CONF-791127--1

LA-UR-79-2799

TITLE: The LASL Thermochemical Hydrogen Status on September 30, 1979.*

AUTHOR(S): Kenneth E. Cox

ER

SUBMITTED TO: To be presented at the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review Meeting, Reston, Virginia, 12-14 November 1979., and to be published in the Proceedings.

DISCLAIMER

[illegible]

*Work performed under the auspices of the U.S. Department of Energy, Division of Energy Storage Systems.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos Scientific Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545
An Affirmative Action/Equal Opportunity Employer

Form No. 836 R3
St. No. 2629
12/78

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

THE LASL THERMOCHEMICAL HYDROGEN PROGRAM STATUS ON SEPTEMBER 30, 1979*

Kenneth E. Cox

University of California
Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545

Abstract

The work described in this report was accomplished during the period October 1, 1978 - September 30, 1979. Most of the effort was applied to a study of the Los Alamos Scientific Laboratory (LASL) hybrid bismuth sulfate cycle. The work included a conceptual design of the cycly and experimental work to verify the design conditions. Key findings were:

- A 50.8% efficiency was obtained when an improved cycle design was coupled to a fusion energy source at 1500 K.
- Experimental results showed an endothermic heat requirement of + 172 kJ/mol for the decomposition of $Bi_2O_3.2SO_3$ to $Bi_2O_3.SO_3$ and SO_3.
- Reaction times for bismuth sulfate decomposition were determined as a function of temperature. At 1240 K, < 1.5 min were required for the first two stages of decomposition from $Bi_2O_3.3SO_3$ to Bi_2O_3.
- Tests made to determine the feasibility of decomposing $Bi_2O_3.2SO_3$ in a 1 inch diameter rotary kiln showed that $Bi_2O_3.2SO_3$ could be decomposed continuously.

In related work, support was given to the DOE Thermochemical Cycle Evaluation Panel (Funk).

The Second Annual International Energy Agency (IEA) Workshop on Thermochemical Hydrogen Production from Water met on September 24-27, 1979 at Los Alamos.

Fusion Synfuel (Hydrogen) Design Study

Introduction

Thermochemical cycles for hydrogen production have been investigated at the Los Alamos Scientific Laboratory (LASL) since the early 1970s. Process development is sponsored by DOE's Division of Energy Storage Systems (STOR). In recent months, our efforts were concentrated on the development of a thermochemical cycle compatible with a 1500 K heat source derived from a conceptual fusion driver. The major task of this study is to define nonelectrical fusion energy applications. Chief among these applications is the production of synfuel (hydrogen) from fusion power. The study is a joint effort involving thermochemical process development (under STOR) and design and engineering systems for extracting fusion heat (under the Office of Magnetic Fusion Energy).

The LASL Bismuth Sulfate Cycle

The LASL bismuth sulfate cycle has the following steps.

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

$$Bi_2O_3.SO_3 + H_2SO_4(aq) = Bi \quad 2SO_3(s) + H_2O(\ell) \qquad \text{Elec.350K} \quad (2)$$

$$Bi_2O_3 \qquad _3(s) + SO_3(g) \qquad \text{1100-1250K} \quad (3)$$

$$SO \qquad g) + (1/2)O_2(g) \qquad \text{1100-1500K} \quad (4)$$

Thi as originally devised as an alternati se cycles employing H_2SO_4.

LASL cycle, shown schematically in Fig. 1, eral advantages.

- The average endothermic heat requirement for the solid decomposition step is 172 kJ per mol of SO_2 removed.
- $Bi_2O_3.2SO_3$ is the stable solid phase in contact with H_2SO_4 over a 3-52.7 wt% range. In principle, the electrochemical oxidation of SO_2, step (1), could be carried out at a lower voltage. Operation at 10-20 wt% H_2SO_4 would be feasible.
- Sulfuric acid is not handled at high concentrations and temperatures or evaporated.
- Both sulfates present in step (3) remain as solids throughout the reaction.
- Maximum temperatures required for solids decomposition can be lower than in other cycles.

---

* Work performed under the auspices of the U.S. Department of Energy, Division of Energy Storage Systems.

In contrast to the other cycles, the LASL bismuth sulfate cycle involves solid-materials handling. Traditionally, liquids and gases are preferable to solids because of the problems of handling solids. The trade-off must be made between solids-handling and the difficulties (and expense) of handling highly corrosive, boiling H_2SO_4.

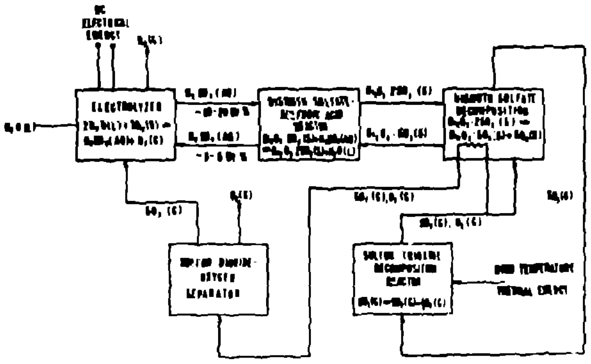

Fig. 1. Schematic of the LASL bismuth sulfate hybrid cycle.

Experimental Verification of Cycle

The experimental bases for the foregoing observations are shown in Figs. 2 and 3. Thermodynamic data on the endothermic heat of reaction for

$$Bi_2O_3.3SO_3(s) = Bi_2O_3.2S_3O(s) + SO_3(g) \quad (5)$$

and reaction (3) were obtained from isothermal batch experiments. The SO_3 pressure is shown as a function of temperature in Fig. 2. Straight-line plots of log P_{SO_3} vs 1/T give a value of 161 kJ/mol (38.4 kcal/mol) for the $Bi_2O_3.3SO_3$ decomposition and 172 kJ/mol (41.2 kcal/mol) for the $Bi_2O_3.2SO_3$ decomposition.

Kinetic data for the decomposition of $Bi_2O_3.3SO_3$ starting material are shown in Fig. 3. The data show the rate of SO_3 removal as a function of time at temperatures of 1050, 1150, and 1240 K. At 1240 K, ~ 1.5 min are required for the decomposition of $Bi_2O_3.3SO_3$ to $Bi_2O_3.SO_3$. Less time (roughly half) would be required for the intermediate step, $Bi_2O_3.2SO_3$ to $Bi_2O_3.SO_3$.

Process Design of Cycle

A thermochemical process design has been developed for the LASL bismuth sulfate cycle. The design aims were to produce an engineering flow sheet, compute mass and energy balances, and obtain a value for the thermal efficiency of the cycle.

A fusion reactor deposits neutrons in a high-temperature boiling lithium blanket at 1500 K. Thermal energy from the isothermal "lithium boiler" is transferred directly to a $SO_3/SO_2/O_2$ process stream for the high-temperature portion of the cycle. One heat exchanger thus provides all the primary thermal energy for the cycle. Heat from a low-temperature (800 K) portion of the fusion blanket provides the electric power generation energy for the electrolysis section located in the low-temperature portion of the cycle.

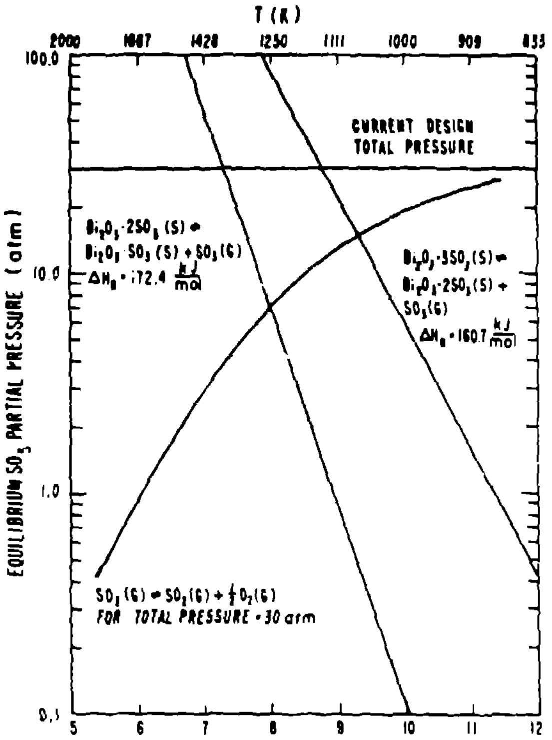

Fig. 2. Equilibrium data for bismuth sulfate and bismuth oxysulfate decomposition.

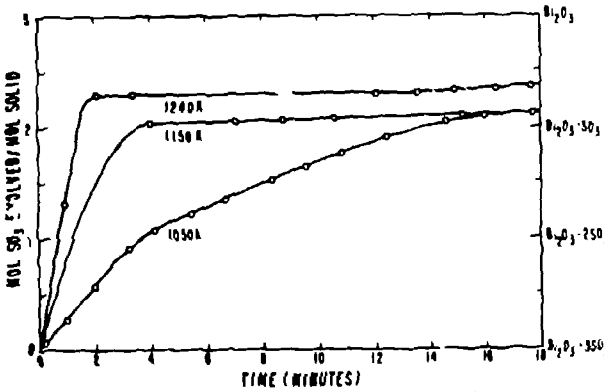

Fig. 3. Kinetics of bismuth sulfate decomposition.

For a representative energy balance and efficiency calculation, we chose the followng process conditions: maximum temperature, 1475 K; pressure, 30 atm; mols SO_2 removed, 1.0; mols H_2O entering, 5.0. The overall energy balance for the cycly is shown schematically in Fig. 4 for these conditions. Details of the design are given below.

The high-temperature portion of the cycle consists of three batteries: Battery A--Solids dewatering, Battery B--Solids decomposition, and Battery C--SO_3 decomposition.

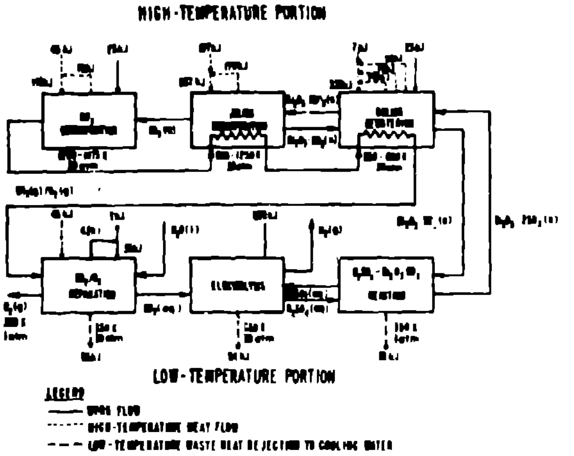

Fig. 4. Cycle energy balance.

A thermal energy balance was performed for each battery to identify the input and output of energy.

Battery A--Solids Dewatering. The function of Battery A is to dry the incoming $Bi_2O_3.2SO_3$ solids and to perform that task by recovering as much heat as possible from hot streams and exothermic reactions.

Battery B--Solids Decomposition. Battery B uses a large amount of heat for decomposing the entering solids to $Bi_2O_3.SO_3$ and SO_3.

Battery C--SO_3 Decomposition. Battery C operates at the highest temperature of the cycle (1475 K). A 25 K difference was arbitrarily chosen for heat transfer.

The low-temperature portion of the cycle operates at 350 K and consists of three batteries: Battery D--SO_2/O_2 separation, Battery E--Electrolyzer, and Battery F--Solids/acid reactor.

Battery D--SO_2/O_2 Separation. The main function of Battery D is to absorb SO_2 from the SO_2/O_2 gas mixture. Heating the purified oxygen stream to 1475 K for generating work in a turbine expander gives a net work gain.

Battery E--Electrolyzer. We assume a working voltage of 0.45 V, at an acid concentration of 15 wt% and a current density of 2000 A/m^2. The electrolyzer is designed for operation at 350 K and 30 atm.

Battery F--Solids/Acid Reactor. $Bi_2O_3.SO_3$ reacting with H_2SO_4 releases heat at 350 K to cooling water.

Overall Efficiency of Cycle

The cycle's efficiency is computed from the values given in Fig. 4. The net heat requirement is 294 kJ and the work requirement is 269 kJ--a total of 563 kJ. The efficiency is η = 286/563 = 0.508 (50.8%).

A parametric analysis was made to evaluate the effect of three major system variables on the cycle's efficiency. The variables chosen for this analysis were the electrolyzer cell voltage, the endothermic heat requirement in the high-temperature portion, and the maximum stream temperature in the cycle.

Of the three variables investigated, the cycle's efficiency was most affected by the electrolyzer voltage and the endothermic heat requirement. The efficiency is extremely sensitive to variation in electrolyzer voltage. The effect of maximum stream temperature variation is important primarily because it varies the equilibrium yield in the $SO_3 = SO_2 + (1/2)O_2$ reaction, hence changes the composition of the gas mixture leaving the high-temperature portion of the cycle. It also affects the rate of solids circulation.

Conclusions of Study

The LASL bismuth sulfate cycle is a promising approach to producing hydrogen from a high-temperature process heat source (1500 K) such as that from a fusion or solar reactor. It avoids the problem of evaporating H_2SO_4 solutions and has an estimated 50% efficiency, based on a flow-sheet analysis. Crucial issues still to be resolved are the demonstration of low-voltage electrolysis under production conditions, the recovery of latent heat of vaporization from drying solid $Bi_2O_3.2SO_3$, and the handling of large amounts of solids in a high-temperature decomposer vessel.

Bismuth Sulfate Decomposition Facility

A facility for studying continuous $Bi_2O_3.2SO_3$ decomposition is being built at LASL. Initially, we planned to carry out the decomposition reactions in a fluidized-bed reactor. Experiments with $Bi_2O_3.2SO_3$ showed "pilling" to take place on fluidization. Since then, we have constructed a 1-inch diameter laboratory-scale quartz rotary kiln. The atmosphere above the decomposing solids can also be controlled. We intend to study the effect of residence time, and temperature on the decomposition rate and yield of $Bi_2O_3.2SO_3$. Preliminary experiments have just begun and indicate complete conversion of the feed to $Bi_2O_3.0.7SO_3$ at temperatures in the range 1000-1100 K.

DOE Thermochemical Cycle Evaluation Panel

LASL support in being provided to the panel chaired by Professor J. E. Funk (Kentucky). At this time, two cycles are undergoing evaluation. They are the G.A. Sulfuric Acid-Iodine process and the LLL Zinc-Selenide process.

IEA Meeting, September 24-27, 1979, Los Alamos

A thermochemical cycle workshop was held at LASL under IEA auspices during the latter part of September. Over 40 persons attended the conference with international delegates from the European Common Market (EEC) Ispra laboratory, West Germany, and Japan. Leading emphasis was placed on sulfuric acid based cycles - sulfuric acid decomposition and materials problems.

In other discussion, the following topics were included:

- Electrochemical SO_2 reactions
- Hydrogen halide decomposition
- New cycles and heat sources
- Complete circuits (bench-scale)
- Techno-economic assessments.

Much technical progress was noted since the First Annual Workshop was held at Ispra, Italy in August 1978. The value of programs to identify new and alternative cycles was recognized and emphasized by the Workshop. Plans for future technical cooperation in these and other areas will be submitted to the IEA Executive Committee for consideration and approval.