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Progress Report

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Thermochemical Processes for Hydrogen Production

October 1, 1979—September 30, 1980

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Charles M. Hollabaugh

Person in Charge:	M. G. Bowman
Principal Investigators:	K. E. Cox
	T. C. Wallace, Sr.
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	W. M. Jones
	C. L. Peterson

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THERMOCHEMICAL PROCESSES FOR HYDROGEN PRODUCTION

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ABSTRACT

Thermochemical cycles for hydrogen production have been investigated at the Los Alamos National Laboratory since the early 1970s. The work consists of experimental and engineering research to define cycles that can be coupled feasibly to high-temperature heat sources for water-splitting to produce hydrogen and oxygen. Process development is sponsored by the Department of Energy, Division of Energy Storage Systems (STOR). In recent months, our efforts were directed toward improving the design and operation of our 1-in-diam laboratory-scale quartz rotary kiln. Our results from the decomposition of bismuth oxysulfate in the kiln have shown the technical feasibility of solid sulfate decomposition in a flow mode with recycled feed in residence times less than 2 min. Other work included (1) engineering studies that compared the published estimates of capital costs and process efficiencies for hydrogen production by thermochemical means and by electrolysis, (2) review of two thermochemical cycles for hydrogen production, and (3) coordination of US contributions to the annual International Energy Agency Technical Workshop on Thermochemical Processes.

EXECUTIVE SUMMARY

The work described here was accomplished during the period October 1, 1979—September 30, 1980. The highlights of the experimental program are described below.

Task 1. A solids decomposition facility was constructed and used to study the handling of $Bi_2(SO_4)_3$ and oxysulfates, and the kinetics of their decomposition. The results of the kiln experiments indicate nearly complete decomposition with residence times under 2 min at temperatures between 973 and 1143 K. There

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*K. E. Cox of Los Alamos National Laboratory died in 1980.

are two versions of this system: one decomposes normal $Bi_2(SO_4)_3$ and the other $Bi_2O(SO_4)_2$, with the same product in either case. The choice between the two versions depends largely on the cell voltage of the electrochemical process being developed by other programs.

Task 2. We evaluated the technoeconomics of the hybrid sulfur cycle and compared them with several published results and with the technoeconomics for water electrolysis processes for hydrogen production.

Task 3. We aided the efforts of the Department of Energy (DOE) Thermochemical Cycle Evaluation Panel in reviewing the Lawrence Livermore National Laboratory (LLNL) zinc selenide cycle as well as the General Atomic Company (GA) sulfur-iodine cycle.

Task 4. M. G. Bowman of Los Alamos National Laboratory, US Technical Contact for the International Energy Agency (IEA) Annex I Agreement on Thermochemical Processes, coordinated US contributions to the 3rd Annual Workshop held at Tsukuba Science City, Japan, June 18-21, 1980. The successful workshop included five delegates from the US and participants from other countries.

TASK 1. SOLIDS DECOMPOSITION FACILITY

At present there are over 30 thermochemical cycles in differing stages of research and development in laboratories around the world. Of these cycles, three have been selected for extensive development, including the construction and operation of closed-loop laboratory models that are capable of producing hydrogen continuously at a 100-ℓ/h rate. These three cycles and their developers are

(1) the hybrid sulfur cycle (Westinghouse Electric Corporation),[1]
(2) the sulfur-iodine cycle (GA),[2] and
(3) the Mark 13 cycle, a sulfur-bromine cycle, [Joint Research Center (JRC), Ispra, Italy].[3]

Two of the cycles, the hybrid sulfur cycle and the Mark 13 cycle, use an electrochemical step for the low-temperature hydrogen-producing reaction. All the cycles include the following steps: (1) concentration of H_2SO_4 solution by vaporization of water at elevated temperatures, (2) decomposition of H_2SO_4 to water and SO_3, and (3) decomposition of SO_3 to SO_2 and oxygen. The high-temperature step, involving the handling and treatment of H_2SO_4 and its components, causes corrosion problems that may be expensive to solve.

A possible means of overcoming the problems connected with the handling and decomposition of H_2SO_4 is the introduction of a metal sulfate into the cycle.[4] This step is accomplished by reacting H_2SO_4 produced by the low-temperature step with the appropriate metal oxide or metal oxysulfate to produce the desired sulfate species. The corrosion problems associated with boiling H_2SO_4 are then avoided. However, containment of SO_3, SO_2, and oxygen in the SO_3 reduction reactor at high temperature still remains a problem.

In principle, it should be possible to reduce the electrolyzer voltage if the electrolyzer (for SO_2 oxidation) is at acid concentrations lower than the current value of 50% achieved in the hybrid cycle. At concentrations lower than 52.7%, $Bi_2O(SO_4)_2$ forms, whereas normal $Bi_2(SO_4)_3$ forms at concentrations higher than 52.7%. The major disadvantage of introducing solids into a previously liquid-gas cycle is difficulties with handling and drying. Typically, if the sulfate particles are small, acid solution is retained within the void space between the particles. Thermal energy must be applied to dry the solids, and an effort must be made to recover the latent heat of the vapor, perhaps by recompression.

Other advantages and disadvantages of the solid sulfate substitution step are listed below.

Advantages

- Isothermal high-temperature operation is possible for better thermodynamic match with fusion and solar energy sources.
- Metal sulfates are less corrosive than H_2SO_4; therefore, materials selection is easier.
- Heat penalties associated with the acid concentration step can be avoided.
- Hybrid cycles have lower operating voltage caused by lower acid concentration in cell.

Disadvantages

- Problems in handling solids include solids in a pressurized system and heat transfer to/from solids.
- Sulfates need drying to remove occluded water and waters of hydration.

Bismuth Sulfate

The bismuth sulfate system was chosen for our initial studies from among many competitive sulfate systems on the basis of the criteria listed below. In general, an ideal sulfate should possess the following characteristics:

- low endothermic heat of decomposition;
- low or negligible solubility in acid solution;
- few or no waters of hydration;
- easy combination of decomposed material (oxide or oxysulfate) with acid to form the starting material;
- low water retention for drying purposes;
- rapid decomposition kinetics at moderate temperatures; and
- availability at low or moderate cost.

A $Bi_2(SO_4)_3$ cycle has already been defined from available data[4,5] and is reviewed here as an aid to understanding the variants possible. The original cycle concept was conceived as an alternative to cycles employing H_2SO_4 and included the following chemical reaction steps.

$$2\ H_2O\ (l) + SO_2(g) = H_2SO_4(aq) + H_2(g) \qquad \text{Elec. } 350\ K \tag{1}$$

$$H_2SO_4(aq) + 1/3\ Bi_2O_3(s) = 1/3\ Bi_2(SO_4)_3(s) + H_2O(l) \qquad 350\ K \tag{2}$$

$$1/3\ Bi_2(SO_4)_3(s) = 1/3\ Bi_2O_3(l) + SO_3(g) \qquad 900\text{-}1500\ K \tag{3}$$

$$SO_3(g) = SO_2(g) + 1/2\ O_2(g) \qquad 900\text{-}1500\ K \tag{4}$$

The concept was used in a system study[6] that explored the possibility of linking a fusion device to a thermochemical cycle for synfuel (hydrogen) production.

During the course of our experimental study,[7] we determined that $Bi_2(SO_4)_3$ decomposes through a series of intermediate oxysulfates rather than directly to Bi_2O_3. Equations (5)-(7) illustrate this progressive decomposition of normal $Bi_2(SO_4)_3$: first, the loss of 1 mol SO_3 to give $Bi_2O(SO_4)_2$; then the loss of another mol of SO_3 to produce $Bi_2O_2SO_4$; and finally, the loss of 0.3 mol SO_3 to give an oxysulfate composition of $Bi_2O_{2.3}(SO_4)_{0.7}$.

$$Bi_2(SO_4)_3 = Bi_2O(SO_4)_2 + SO_3 \tag{5}$$

$$Bi_2O(SO_4)_2 = Bi_2O_2SO_4 + SO_3 \tag{6}$$

$$Bi_2O_2SO_4 = Bi_2O_{2.3}(SO_4)_{0.7} + 0.3\ SO_3 \tag{7}$$

This progressive decomposition occurs at lower temperatures and with lower heat requirements than had been indicated by literature data.[8]

The enthalpies for Eqs. (5) and (6) were determined experimentally in an isothermal batch apparatus where the static gas pressures were obtained as a function of temperature. These equilibrium data, shown plotted in Fig. 1, gave a value of 161 kJ/mol for Eq. (5) and 172 kJ/mol for Eq. (6). Although the enthalpy for Eq. (7) was not determined, it is expected to approximate that of Eq. (6) because the decomposition proceeds rapidly to the bismuth oxysulfate product of Eq. (7), $Bi_2O_{2.3}(SO_4)_{0.7}$.

In addition, it was found that $Bi_2O(SO_4)_2$ is the stable sulfate in contact with H_2SO_4 in the concentration range

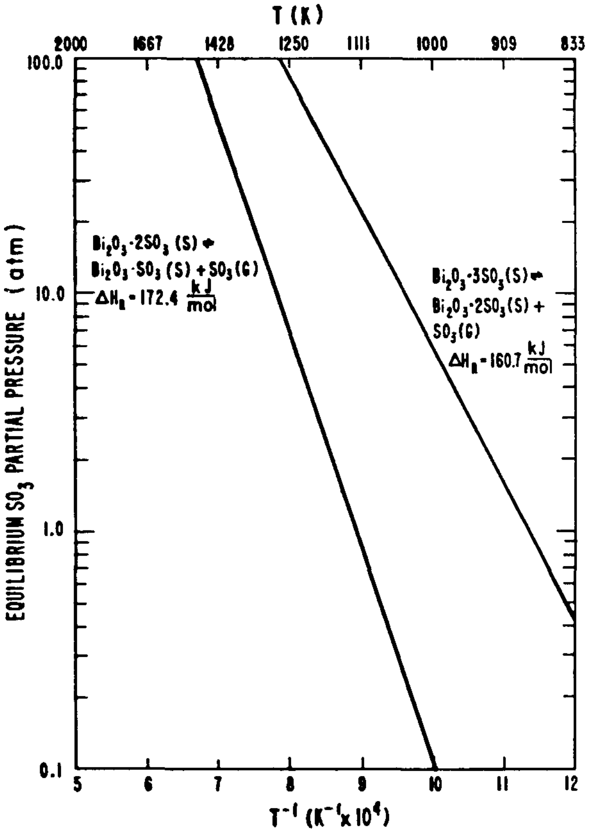


Fig. 1.
Decomposition pressures for $Bi_2(SO_4)_3$ and $Bi_2O(SO_4)_2$.

of 3.0 to 52.7 wt%. This oxysulfate contains three waters of hydration. At acid concentrations higher than 52.7 wt%, the stable sulfate is $Bi_2(SO_4)_3$ with no waters of hydration.

The progressive nature of the decomposition of $Bi_2(SO_4)_3$ and oxysulfates provides several alternatives to the original concept. These are shown in Fig. 2, which illustrates that one can devise alternatives by cycling back and forth between any two species in the decomposition chain.

Alternative 1 requires a high acid concentration, but the sulfate produced has no waters of hydration to be removed. Very low acid concentrations can be used with Alternative 2 but at the expense of removing three waters of hydration for each 1.3 mol of hydrogen produced. Clearly, the choice between the two alternatives is tied to the acid concentrations, and in turn, to the electrolyzer cell voltage in the hybrid process. The development of the electrolyzer is not part of this program. It should be emphasized that the solids in both cases have adsorbed solution that must be dried although Alternative 1 would have less solution per mol of hydrogen produced than Alternative 2.

Preliminary kinetic data for these decompositions were obtained by dropping a holder containing a small sample (0.25 g) of $Bi_2(SO_4)_3$ into a preheated furnace held at a set temperature. Measurements showed that the sample came to temperature equilibrium with the furnace temperature within 2 min. In Fig. 3, the SO_3 evolution rate is plotted as a function of time for runs at three different temperatures. Less than 2 min were required for the decomposition of $Bi_2(SO_4)_3$ to $Bi_2O_2SO_4$ at 1240 K. Less time (roughly half) is estimated for Eq. (5).

These results indicate that the reaction rate for the decomposition of $Bi_2(SO_4)_3$ or $Bi_2O(SO_4)_2$ is determined by temperature-dependent kinetics rather than by heat-transfer effects. In large industrial reactors, however, heat transfer to the solid particles will play an important role, which must be considered in the design.

To show the feasibility of decomposing a solid in a continuous manner, we constructed a rotary kiln and tested its operation with $Bi_2O(SO_4)_2$.

Rotary Kiln

A solids-handling facility was set up to evaluate the technical feasibility of the sulfate decomposition reaction in a continuous or flow mode and to determine whether recycled (decomposed) solids could be used again in the cycle. The initial scheme tested involved the use of a fluidized-bed solids/gas contacting scheme. The tests were run in a batch mode with an inert gas, nitrogen, as the fluidizing medium. Attempts at fluidizing the sulfate particles made during our first preparation were unsuccessful. Examination of the morphology of these particles under an optical microscope, and later by Scanning

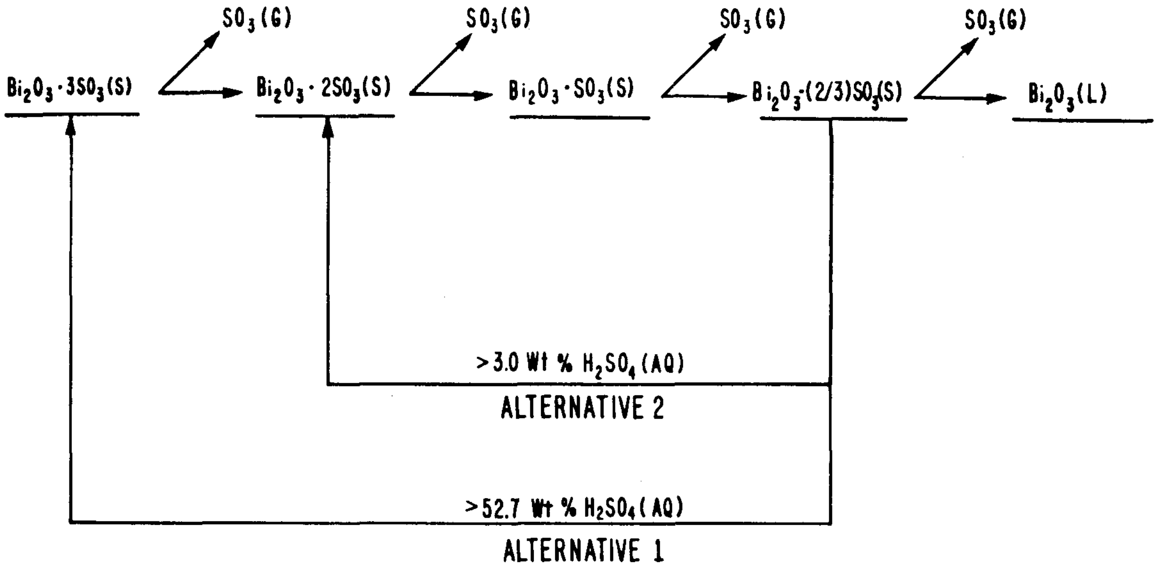


Fig. 2.
Bismuth sulfate decomposition alternatives.

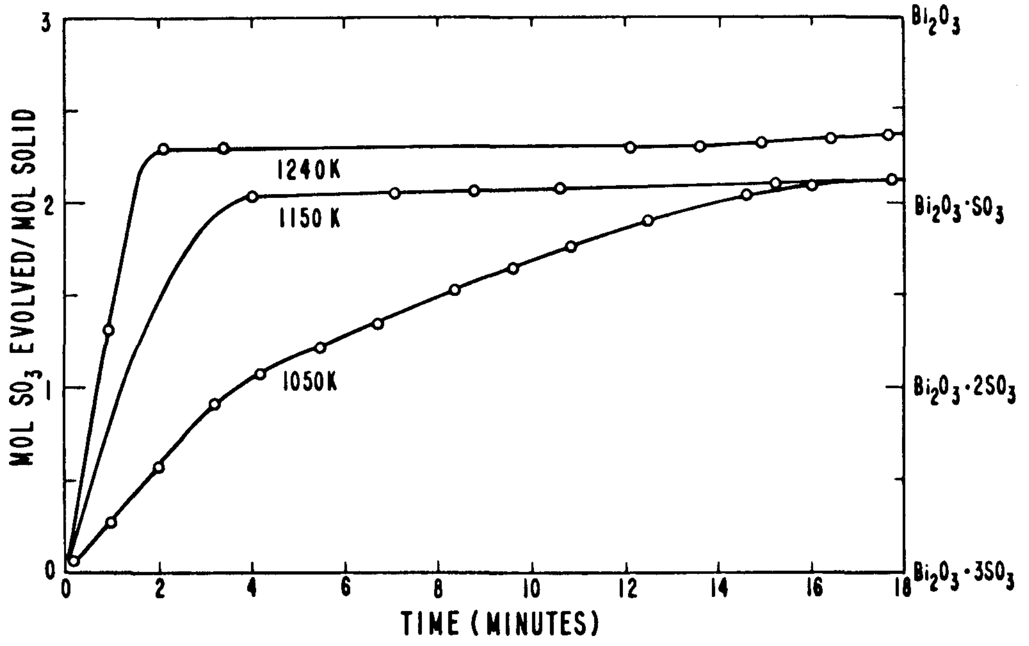


Fig. 3.
Kinetics of $Bi_2(SO_4)_3$ decomposition.

Electron Microscopy (SEM), showed them to be highly acicular with aspect ratios varying from 7 to 10. When the fluidizing gas was introduced, the bed of particles would tumble, and the particles would roll into larger spherical masses or pills. The sulfate particles appeared to interlock rather than to behave as individual elements. As a result, the fluidization experiments were shelved in favor of a more general solids-decomposition scheme, employed widely in industry for processes such as roasting, calcination, etc., which uses a rotary kiln as the solids-handling device.

A bench-scale rotary kiln was constructed from a 25-mm-diam quartz tube, 1.5 m long.[9] The overall kiln is shown in Fig. 4. At the head or feed end of the kiln, the quartz tube was fitted into a screw feeder made by inserting a Teflon screw in a tapered Teflon plug. A more detailed view of the feeder arrangement can be seen in Fig. 5. A V-shaped hopper was used for feed material storage, and the assembly was attached to the top of a vibrator to aid in moving the solid particles. A key feature in the design of the plug was to allow rotary motion of the kiln and yet provide a gas seal. The seal was important because we wished to recover the gases evolved from the decomposing solids (SO_3), as well as to provide a controlled atmosphere inside the kiln and keep moisture out. The Teflon plug was fitted to a standard taper-joint at the end of the quartz tube.

A 33-cm long, center portion of the kiln tube, enclosed by a tubular furnace, was the working kiln. The furnace temperature could be set as desired for a decomposition run. Passage of material through the heated kiln can be seen in Fig. 6. The upper portion of the furnace has been momentarily raised to show the sulfate particles passing downward through the quartz-tube section. Figure 7 shows the downstream or collection end of the kiln apparatus. A flask-shaped device added to the end of the tube collected the product. Two glass vials 180° apart were the sample-removal ports for the decomposed product. An electric motor, geared through a drive mechanism, rotated the kiln by a chain sprocket attached to the quartz tube. The speed of kiln rotation could be varied by this arrangement. The whole mechanism was mounted on a metal chassis that could be lowered or raised by elevating screws at the feed end of the kiln, allowing for variable slope. Figure 7 also shows a small rotary seal, fitted to the downstream end of the tube, that permitted the introduction of an inert gas to sweep away the gaseous decomposition products. A gas-absorber tube filled with Ascarite was sometimes used to collect the SO_3 formed; on other occasions this gas was vented to the fume hood enclosing the entire bench-scale kiln.

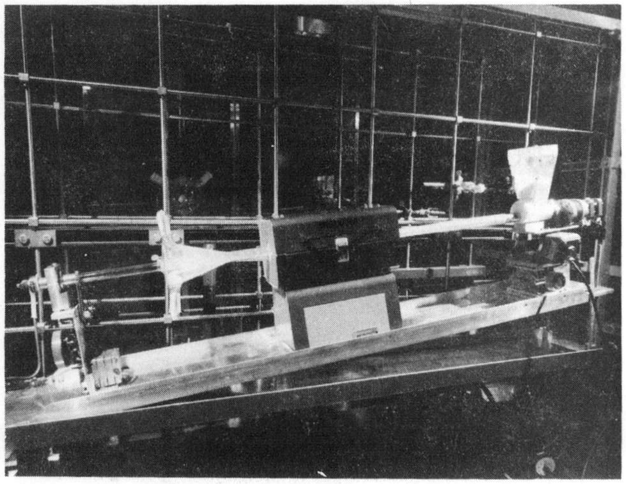


Fig. 4.
Rotary kiln for $Bi_2(SO_4)_3$ decomposition.

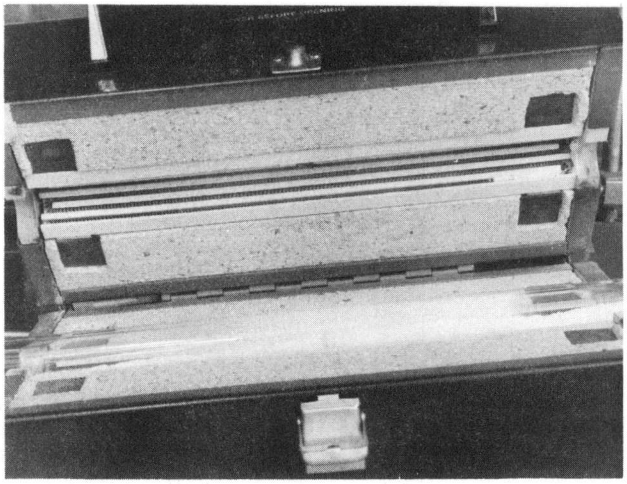


Fig. 6.
Passage of solids through rotary kiln.

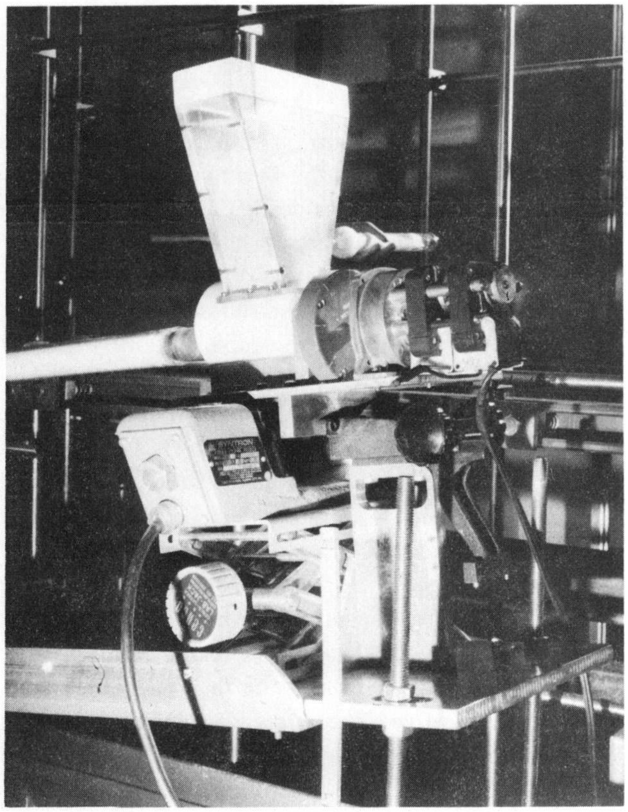


Fig. 5.
Solids feeder for rotary kiln.

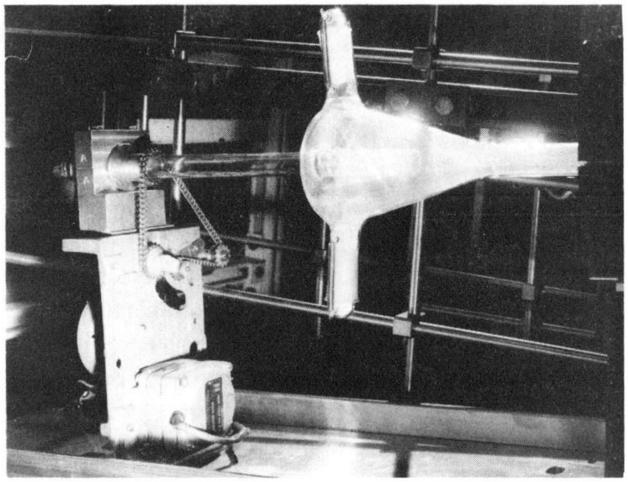


Fig. 7.
Rotary kiln collection end.

Feed Preparation

Prior to running experiments in the kiln, we had to define a procedure that would provide a uniform feed material for both feed composition and morphology (particle shape and size). The starting $Bi_2O(SO_4)_2$ was initially prepared from Bi_2O_3 reagent-grade chemical, as recycled (decomposed sulfate) was unavailable.

Two differing methods were used in the preparation of the feed sulfate. In the first preparation, Bi_2O_3 reagent was slowly added to a stirred H_2SO_4 solution of known concentration to yield a given weight of product as well as a final acid concentration. The precipitated sulfate was filtered, washed to remove acid, and dried overnight at 623 K. This method produced the acicular particles used in the initial fluidization experiments, which, when undigested, were approximately 1 μm in diam by 5-10 μm long as determined by SEM photomicrographs. Water retention by this material was large (in excess of 10 mol H_2O/mol of sulfate) because of the high void volume. This method of preparation produced a material with a stoichiometric formula close to $Bi_2O(SO_4)_2$. We had great difficulty fluidizing the particles or feeding them in the screw feeder. Although we used a vibrator, packing of the particles caused bridging and plugging of the feeder; in fact, the motion sometimes made matters worse by further compacting the particles.

The second method of preparation successfully resolved these difficulties. It consists of adding H_2SO_4 of known strength to an aqueous slurry of Bi_2O_3 particles, holding the slurry near the boiling point of the liquid (363-373 K), and allowing a period of digestion for particle growth. Results of the second method can be seen in Table I. High $Bi_2O(SO_4)_2$ yields obtained in all cases are well within the experimental error. The rise in stoichiometric product composition is caused by an additional processing change. Because washing is not an integral feature of the final process flow sheet, drying of the wet filter cake was performed without it. As it is drying, the acid present in the occluded liquid concentrates and further reacts with the originally precipitated $Bi_2O(SO_4)_2$ to yield a mixture of this material and some $Bi_2(SO_4)_3$ represented by the product compositions shown in Table I.

Bulk density tests also were carried out to help characterize the feed material. The higher the bulk density of the sample, the lower the void fraction, indicating that the particles in the sample possess a more uniform shape. The tap density value reflects particle density after 5000 taps and is another indication of the particles' morphology. The major disadvantage noted in these preparation runs was the amount of liquid retained (occluded solution by the product), which approximated 10 mol H_2O/mol of dry product. All material prepared by the second method proved easy to feed.

Kiln Operation

The key variables affecting the operation of a kiln in which solid species undergo decomposition are operating temperature and solids residence time. An empirical equation linking the residence time to the major dependent variables is given by[10]

$$t = \frac{0.19\ L}{NDS} \tag{8}$$

where t = residence time (min), L = kiln length (m), N = rotational speed (rpm), S = slope of kiln (m/m), and D = kiln diameter (m).

TABLE I

PREPARATION OF BISMUTH OXYSULFATE FEED (METHOD 2)

	80/1	80/5	80/6	80/7	80/8	80/9	80/10
Filtration temp (K)	326	327	307	309	309	306	307
Ratio, filtrate/cake	5.00	5.27	5.10	5.18	5.02	4.97	5.32
$Bi_2O_{3-X}(SO_4)_X$, X =	2.07	1.99	2.00	2.10	2.14	2.13	1.99
Yield (%)	97.5	96.8	97.2	96.2	96.1	96.7	96.9
Mol H_2O/mol product[a]	9.98	10.1	11.2	10.6	9.67	10.2	8.04
Bulk density (g/ml)	1.15	1.34	1.28	1.34	1.40	1.53	1.37
Tap density (g/ml)	1.78	2.01	1.95	1.94	2.10	2.16	2.16

[a] In filter cake.

Preliminary experiments were conducted to establish the feed characteristics, and the best kiln slope and rotation speeds to provide reproducible data useful in relating the residence time and temperature to the decomposition during transit of the kiln by the solid feed. We chose the steepest slope (7.9°) that could be used without sliding, but that allowed good downward progress without back-up. Sliding tends to increase at higher temperatures because the SO_3 cushions the particles and removes some of the normal influence of the friction from the rotating walls of the kiln. Caking occurred at the upper end of the tube furnace, seemingly where the evolved SO_3 reacted with the feed to produce a higher sulfate with different sliding and packing characteristics. This problem disappeared when an aspirator tube was placed in the hot zone of the kiln so that the kiln operated slightly below atmospheric pressure.

We estimated residence times by timing the movement of powder along the kiln. A 50-mm portion of the kiln, extending beyond the tube furnace, and of the same bore as that within the furnace, was used as a zone through which the transits were timed. Residence times calculated according to Eq. (8) exceeded the measured values by from 1 to 35%. In light of the great disparity in size of the laboratory kiln compared to commercial ones, this is considered quite good agreement.

Using the composite feed and the same kiln inclination, we made a matrix of kiln experiments that explored the effect of four temperatures and three rotational speeds. The temperatures chosen were 993, 1023, 1073, and 1123 K. The highest temperature is about the maximum that can be used in this system without encountering molten product, which starts to appear around 1153 K, resulting in attack on the quartz tube. The results are shown in Table II.

The feed material had a composition of $Bi_2O_{0.94}(SO_4)_{2.06}$. Based on previous results, we assumed that the oxysulfate would not decompose to a composition beyond $Bi_2O_{2.28}(SO_4)_{0.72}$; thus the percentage of decomposition is based on a maximum of 1.34 mol SO_3 evolved. Examination of the data in Table II reveals that over 90% conversion is obtained in less than 2 min at a temperature of about 1100 K.

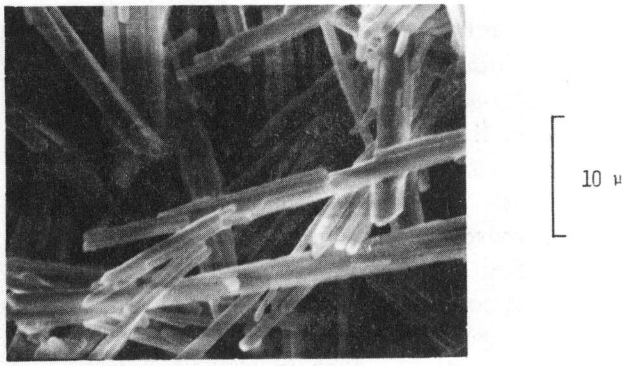
Morphology of Bismuth Sulfate

A study was made of the morphology of the particles formed by the two methods of preparation and after passage through the kiln. Samples of the $Bi_2O(SO_4)_2$ preparations were viewed on the SEM, and photomicrographs of representative particles were taken. Materials prepared by the first method are shown in Fig. 8. These particles have acicular shapes and are 1 μm in diam by 5-10 μm long. The decomposed material from this preparation (also shown in Fig. 8) appears to have the same overall dimensions as before, but the particles are

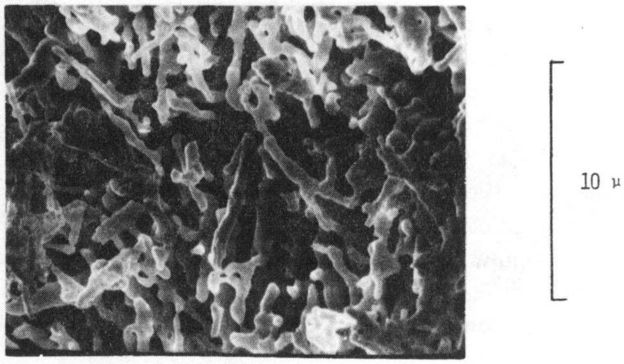
TABLE II

DECOMPOSITION OF BISMUTH OXYSULFATE IN A ROTARY KILN

Experiment	Set Temp (K)	Time in Hot Zone (s)	Product	SO_3 Evolved (moles/mol)	Decomposition (%)
80/37	993	67	$Bi_2O_{1.86}(SO_4)_{1.14}$	0.92	69
80/38	993	138	$Bi_2O_{2.02}(SO_4)_{0.98}$	1.08	81
80/36	1023	51	$Bi_2O_{1.60}(SO_4)_{1.40}$	0.66	49
80/27	1023	66	$Bi_2O_{1.61}(SO_4)_{1.39}$	0.67	50
80/28	1023	128	$Bi_2O_{2.07}(SO_4)_{0.93}$	1.13	84
80/34	1073	46	$Bi_2O_{2.03}(SO_4)_{0.97}$	1.09	81
80/29	1073	66	$Bi_2O_{2.14}(SO_4)_{0.86}$	1.20	90
80/30	1073	128	$Bi_2O_{2.24}(SO_4)_{0.76}$	1.30	97
80/33	1123	62	$Bi_2O_{2.22}(SO_4)_{0.78}$	1.28	96
80/31	1123	80	$Bi_2O_{2.25}(SO_4)_{0.75}$	1.31	98
80/32	1123	152	$Bi_2O_{2.19}(SO_4)_{0.81}$	1.25	93

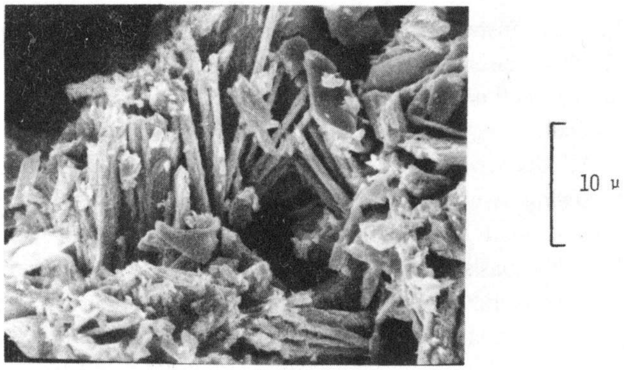


$Bi_2O_{0.97}(SO_4)_{2.03}$ - FEED

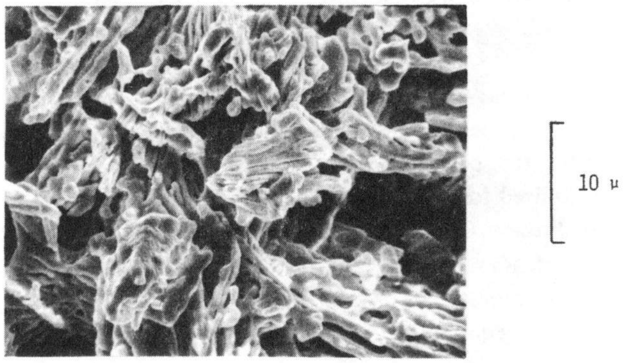


$Bi_2O_{2.28}(SO_4)_{0.72}$ - PRODUCT

Fig. 8.
$Bi_2O(SO_4)_2$ preparation method 1. Kiln feed and product.



$Bi_2O_{0.93}(SO_4)_{2.07}$ - FEED



$Bi_2O_{1.93}(SO_4)_{1.07}$ - PRODUCT

Fig. 9.
$Bi_2O(SO_4)_2$ preparation method 2. Kiln feed and product.

rounded probably because of some sintering.

Material prepared by the second method is shown in Fig. 9 together with its decomposed counterpart. In this case, the particles are much less acicular than those prepared by the first method (Fig. 8). The decomposed material retains the shape and size of the original, although there is some sintering as there was with the first method.

New Approach

Because the decomposition rate of the bismuth sulfates is so high, we anticipate that on a larger scale the heat transfer rates to the solid will be the rate limiting factor for decomposition. Rotary kilns are fundamentally geared to relatively slow processes where heat transfer is not so critical; consequently, they may not be the best choice for handling the decompositions of the sulfates. One alternative is a fluidized bed. Our early attempts at fluidization were not successful because we tried to fluidize the small acicular particles directly. A better approach is to feed these small particles into a well-fluidized bed of larger inert particles.

TASK 2. TECHNOECONOMIC EVALUATION OF CYCLES

We made a comparative study of the capital costs and efficiency estimates for water electrolysis and thermochemical splitting of water to produce hydrogen.

Methodology

Data on water electrolysis and on the hybrid sulfur cycle have occurred most often in the literature; this study is mainly based on comparison of these methods.

In many instances, data were estimated simultaneously as water electrolysis forms a "baseline" against which the competitiveness of thermochemical processes can be judged.

All data were placed on a common basis with the following assumptions:

- a plant capacity of 100 000 Nm^3/h of hydrogen (the basis chosen by JRC);
- conversion of all data to mid-1979 dollars using the Chemical Engineering Plant Cost Index;[11] and
- total investment cost broken down into its components and expressed as specific investment $/kW H_2.

The following breakdown was employed to categorize the individual components of water electrolysis and thermochemical plants.

- Nuclear (N)—This category included the cost of the nuclear reactor and its auxiliaries plus the costs of the primary and secondary helium loops required for heat transfer.
- Power Generation and Conditioning (P)—This category included the cost of the electrical generators plus the costs of the transformers, rectifiers, etc., required to condition the electricity.
- Electrolyzer (E)—This category included the electrolyzer system required to produce a 99%-pure hydrogen product at 30 atm pressure.
- Chemical Plant and Heat Exchange Equipment (C)—For a hybrid or "pure" thermochemical cycle, this category included the reactors, separators, and heat exchangers making up the plant plus the piping, pumps, and instrumentation. The hydrogen product is delivered to a pipeline at 30 atm. All capital costs derived are for a "grass roots" plant.

Results

Data on the estimated investment costs and efficiencies derived for the different processes were drawn from a number of original references in the literature.[12-18] Explicit assumptions were made regarding cycle as well as heat source conditions, and relevant information regarding these assumptions is given below.

Case I. Westinghouse Sulfur Cycle — Study 1[12]
Cycle Efficiency: 45.2%
Assumptions:
Nuclear Heat Source
- Prestressed concrete reactor vessel
- Reactor outlet helium temperature – 1283 K
- Turbogenerators in primary helium loop

Acid Electrolyzer
- Acid concentration: 75 wt%
- Voltage: 0.45 V
- Current density: 2000 Am^{-2}

Case II. Schulten Methanol Cycle[13]
Cycle Efficiency: 37.5%
Assumptions:
Nuclear Heat Source
- Per Case I

Thermochemical Cycle
- All reactions to equilibrium
- A key reaction ($CH_3OH + SO_2 + H_2O = H_2SO_4 + CH_4$) not technically feasible

Case III. Westinghouse Sulfur Cycle—Study 2[14]
Cycle Efficiency: 54.1%
Assumptions:
Nuclear Heat Source
- Per Case I

Acid Electrolyzer
- Acid concentration: 80 wt%
- Voltage: 0.48 V
- Current density: 2000 Am^{-2}

Case IV. Exxon Study[15]
Assumptions:
Heat Source
- Unspecified, electricity cost assumed at 2.7 ¢/kWh

Electrolyzer
- Advanced type solid polymer electrolyte (SPE), efficiency: 77.6%
- Advanced type (SPE), efficiency goal: 90%

Case V. Westinghouse Sulfur Cycle—Study 3[16]
Cycle Efficiency: 46.8%
Assumptions:
Nuclear Heat Source
- Per Case I

Acid Electrolyzer

- Acid concentration: 80 wt%
- Voltage: 0.6 V (Case 2)
- Current density: 2000 Am^{-2}

Water Electrolysis (H_2SO_4 electrolyte)

Cycle Efficiency: 40.8%

Assumptions:

Water Electrolyzer

- Acid concentration: 28 wt%
- Voltage: 1.68 V
- Current density: 2000 Am^{-2}

Case VI. Mark 11 — V6 Hybrid Sulfur Cycle[17]

Cycle Efficiency: 41.7%

Assumptions:

Nuclear Heat Source

- No electricity generation in primary helium loop
- Use of bottoming cycle for additional electricity generation

Acid Electrolyzer

- Acid concentration: 75 wt%
- Voltage: 0.62 V
- Current density: 4000 Am^{-2}

Advanced Water Electrolysis

Efficiency: 32.7%

Assumptions:

Electrolyzer

- Voltage: 1.64 V
- Current density: 2000 Am^{-2}

Mark 13 — V2 Cycle Hybrid Cycle

based on sulfuric acid and bromine

Efficiency: 37.2%

Assumptions:

Acid (hydrogen bromide) Electrolyzer

- Acid concentration: 80 wt%
- Voltage: 0.8 V
- Current density: 4000 Am^{-2}

Case VII. General Electric Study[18]

Hybrid Sulfur Cycle, Cycle Efficiency: 42.5%

Nuclear Heat Source

- Per Case V

Acid Electrolyzer

- SPE Type
- Acid concentration: 80 wt%
- Voltage: 0.73 V
- Current density: 4000 Am^{-2}

Water Electrolysis, Efficiency: 40.2%

- SPE type
- Voltage: 1.665 V
- Current density: 10 000 Am^{-2}

Figure 10 presents data for the specific investments for thermochemical cycles. The investments range from a low of \$589/kW H_2 to a high of \$1089/kW H_2. Efficiency estimates ranged from 37.2 to 54.1%. Examination of these data shows that optimistic assumptions were made to create the low-investment/high-efficiency values. In Case III for the hybrid sulfur cycle, a voltage under 500 mV was assumed for the electrolyzer. In reality, the voltages achieved are closer to 800 mV at 50 wt% acid, and the research goal is 600 mV. Raising the design voltage to this level would bring the capital investment closer to \$1000/kW H_2 and the efficiency to 40%.

The one "pure" thermochemical cycle included in this sample, the Schulten-Methanol cycle (Case II), suffers in comparison with hybrid cycles. Its investment cost is high (\$938/kW H_2) and its efficiency is low (37.5%). It must be emphasized, however, that the cycle was studied primarily to develop the methodology for technoeconomic evaluation. Certainly, it is not representative of thermochemical cycles in general because it suffers from most of the weaknesses to be avoided in choosing cycles for practical development.

Figure 10 shows the cost breakdown for each cycle. For the six hybrid cycle cases, the investment allotted to the electrolyzer and the chemical sections of the plant were found to be almost the same. The major deviation was found in the pricing of the nuclear portion of the plant. The nuclear plant costs in Case VI (Mk 11 and 13) may be too high because they were obtained from the annual charges assigned by the authors.[17] Figure 11 shows results for the water electrolysis plants. Their efficiencies are lower than those of the thermochemical cycles (Fig. 10) and range from 32.7 to 40.8%. The efficiency for water electrolysis is the product of the electricity generation efficiency and the electrolyzer efficiency. The investment costs for water electrolysis appear to be in the same range as those computed for hybrid thermochemical cycles ranging from \$692/kW H_2 to \$1089/kW H_2. The data on the extreme right-hand side of Fig. 11 are for stand-alone electrolyzer plants where electricity is purchased directly.[15]

There is a large difference between the cost obtained for conventional electrolysis (\$681/kW H_2) and the costs estimated for advanced electrolyzers using SPE technology. Conventional electrolyzers have efficiencies in the 70-80% range, whereas SPE has a goal of 90% efficiency, which will help lower the overall cost if it is achieved.

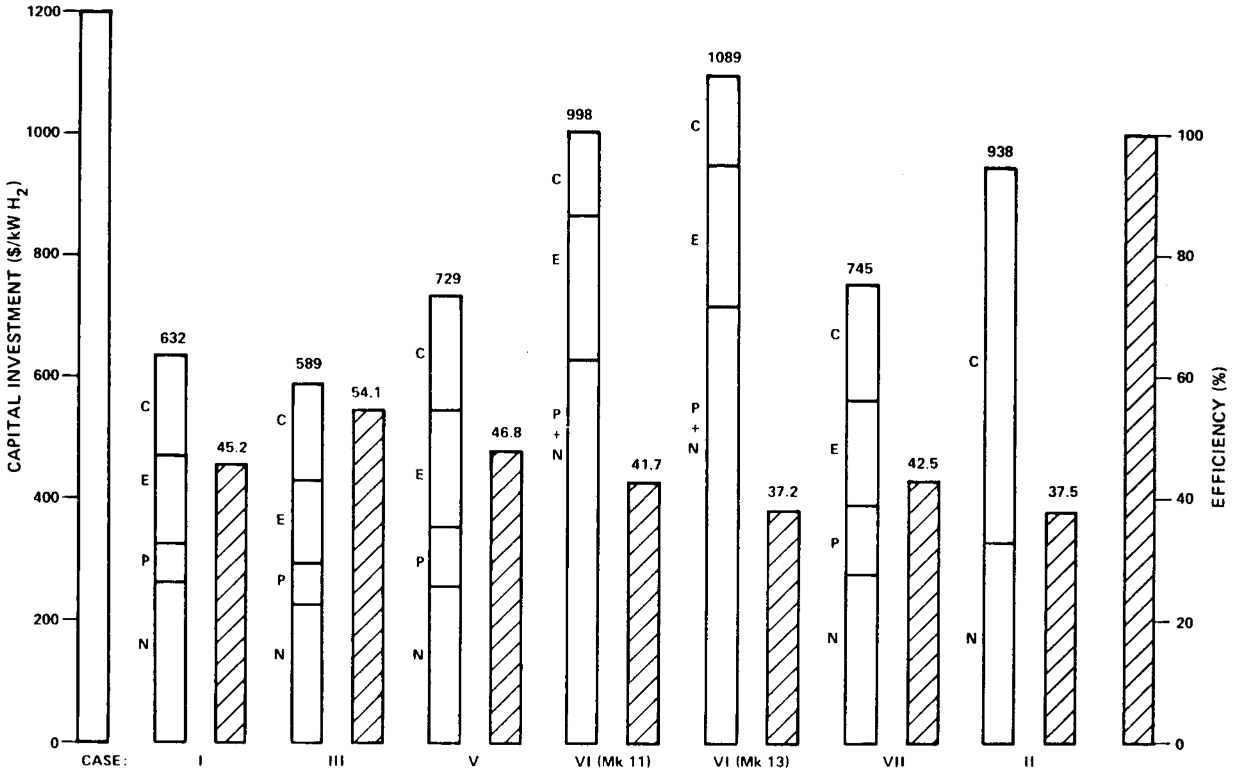


Fig. 10.
Investment and efficiency estimates for thermochemical cycles.

This study does not take into account the technique of high-temperature water electrolysis. As experimental data on these systems are relatively scarce, economic projections are even more speculative than for SPE or thermochemical cycles. Figure 12 presents data from studies in which competitive hydrogen production schemes were compared by the same authors. These data are grouped in pairs. In the first set of data (Case V), Westinghouse Electric Corp. compared the cost for the hybrid sulfur cycle against that for an advanced water electrolyzer using H_2SO_4 as the electrolyte. The costs were strikingly similar even though their efficiencies differed.

To understand the investment difference between water electrolysis and hybrid thermochemical cycles see Fig. 13, in which a water electrolysis process is powered by the same heat source as a hybrid cycle. For water electrolysis, heat is first converted into electricity. An investment must be made for the heat source, for the power generation and power conditioning equipment (transformers and rectifiers), and for the electrolyzers. In a hybrid cycle, the same investment is made for the heat source. (The efficiencies are assumed equal in both cases.) Only part of the heat is necessary for electrolytic step; thus, the power generation and conditioning investment is significantly less than for water electrolysis. The electrolyzer cost for a hybrid cycle, however, remains the same as for water electrolysis because the same amount of current must be used to produce the same quantity of hydrogen.

The major tradeoff in investment cost is therefore quite simple to evaluate. The larger amount of power generation and conditioning equipment for water electrolysis is balanced by the cost of the chemical plant for a hybrid cycle. The first set of data in Fig. 12 indicates that this tradeoff occurs.[16] The second set of data[18] assumes an advanced SPE water electrolyzer and a hybrid cycle using a similar SPE electrolyzer. The data indicate a higher cost for the hybrid cycle as compared to SPE electrolysis even though the efficiency of the former is higher than that of the latter. Another comparison was done by JRC. They compared a hybrid cycle (Mk 11) similar to Westinghouse's hybrid cycle to advanced water electrolysis. The investment costs for these two processes appears equivalent, even though the hybrid cycle has a greater efficiency.

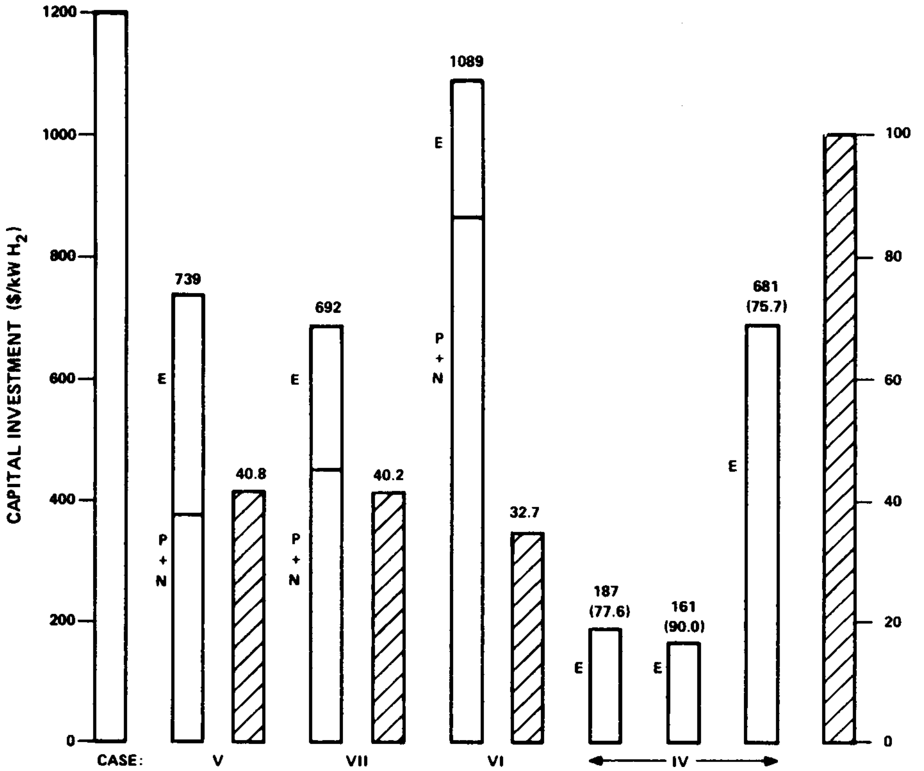


Fig. 11.
Investment and efficiency estimates for water electrolysis.

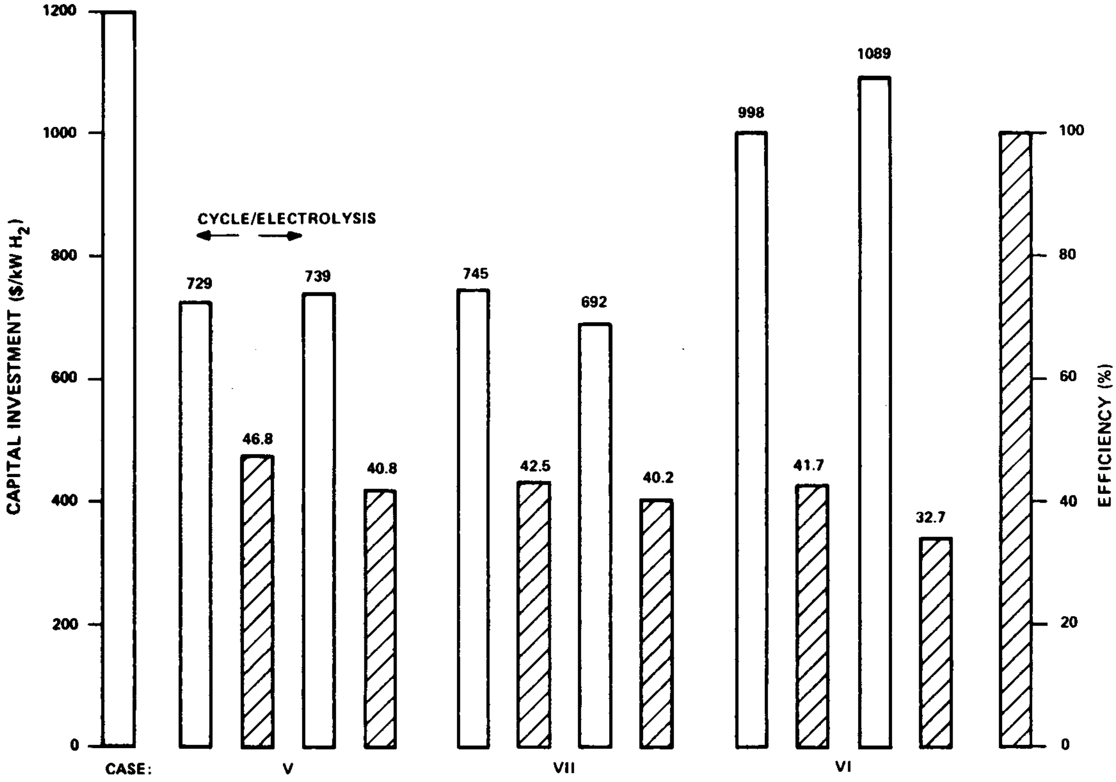


Fig. 12.
Comparative data for investment and efficiency. Thermochemical cycles and water electrolysis.

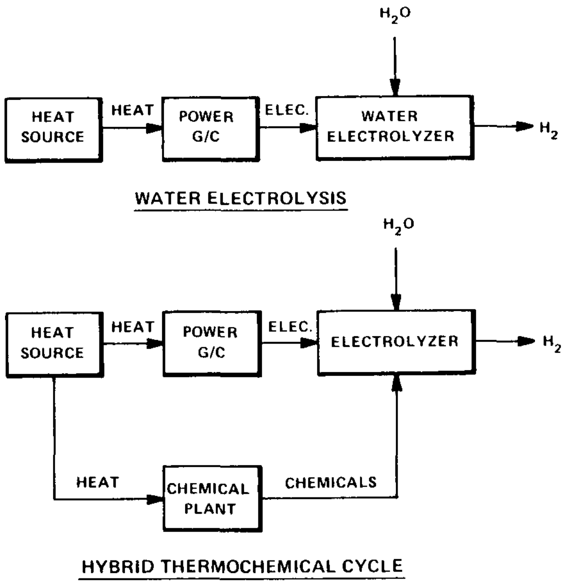


Fig. 13.
Comparison of water electrolysis and hybrid thermochemical cycle processes.

In the above results, one must always take into account the assumptions. For hybrid cycles as for water electrolysis, key parameters are the electrolyzer voltage and current density. Doubling the current density leads to roughly half the cost for electrolyzers. GE used a current density of 10 000 Am^{-2} in their SPE water electrolysis design.[18] For the hybrid cycle, a 4000 Am^{-2} current density was used. Although the specific cost of GE's SPE electrolyzer was greater than that of the hybrid cycle, their overall cost was estimated lower because of operation at higher current density.

Summary

The cost data show slight differences in investment between the two methods of hydrogen generation. All the costs were in the \$589-1089/kW-H_2 range. In general, efficiencies are higher for thermochemical cycles than for water electrolysis. These range from 37.2 to 54.1% for thermochemical cycles and from 32.7 to 40.8% for water electrolysis.

The values of cost or efficiency derived are only as good as the assumptions. Values of the SO_2 electrolyzer voltage assumed in early studies on the hybrid sulfur cycle were below 0.5 V at acid concentrations of 75-80 wt%. These voltages are impossible to attain under the assumed conditions. In these cases, costs and efficiencies must be revised to reflect conditions that are more realistic.

The major tradeoff between hybrid thermochemical cycles and water electrolysis appears in the specific investment for the chemical portion of the plant, typically the sulfuric acid concentrator, acid decomposer, and sulfur dioxide/oxygen separation unit. This cost must be balanced against the cost of the additional power generation and power conditioning facilities required in the case of water electrolysis. The chemical portion of the plant is fairly constant in cost at \$133 to \$186/kW H_2. Unfortunately, few data are available for power equipment required in water electrolysis systems to quantify this tradeoff. The specific investment for the electrolyzer portion for both processes is also similar, ranging from \$142 to \$187/kW H_2 for advanced electrolyzers; however, values of \$238/kW H_2 and \$365/kW H_2 were obtained for SPE and H_2SO_4 electrolysis in later studies.

There does not appear be be any simple method to determine investment costs or efficiencies for new technologies such as thermochemical cycles or advanced water electrolysis. Computer codes will speed the process of cost estimation, but a flow sheet reflecting reliable operating conditions is still the prime requirement in technoeconomic evaluation.

TASK 3. DOE THERMOCHEMICAL CYCLE EVALUATION PANEL

Los Alamos National Laboratory support was provided to this panel chaired by J. E. Funk (University of Kentucky). In this reporting period, two cycles have undergone evaluation, the LLNL zinc selenide cycle and the GA sulfur-iodine cycle.

TASK 4. IEA ANNEX I AGREEMENT ON THERMOCHEMICAL PROCESSES

The third annual IEA Annex I Workshop on Thermochemical Processes was held in Tsukuba Science City, Japan, June 18-21, 1980. Attendees from the United States were

M. G. Bowman, Los Alamos National Laboratory;
C. F. V. Mason, Los Alamos National Laboratory;
G. Besenbruch, General Atomic Company;

G. Parker, Westinghouse Electric Corporation; and

O. Krikorian, Lawrence Livermore National Laboratory.

M. G. Bowman, US Technical Contact for Annex I, coordinated US participation at this workshop.

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