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TITLE: The LASL Thermochemical Hydrogen Program Status on September 30, 1980*

MASTER

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THE LASL THERMOCHEMICAL HYDROGEN PROGRAM STATUS ON SEPTEMBER 30, 1980*

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Abstract

The work described here was accomplished during the period October 1, 1979--September 30, 1980. Highlights of the experimental program were:

- o A solids decomposition facility was constructed and used to study the handling of bismuth oxysulfates and the kinetics of their decomposition.
- o The results of our kiln experiments showed that a substantial amount of bismuth oxysulfate decomposition occurs with residence times under 2 min. at temperatures between 973 and 1143 K.

The LASL bismuth sulfate sub-cycle thus appears a candidate for hydrogen production utilizing a solar heat source. In the evaluation phase of our work, the technoeconomics of the hybrid sulfur cycle were determined and compared with several published results as well as compared to the technoeconomics for water electrolysis processes for hydrogen production.

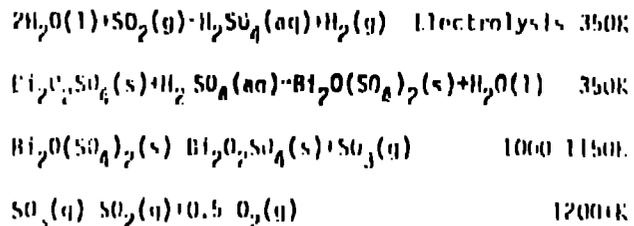
We aided the efforts of the Department of Energy (DOE) Thermochemical Cycle Evaluation Panel in reviewing the Lawrence Livermore Laboratory (LLL) zinc selenide cycle as well as the General Atomic (GA) sulfur-iodine cycle.

M. G. Bowman, U. S. Technical Contact for the International Energy Agency (IEA) Annex I Agreement on Thermochemical Hydrogen Production, coordinated U. S. contributions to the 3rd Annual Workshop held at Tsukuba Science City, Japan, June 18-21, 1980. The successful workshop was attended by five delegates from the U. S. and also included international participation.

1. Solids Decomposition Facility

The metal sulfate sub-cycle currently being studied as part of our applied program under the Office of Advanced Conservation Technologies is a bismuth oxysulfate cycle. In a related program under the Office of Energy Research, more basic studies of alternative sulfates are being conducted to determine whether they offer advantages for the applied program.

The present version of the bismuth oxysulfate cycle may be described as follows.



*Work performed under the auspices of the US DOE.

The bismuth oxysulfate system is desirable because it decomposed rapidly at moderately high temperatures, and the decomposed product reacts rapidly with dilute sulfuric acid solutions, giving an insoluble product. This is important in minimizing solution concentration steps.

Two disadvantages are the rather high cost of bismuth compounds although this becomes a plant inventory rather than an operating cost, as nearly all of the bismuth is recovered and recycled. The other is the water-retention problem and the fact that the disulfate forms a trihydrate.

A laboratory-scale rotary kiln was constructed from a 25-mm o.d. quartz tube, so supported that it could rotate freely inside a 350-mm long, 25.4-mm tube furnace. This furnace was capable of temperatures to 1203 K. The quartz tube terminated in a standard taper female joint which rotated on a male counterpart machined from Teflon. This afforded a gas-tight rotary seal without need of lubrication. The Teflon joint extended to a Teflon body which supported a rectangular hopper constructed from Lexan polycarbonate sheet. A Teflon auger passed through the body and the tapered joint. The auger was rotated by a geared drive so that the feed rate could be varied in steps. Also, built into the body and out through the tapered joint was a gas passage, which could support a quartz tube protruding into the center of the quartz kiln, providing a leak-free exit for SO₃ and carrier gas. The kiln is shown in Fig. 1.

A matrix of kiln experiments using composite feed and the same kiln inclination were made. These explored the effect of four set temperatures and three rotational speeds. Temperatures of 993, 1023, 1073, and 1123 K were chosen.

The results of these experiments are presented in Fig. 2. Previous experiments of this type have shown that the maximum decomposition that will occur in a few minutes such as in a kiln experiment, never seems to go beyond a composition of approximately Bi₂O₇·2H(SO₄)_{0.77}. Since the feed composition is Bi₂O₇·0.94(SO₄)_{2.06}, it is assumed that a maximum of 1.34 moles of SO₃ can be driven off in the laboratory-scale kiln with this feed.

The main conclusions to be drawn from this matrix of experiments is that a substantial amount of decomposition was obtained in short (less than 2 min.) reaction times at 973 K to 1143 K. In addition, by proper procedures, which appear to be industrially compatible, bismuth monoxydisulfate can be prepared with an altered morphology and particle size conducive to good solids handling characteristics.

Our latest work has been done with reconstituted feed with a composition, Bi₂O₇·0.6(SO₄)_{2.4}·H₂O made from five batches that had been run through the kiln and treated with 3 M sulfuric acid. This material decomposed to Bi₂O₇·2.5(SO₄)_{1.75} at 1143 K however, the solid showed different handling characteristics than the earlier feed prepared from reagent grade Bi₂O₃. Further experimentation will

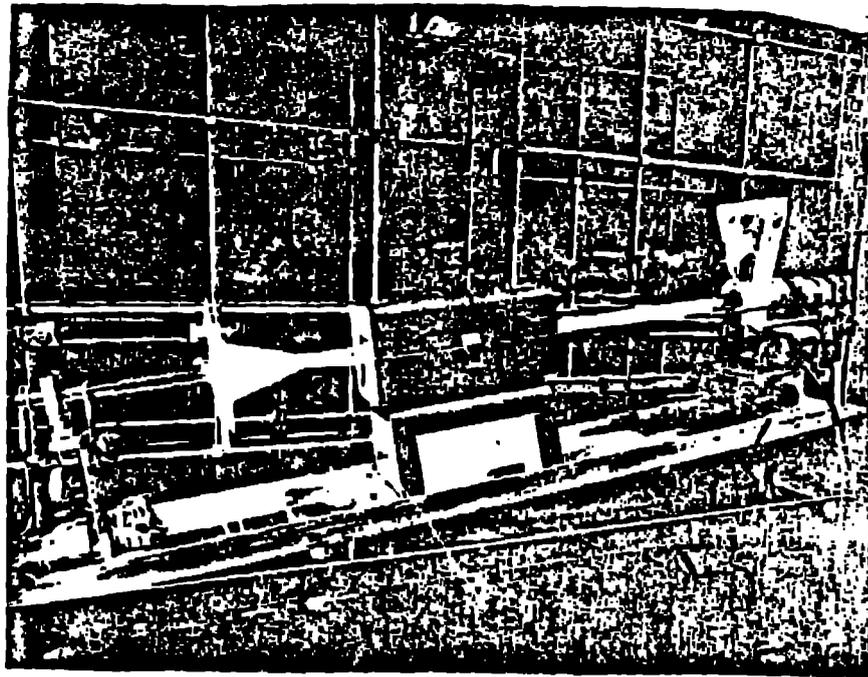
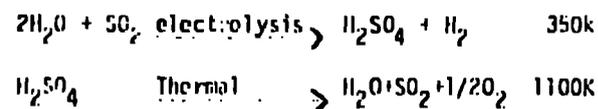


Figure 1. LASL Solids Decomposition Facility (Rotary Kiln)

chemical cycles were higher at 40 - 55% than for water electrolysis systems at 30 - 40%.

In the techno-economic evaluation of thermochemical cycle technology, the hybrid sulfur cycle, known commonly as the "Westinghouse Sulfur Cycle" and the "JRC Mark II Cycle," has received the most attention. This cycle is characterized by the following reaction sequence:



In both the Westinghouse and the JRC versions, the process operates off nuclear heat delivered as a high-temperature helium gas stream from a HTGR or a Very-High Temperature Reactor (VHTR). If instead solar heat is considered for a thermochemical cycle, an additional factor must be considered. This is the cost of solar heat at the temperature required for the process. Solar heat is intermittent both on a daily basis (night and day) as well as during cloudy periods during the day. The lower capacity factor for solar plants (as contrasted to nuclear plants) will have a larger effect on capital cost as compared to a nuclear plant. Solar-thermochemical schemes are just now receiving attention and this potentially promising technology has in its favor the capability of delivering heat at a practically isothermal temperature to a thermochemical cycle allowing consideration of cycles involving solid oxide or sulfate decompositions.

Detailed summaries of the estimated investment costs and efficiencies derived for the different processes are presented in bar chart format in Figs. 3 and 4 on the basis of \$ Investment/KWh₂ (1979 \$) and (%) efficiency. The data were drawn from a number of original references in the literature.

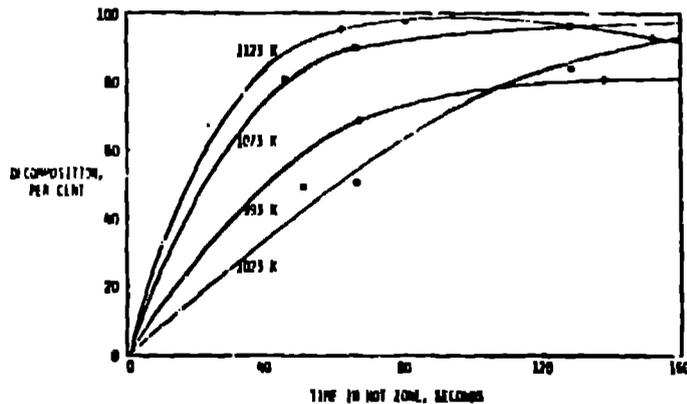


Figure 2. Decomposition Rate in Kiln.

relate these characteristics to practical operating conditions.

In summary, it appears that the LASL bismuth sulfate sub-cycle offers a practical means to minimize some of the difficulties in handling sulfuric acid that are associated with cycles such as the hybrid sulfur cycle and the sulfur-iodine cycle. If solids handling problems are not too severe, this cycle appears well adapted for hydrogen production from a solar thermal energy source.

II. Cycle Evaluation

A survey of capital cost estimates and process efficiencies for two different technologies for the production of hydrogen has been performed. Thermochemical cycles show costs ranging from \$600 - 1100/MWh while advanced methods of water electrolysis were estimated in the range of \$700 - 1100/MWh. In general, efficiencies for thermo-

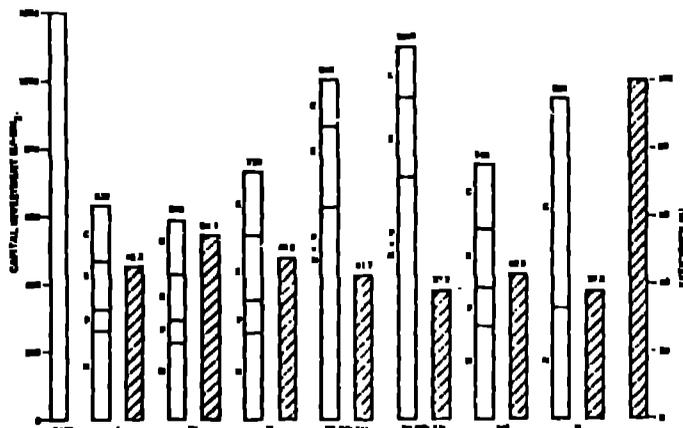


Figure 3. Investment and Efficiency Estimates for Thermochemical Cycles.

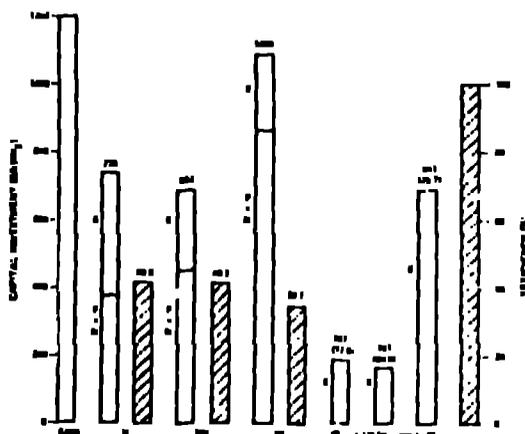


Figure 4. Investment and Efficiency Estimates for Water Electrolysis.

The cost data show slight differences in investment between two methods of hydrogen generation. All costs were in the range, \$589 - 1039/kW H₂. Efficiencies are in general, higher for thermochemical cycles than for water electrolysis. These range from 37.2% to 54.1% for thermochemical cycles and from 32.7 to 40.0% for water electrolysis.

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

There does not appear to be any simplistic 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 flowsheet reflecting reliable operating conditions is still the prime requirement in techno-economic evaluation.

III. DOE Thermochemical Cycle Evaluation Panel

LASL support is being provided to this panel that is chaired by Dr. J. E. Funk (University of Kentucky). Two cycles have undergone evaluation in this reporting period, the LLL zinc selenide cycle and the GA sulfur iodine cycle.

IV. IEA Annex I Workshop

The third annual IEA, Annex I Workshop on Thermochemical Hydrogen Production was held in Tsukuba Science City, Japan, 18-21 June, 1989.

Attendees from the United States were:

H. G. Bowman, Los Alamos Scientific Laboratory
 C.F.V. Mason, Los Alamos Scientific Laboratory
 G. Besenbruch, General Atomic Company
 G. Parker, Westinghouse Electric Corporation
 O. Krikorian, Lawrence Livermore Laboratory

H. G. Bowman, U. S. technical contact for Annex I coordinated U. S. participation at this Workshop.

PROJECT SUMMARY

Project Title: Thermochemical Processes for Hydrogen Production
Principal Investigator: Melvin G. Bowman
Organization: Los Alamos Scientific Laboratory
P. O. Box 1663, MS-756
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FTS 843-6014

Goals: The overall objective of this program is to contribute to the development of practical thermochemical cycles for the production of hydrogen from water using primary heat sources.

Status: The principal program tasks are:

1.0 Experimental: Studies are being conducted to obtain accurate thermochemical data and practical kinetic data for key reactions in cycles that match the heat delivery characteristics of different heat sources. Currently, reactions for the formation and decomposition of bismuth oxysulfates are being studied as steps that minimize heat requirements for solution concentration in sulfuric acid cycles designed to couple with solar heat sources. Studies in a solids decomposition facility consisting of a rotary kiln have shown that $\text{Bi}_2\text{O}(\text{SO}_4)_2$ will decompose in less than 2 minutes at temperatures ranging from 973 to 1143 K. Activities for FY-81 will consist of additional bismuth oxysulfate decomposition experiments and studies of bismuth oxysulfate reactions with sulfuric acid at different temperatures and acid strengths. Design studies will be initiated to determine the suitability of different solids decomposition systems for solar heat input.

2.0 Process Evaluation: Technoeconomic studies have been conducted to determine differences in estimated capital costs and efficiencies between water electrolysis and thermochemical cycles as paths for hydrogen production from primary heat sources. The differences found were relatively minor and within estimation error. The final best method will depend on technical advances made in both branches of technology.

3.0 I.E.A. Information Exchange: As a continuing activity reports and papers are exchanged between U. S. Laboratories and other countries participating in Annex I. of the I.E.A. Agreement on Hydrogen Production. The fourth Annex I workshop is tentatively scheduled to be held in Juelich, Germany, during the summer of 1981.

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