day. As we need 9.2 mol of  $H_2$  per MMBtu produced, this gives about 300 lb per mol of  $H_2$  per day.

The minimum requirements of materials to be processed per mole of  $H_2$  are simply the sum of the molecular weights in each process as written in Table I. We must be careful, as one stoichiometric relation can involve several stages. But we can immediately note that even the simple sum as given in the table must be less than 300. Since conversion is seldom complete, 200 to 250 is a more reasonable number. It is clear that we can have no recycles of high molecular weight materials since that would involve large thermal losses.

Furthermore, we cannot afford any large losses for separation processes. These requirements would by themselves rule out most of the processes that have been considered till now. The Schulten cycle would almost survive ( $\sum M_w = 288$ ). However, this cycle fails if we look closer. Methanol production involves high recycles. But more important, the steam requirements would ruin the thermal efficiency. Steam reforming of methane (step 1) is a commercial process and the irreversible losses associated with it are about 300 000–400 000 Btu/MMBtu of  $H_2$  produced. We have to multiply these losses by four since we get only 1 mole of net  $H_2$  for every mole of  $CH_4$  reformed instead of 4 moles in hydrogen production in an open cycle. For every 1 MMBtu of net  $H_2$  we use 300 lb

of steam in the reformer. The losses associated with the steam production alone are equal to our total allowable heat loss. For the Schulten cycle commercial experience can be used to realize that the efficiency must be lower than our goal. Steps 1 (steam reforming) and 2 (methanol production) are similar to the commercial production of methanol from methane. The overall thermal efficiency of this process is about 65%. Translating this figure into our stoichiometry gives process losses in this step of 1.2 MMBtu of  $H_2$  compared with the maximum of 0.8 MMBtu. Employing data from existing processes is a very useful way of checking results.

Based on the foregoing it is not surprising that a more thorough evaluation involving detailed flowsheeting showed that the Schulten process has no chance to compete with advanced electrolysis (see Funk (1976), which estimates an efficiency of  $\eta_H = 0.37$ ). We are not aware of any process that passes the second-stage screening. Our goal here is not to prejudge the possibility of such a process's existence, but rather to establish a priori a criterion for evaluation.

One main problem of thermochemical cycles proposed till now is the tremendous amount of material to be processed. If for comparison we look at the steam power cycle of the electrolysis process, only about 2000 lb of steam must be processed for the thermal part of the cycle per MMBtu of  $H_2$ , or about 250 lb of steam per mole of  $H_2$  per day. Pure steam has the further advantage that it can be generated and condensed with very high heat transfer coefficients and therefore low driving forces.

## X. Economic Considerations of Thermochemical Cycles

Till now we considered only thermal efficiency. We can also consider the chance of significant cost reduction at the same thermal efficiency. We must also ask what constraints we have to put on our process in order not to nullify any potential economic advantage due to thermal efficiency, should we find a process that has a potential for higher thermal efficiency. Again we have to establish a reasonable goal for cost reduction due to a new process, and we will again use the 20% criterion. Having established our goal, we then have to look to where our potential savings could come from and evaluate our chances of achieving them.

Let us start with the nuclear reactor itself. It makes up a big part of the cost of an electrolysis plant (over 70%, Table III). If we deduct from this cost the identifiable costs of electricity generation, we still have about 60% of the total cost. What are the conditions for a 20% reduction in costs? We will neglect here, for purposes of initial screening, the fact that operating costs in chemical plants are higher compared with those of electricity generation and electrolysis and judge costs solely by investment. A 20% reduction in costs requires a 20% reduction in total investment. We can ask the question in two ways: (1) What price can we pay for a thermochemical process that has the same efficiency as advanced electrolysis? (2) What price can we afford to pay for a thermochemical process that increases the efficiency and reduces the size of the nuclear reactor by 20%?

In case 1 we are limited for the thermochemical part to a total investment of \$2880–\$4000 per MMBtu of  $H_2$  per day. In the second case we can increase this figure to \$4320–\$5440. To simplify matters we will use a number of \$4000 for the analysis.

Again we can do our screening in several stages. In the first let us look at general process requirements. We will base all numbers on a figure of 1.0 MMBtu of  $H_2$  produced.

In this case large amounts of heat must be transferred. For the case of a 20% higher efficiency, the heat input to the process is 2 MMBtu. Since our product has a  $\Delta H$  of 1 MMBtu, an additional 1 MMBtu must be removed in cooling systems. Second, heat must be transferred between feed and product streams. We therefore deal with total heat transfer requirements of at least 4 MMBtu/day or 167 000 Btu/h per MMBtu of  $H_2$  per day.

The desire for high thermal efficiency mandates lower temperature gradients. Let us assume 100 °F as an average driving force. What constraints does this temperature put on our process? Heat exchange will be an important cost item and based on experience with similar processes, we cannot afford to spend more than one-third of our investment on heat exchangers. Let us assume as an upper limit, that we have 40% of \$4000 at our disposal or \$1600. Heat exchangers in large installations that are appropriate to the discussion here are about \$15–\$20 per square foot, installed carbon steel, \$40–\$60 for high-alloy steels, and up to \$150 for special alloys such as Inconel. That implies we can afford at best 100 ft<sup>2</sup> of a simple steel heat exchanger, 40 ft<sup>2</sup> for an alloy steel, and less than 20 ft<sup>2</sup> for special alloys. These figures translate into a required heat transfer coefficient of 17 Btu/h ft<sup>2</sup> °F for carbon steels, 40 Btu/h ft<sup>2</sup> °F for high-alloy steels and above 100 Btu/h ft<sup>2</sup> °F for specialty alloys.

Simple carbon steels are almost out for the higher temperatures employed. We also cannot afford specialty alloys unless we deal with systems that have an inherently high heat transfer coefficient. We realize here the big advantage of the steam cycle with its high heat transfer coefficient, and we might remember that even there thermal efficiency was constrained by the fact that top temperature was limited to avoid the use of costly materials.

We realize here another design constraint on our process. In gas heat exchangers high transfer coefficients are related to high pressure losses that we cannot afford. We must therefore balance heat exchanger costs with the desire for high thermal efficiency. The constraint due to heat exchange cost is a severe limitation on the type of cycle we can choose and eliminates highly corrosive processes requiring special materials and also processes with high recycles, since in these cases the heat transfer load would increase.

If we look at the heat transfer requirements of the Schulten process, which we can get from a mass and heat balance, we see that it requires 6.9 MMBtu per day of heat transfer per MMBtu of  $H_2$ . In addition, part of the heat transfer, especially in step 4, occurs under very corrosive conditions. Therefore, we can conclude that the process has no chance of leading to substantial cost reduction compared with electrolysis. We come to similar conclusions for any other process proposed so far, since all of them have much larger heat transfer requirements than our minimum assumed and all involve very corrosive conditions for heat transfer such as the decomposition of  $H_2SO_4$  or the formation of HCl at high temperature in the Mark 9 or the Agnes processes.

If any process would have survived this step, we would go on to the next two criteria, which deal with another feature of these processes, namely, the large quantities of material processed. The importance of minimizing these quantities was mentioned with respect to thermal efficiency. Just as there are minimal energy losses related to each pound of material handled, there are minimum investment costs associated with it. If we look at Table IX we find that there are very few processes that can handle 1 lb of material per day at an investment of less than

\$1/lb/day. These are processes like crude distillation or a naphtha pretreater. Simple crystallization such as ammonium sulfate already requires \$4/lb/day. The processes mentioned in Table I or any of the cycles proposed are far more complex. If we assume a minimum investment cost of \$2 per lb fresh feed processed per day, then \$4000 allows us to deal with 2000 lb/day, or 250 lb per mole of  $H_2$  produced. The limit of \$2/lb requires that we deal with simple noncorrosive processes with low recycle. These figures translate into the stoichiometric constraint,  $\sum M_{wi} < 250$ , as we need 8 mol of  $H_2$  per MMBtu of product. This constraint is by chance identical to the constraint derived by considering thermal losses. None of the proposed processes fulfills this criterion.

We have here several ways to derive economic constraints suitable for screening ideas and for first evaluation. Some of these were overlapping and it is advisable to look at as many of these constraints as is feasible, as they provide insight into the properties that the desired process must have. If a process survives, and we are faced with a specific flowsheet, we can take our analogy somewhat further. We can use Table IX or similar sources to look for steps that are similar or identical to establish minimum costs.

Thus the Schulten process contains two steps that are well known: steam reforming or methane and methanol production. The combined cost of these two steps in a natural gas plant is about \$15–\$20/lb/day, which gives a total cost of \$3900–\$5200 per MMBtu of  $H_2$ . Our plants are much bigger than standard methanol plants but size effects in methanol plants from natural gas are small. Even if we halve the investment cost, we are left with too little money for the two corrosive steps. Similarly, we can put some minimum cost on the sulfuric acid decomposition by looking at a sulfuric acid plant, as we noted before, which should be well above \$3000.

We can find such close analogies for almost every step in any of the proposed cycles and we will again see that the only cycle surviving is the totally hypothetical two-step process given in eq 4. This is a fast and powerful method for preliminary evaluation. Table X presents some recently proposed cycles from Cox (1978). We do not have complete process information for those cycles, nor is that necessary. We can just use our criterion of  $\sum M_{wi}$  which is given in Table X, and we will see that all of them exceed our maximum by a factor of 4 or more, without counting recycles. All of them involve corrosive high-temperature steps; therefore, none of them has any realistic hope for high thermal efficiency or lower cost compared with electrolysis.

We can sum up our results by saying that none of the cycles proposed thus far has any chance of being economically attractive compared with electrolysis.

## XI. Summary and Discussion

In the preceding we tried to perform a differential economic analysis on a class of new processes proposed for development, namely, thermochemical and hybrid thermochemical cycles for the production of hydrogen from nuclear reactors. Although a considerable effort is still going on in developing such processes, no one process has reached the stage where complete data are available to construct a reasonably reliable flowsheet, even in a preliminary way. What we tried to do here was to investigate the potential of such processes to lead to cheaper hydrogen as compared with electrolysis of water. The conclusion arrived at was that none of these processes proposed so far appears to have any cost advantage over electrolysis of water. The properties required for such a process to be

Table X. Thermochemical Cycles under Development

	sum mol wt
1. Institute of Gas Technology (USA). Cycle H-5	
1. $\text{CuO} + 6\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{H}_2$	} 741
2. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 + 5\text{H}_2\text{O}$	
3. $\text{CuSO}_4 \rightarrow \text{CuO} + \text{SO}_3$	
4. $\text{SO}_3 \rightarrow \text{SO}_2 + 1/2\text{O}_2$	
2. Argonne National Laboratory (USA). Cycle ANL-4	
1. $2\text{NH}_3 + 2\text{KI} + 2\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{I} + 2\text{KHCO}_3$	} 1773
2. $2\text{KHCO}_3 \rightarrow \text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$	
3. $\text{Hg} + 2\text{NH}_4\text{I} \rightarrow 2\text{NH}_3 + \text{HgI}_2 + \text{H}_2$	
4. $\text{HgI}_2 + \text{K}_2\text{CO}_3 \rightarrow 2\text{KI} + \text{Hg} + \text{CO}_2 + 1/2\text{O}_2$	
3. Hitachi (Japan). $\text{Na}_2\text{CO}_3\text{-I}_2$ Cycle	
1. $2\text{NaI} + 2\text{NH}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 + 2\text{NH}_4\text{I}$	} 1287
2. $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$	
3. $2\text{NH}_4\text{I} + \text{Ni} \rightarrow \text{NiI}_2 + 2\text{NH}_3 + \text{H}_2$	
4. $\text{NiI}_2 \rightarrow \text{Ni} + \text{I}_2$	
4. Oak Ridge National Laboratory (USA). Cu/Cu (Ba, F) Cycle	
1. $2\text{Cu} + \text{Ba}(\text{OH})_2 \rightarrow \text{BaCu}_2\text{O}_2 + \text{H}_2$	} 1377
2. $\text{BaCu}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2 + \text{Cu}_2\text{O}$	
3. $2\text{Cu}_2\text{O} + 4\text{HF} \rightarrow 2\text{CuF}_2 + 2\text{Cu}^0 + 2\text{H}_2\text{O}$	
4. $2\text{CuF}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CuO} + 4\text{HF}$	
5. $2\text{CuO} \rightarrow \text{Cu}_2\text{O} + 1/2\text{O}_2$	
5. Los Alamos Scientific Laboratory (USA). LASL Cerium-Chlorine Cycle	
1. $2\text{CeO}_2 + 8\text{HCl} \rightarrow 2\text{CeCl}_3 + 4\text{H}_2\text{O} + \text{Cl}_2$	} 1644
2. $\text{BaCeCl}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{CeOCl} + 4\text{HCl}$	
3. $2\text{CeOCl} + 2\text{H}_2\text{O} \rightarrow 2\text{CeO}_2 + 2\text{HCl} + \text{H}_2$	
4. $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + 1/2\text{O}_2$	

attractive were also elucidated.

This conclusion could be arrived at without any detailed knowledge about a specific flow sheet of the new process and without any extensive engineering effort. It is important to try to thoroughly understand the cost-benefit tradeoffs that apply to available technology and the potential inherent advantages that would make a new process attractive.

In the case of hybrid cycles the similarities are so strong that we were able to directly evaluate the potential advantage of this new process and show that hybrid cycles are inherently not attractive as compared to straight electrolysis.

In the case of thermochemical cycles we were able to define simple screening criteria that such processes have to meet before they could have any chance of being at-

tractive. Regrettably, none of the processes proposed till now meets these criteria.

We tried here to present a systematic method of economic and technical screening of new processes which are still at a conceptual stage. This method is more illuminating and reliable than straightforward cost estimates and provides the results in a form that can be understood by the researcher and by the management.

### Literature Cited

- Appleby, A. J., et al. *Int. J. Hydrogen Energy* **1978**, *3*, 21-37.
- Chalmers, A. "Design and Fabrication of a Water Electrolysis Unit for an Integrated Life Support System", Advanced Electrochemical Products Div., Milwaukee, 1968; NASA CR 66654.
- Chao, R. E. *Ind. Eng. Chem. Prod. Res. Dev.* **1974**, *13*, 94.
- Cornell, H. G., et al. "Production Economics for Hydrogen Ammonia and Methanol during the 1980-2000 Period"; Exxon Research and Engineering Co., April 1977; Contract No. 368150-S.
- Cox, K. E. "Photochemical Process for Hydrogen Production"; Los Alamos Scientific Laboratory Report LA-2996-JR, 1978.
- Diamond Shamrock "Diamond Shamrock Modified Diaphragm Cells", Diamond Shamrock Co., Chardon, Ohio, 1977.
- Donat, G., et al. *Per. Energle* **1977**, *293*, 1017.
- Eisenstadt, M. N.; Cox, K. E. *Solar Energy* **1975**, *17*, 59-65.
- ERDA, Ad Hoc Committee, "An Evaluation of the Use of Hydrogen as a Supplement to Natural Gas"; prepared for ERDA 1977, TID 27747.
- Farbman, G. H. "The Conceptual Design of an Integrated Nuclear-Hydrogen Production Plant using the Sulfur Cycle Water Decomposition"; Westinghouse Electric Corp., April 1976; NASA CR-134976.
- Farbman, G. H., et al. "Hydrogen Production using Electrolysis versus a Hybrid Cycle"; EPRI Report EM 789, 1978.
- Funk, J. E. "Thermodynamics of Multi-Step Water Decomposition Processes"; 163rd National Meeting of the American Chemical Society, Division of Fuel Chemistry, Boston, April 1972.
- Funk, J. E. "A Technoeconomic Analysis of Large Scale Thermochemical Production of Hydrogen"; EPRI EM-287, 1976.
- Glandt, E. D.; Myers, A. L. *Ind. Eng. Chem. Process Des. Dev.* **1976**, *15*, 100.
- Gregory, D. P. *Sci. Am.* **1973**, *228*, 13-219.
- Guthrie, M. K. *Chem. Eng.* **1970**, *12*, 140-156.
- Hardie, D. W. F. "Electrolytic Manufacture of Chemical from Salt"; The Chlorine Institute, Inc., 1976.
- Hydrocarbon Process.* **Sept 1978**, 57.
- Kuhn, A. T. "Industrial Electrochemical Process"; Lectures in Electrochemistry, University of Salford, England; Elsevier Publishing: New York, 1971.
- Linhoff, B.; Flower, J. R. *AIChE J.* **1978**, *24*, 642.
- Marchetti, C. *Chemical Economy Eng. Rev.* **1974**, 288.
- Nuttel, L. J. *Int. J. Hydrogen Energy* **1977**, *2*, 395-403.
- Shinnar, R. *Science* **1975**, *188*, 1036-1037.
- Stuart, A. K. "Modern Electrolyzer Technology in Industry"; 163rd National Meeting of the American Chemical Society, Division of Fuel Chemistry, Boston, April 1972.
- Uhde, F. G. "Alkaline Chloride Electrolysis by the Diaphragm Process"; Friedrich Uhde GmbH, West Germany, 1976.
- Uhde, F. G. "Alkaline Chloride Electrolysis by the Mercury Process"; Friedrich Uhde GmbH, West Germany, 1976.
- Warde, C. J.; Brecher, L. E. "High Efficiency Cell for Hydrogen Production"; Westinghouse Research Laboratories, 1976.
- Wentoff, R. H.; Hanneman, R. E. *Science* **1974**, *1985*, 311.

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