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TITLE: ADVANCED THERMOCHEMICAL HYDROGEN CYCLES

MASTER

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CONTRACT W-7405-ENG. 36

PROJECT SUMMARY

Project Title: Thermochemical Processes for Hydrogen Production

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Goals: The overall objective of this program is to contribute to the development of practical thermochemical cycles for the production of hydrogen from water. Specific goals are:

- Investigate and evaluate the technical and economic viability of thermochemical cycles as an advanced technology for producing hydrogen from water.
- Investigate and evaluate the engineering principles involved in interfacing individual thermochemical cycles with the different thermal energy sources; high temperature fission, solar and fusion.
- Conduct a continuing research and development effort to evaluate the use of solid sulfates, oxides and other compounds as potentially advanced cycles and as alternates to H_2SO_4 based cycles.

Status: Basic thermochemistry studies have been completed for two different steps in the decomposition of bismuth sulfate. Two different bismuth sulfate cycles have been defined for different sulfuric acid strengths. The eventual "best" cycle will depend on energy required to form sulfuric acid at different concentrations.

- A solids decomposition facility has been constructed and practical studies of solid decompositions are being conducted. The facility includes a rotary kiln system and a dual-particle fluidized bed system.
- Evaluation of different types of cycles for coupling with different heat sources is continuing.

Contract No.: AI-10-05-15-0

Contract Period: FY-1981 **Funding Level:** $150 K

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ADVANCED THERMOCHEMOCAL HYDROGEN CYCLES

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The Los Alamos program on the "Thermochemical Production of Hydrogen" is designed to provide experimental and/or analytical information in direct support of cycles selected by the Division of Chemical/Hydrogen Energy Systems for process development and evaluation and to identify and conduct experimental and analytical feasibility studies of advanced or longer range cycles with potential advantages for matching the individual heat delivery characteristics of solar thermal, high temperature fission, and fusion energy sources. Recent progress and current activities are described below.

1.0 Bismuth Sulfate Chemistry. We have completed studies of the thermochemistry of bismuth sulfate decomposition and determined that bismuth sulfate decomposes through a series of intermediate oxysulfates rather than directly to bismuth oxide. Equations 1, 2, and 3 of Figure I illustrates this progressive decomposition. Enthalpies for reactions 1 and 2 were determined experimentally by measuring equilibrium gas pressures as a function of temperature. The values obtained are 161 and 172 kJ/mol for reaction 1 and 2, respectively. Although the enthalpy for reaction 3 was not determined, it is expected to approximate that for reaction 2 since the decomposition proceeds rapidly to the bismuth oxysulfate product of reaction 3.

We have found that $Bi_2O(SO_4)_2$ is the stable sulfate in contact with sulfuric acid in the concentration range of 3.0 to 52.7 wt% at ambient temperatures. 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. From our studies it is clear that there are two alternate bismuth sulfate cycles based on the initial formation of sulfuric acid. These are described as Alternate I and Alternate II in Figure I. Both cycles contain an additional step for the decomposition of SO_3 to SO_2 and O_2.

Alternate I requires higher strength sulfuric acid, but for each mole of SO_3 finally decomposed, requires a lower bismuth inventory and less energy for drying the solid sulfate. Alternate II requires lower strength sulfuric acid. Thus, its potential advantage depends on the possibility that significantly less energy may be required to form dilute sulfuric acid. Studies to determine the energy required to form sulfuric acid as a function of concentration are being made in other programs, primarily in other laboratories.

2.0 Solids Decomposition Facility. Most of the recent worldwide effort on applied process development has been focused on sulfuric acid cycles. Encouraging progress is being made. In principle, however, more efficient cycles are possible, particularly for high temperature isothermal heat sources. For example, several laboratories are considering the use of solid sulfates in sulfuric acid based cycles to avoid the concentration of sulfuric acid which is an energy intensive step. Methods for forming sulfates more directly are also under study. A second example is related to a recognition that cycles based on solid oxide decomposition as the high temperature step offer unique advantages for coupling with a solar furnace since the oxide can be heated and decomposed in air at temperatures where the oxygen dissociation pressure exceeds the pressure of oxygen in the atmosphere. Thus, the oxide can be heated directly by solar radiation entering through an "air window" and the usual difficult problem of transmitting heat to a process, either through a container wall or a quartz window, can be greatly simplified.

The key to practicality for advanced solid sulfate cycles will be determined to a large extent by the availability of practical methods for handling solids. Consequently, most of our current experimental effort under C/HES involves the testing of methods for promoting solid decomposition reactions.

2.1 Rotary Kiln Facility. A laboratory-scale rotary kiln was was constructed from a 25 mm diameter quartz tube which is coupled to a "screw feeder" through a gas tight rotary seal. Figure II is a schematic of the system.

The rotary kiln has been used in experiments to decompose $Bi_2O(SO_4)_2$, $La_2(SO_4)_3$, $ZnSO_4$ and Co_3O_4. Results of typical experiments are presented in Figures III, IV, V & VI.

2.2 Fluidized Bed Facility. A "dual particle" fluidized bed facility has been constructed and tested at temperatures up to 1425K. In the system, a bed of spherodized particles (stabilized ZrO_2) is fluidized by a carrier gas (initially argon) which carries the finer particle feed material through the bed. The decomposed feed material is collected down stream in a cyclone separator. Figure VII is a schematic of the system.

The dual-particle fluidized bed has been tested in experiments to decompose $ZnSO_4$. Results of these initial studies are presented in Figure VIII. Results of the earlier $ZnSO_4$ kiln experiments are also included for ease of comparison.

It should be noted that the sulfate decomposition reactions have been written to show SO_3 evolution (rather than a mixture of SO_3, SO_2 and O_2). The actual gas compositions for the different experiments will be determined in future experiments. We also plan to determine the effects of adding catalysts, not only on the composition of the evolved gases, but also on decomposition rates.

3.0 Matching Cycles with Thermal Energy Sources. As indicated above, cycles based on solid decomposition almost require a source of high temperature isothermal heat rather than heat from a circulating gas cooled reactor. In contrast, sulfuric acid cycles are better suited for heat delivered from a cooling gas stream. Of course, an isothermal heat source can be used for sulfuric acid cycles, but (in an ideal sense) with a loss of potential efficiency. Comparisons of heat requirements versus temperature for H_2SO_4 decomposition and for $Bi_2O(SO_4)_2$ decomposition are given in Figures IX-XII. Figure XIII presents simplified "load line" curves that illustrate the comparisons. It should be noted that the large heat requirement for drying sulfuric acid is not included.

4.0 Acknowledgement. The experimental work described herein was performed by C. M. Hollabaugh, W. M. Jones and C. L. Peterson.

FIG. I. DECOMPOSITION OF $Bi_2(SO_4)_3$

$Bi_2(SO_4)_3 = Bi_2O(SO_4)_2 + SO_3$ (1)

$Bi_2O(SO_4)_2 = Bi_2O_2SO_4 + SO_3$ (2)

$Bi_2O_2SO_4 = Bi_2O_{2.3}(SO_4)_{0.7} + 0.3\ SO_3$ (3)

ALTERNATE I

$Bi_2O_{2.3}(SO_4)_{0.7} + 2.3\ H_2SO_4 = Bi_2(SO_4)_3 + 2.3\ H_2O$

$Bi_2(SO_4)_3 = Bi_2O_{2.3}(SO_4)_{0.7} + 2.3\ SO_3$

ALTERNATE II

$Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ H_2SO_4 = Bi_2O(SO_4)_2 + 1.3\ H_2O$

$Bi_2O(SO_4)_2 = Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ SO_3$

FIG. II. LABORATORY ROTARY KILN

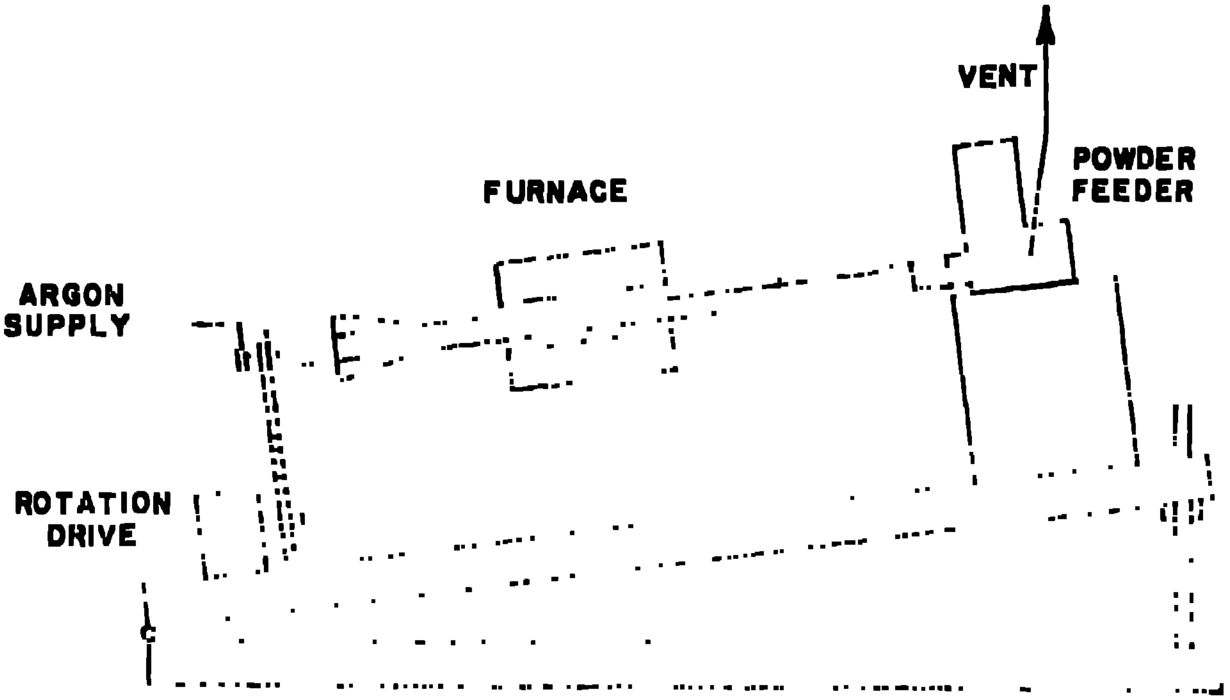

FIG. III. DECOMPOSITION OF $Bi_2O(SO_4)_2$ IN ROTARY KILN

$$Bi_2O(SO_4)_2 = Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ SO_3$$

TEMP (K)	TIME (s)	DECOMPOSITION (%)
993	67	63
993	138	81
1023	51	49
1023	66	50
1023	128	84
1073	46	81
1073	66	90
1073	126	97
1123	62	96
1123	80	98
1123	152	93

FIG. IV. DECOMPOSITION OF $LA_2(SO_4)_3$ IN ROTARY KILN

$$LA_2(SO_4)_3 = LA_2O_2SO_4 + 2SO_3$$

TEMP (K)	TIME (s)	DECOMPOSITION (%)
1263	66	11.5

FIG. V. DECOMPOSITION OF $ZNSO_4$ IN ROTARY KILN

$$ZNSO_4 = ZNO + SO_3$$

TEMP (K)	TIME (s)	DECOMPOSITION (%)
1223	60	45.6
1283	60	92.1

FIG. VI. DECOMPOSITION OF Co_3O_4 IN ROTARY KILN

$$Co_3O_4 = 3\ CoO + 1/2\ O_2$$

TEMP (K)	TIME (s)	DECOMPOSITION (%)
1283	60	100
1263	60	96

FIG. VII. FLUIDIZED BED SYSTEM

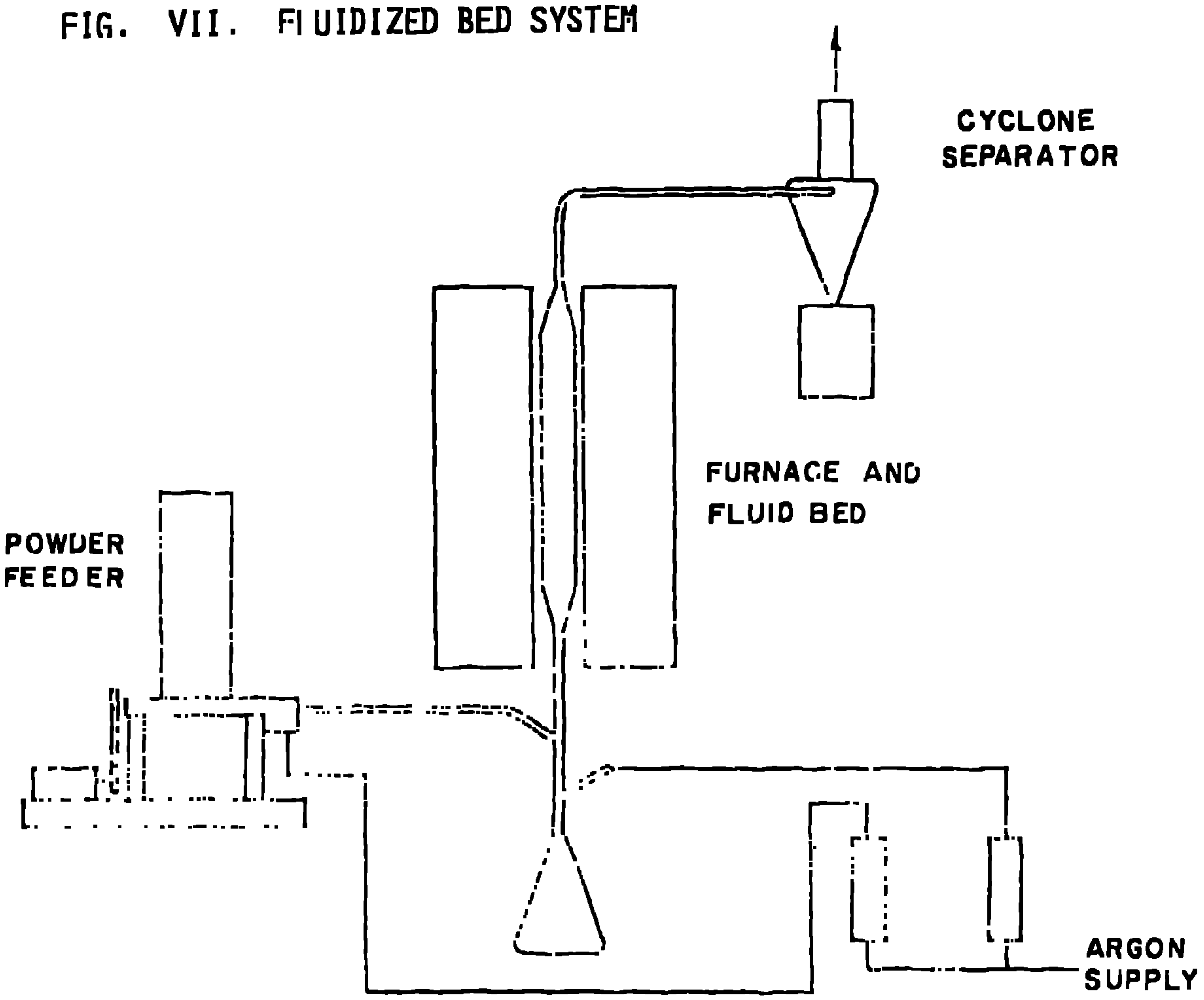

FIG. VIII. DECOMPOSITION OF $ZnSO_4$

$$ZnSO_4 = ZnO + SO_3$$

FLUIDIZED BED (1223 K)

SOLID RATE (G/S)	RATIO ($Ar/ZnSO_4$)	TIME (S)	P (ATM) $SO_3 + SO_2$	% DEC.
0.017	64.2	0.35	0.011	93
0.042	25.7	0.35	0.026	91
0.065	16.7	0.34	0.034	77
0.090	12.0	0.34	0.042	70
0.098	11.1	0.34	0.039	60

ROTARY KILN

TEMP (K)	MOL. RATIO ($Ar/ZnSO_4$)	TIME (s)	P (ATM) $SO_3 + SO_2$	% DEC.
1223	0.89	60	0.24	46
1283	0.78	60	0.38	92

FIG. IX. DECOMPOSITION OF $H_2SO_4(\ell)$

ASSUME: (1) VAPORIZATION OF 100% H_2SO_4 AT 700K TO FORM EQUILIBRIUM GAS MIXTURE AT A PRESSURE OF 10.6 ATM. (2) THE GAS HEATED TO ACHIEVE EQUILIBRIUM AT 1300K AND 10.6 ATM. GAS COMPOSITIONS WOULD BE:

COMPONENT	700K	1300K
H_2SO_4 (G)	4.02 ATM	---
H_2O (G)	3.27	4.36 ATM
SO_3 (G)	3.21	0.63
SO_2 (G)	0.06	3.73
O_2	0.03	1.87

IF GAS CONTAINS 1 MOLE OF SO_2 AT 1300K, THE UNDISSOCIATED SO_3 WOULD BE 0.17 MOLE. THUS, 1.17 MOLES OF $H_2SO_4(\ell)$ WOULD NEED TO BE VAPORIZED AT 700K AND HEATED TO 1300K TO YIELD 1 MOLE OF SO_2.

FIG. XI. BISMUTH SULFATE DECOMPOSITION

$$Bi_2O(SO_4)_2 \rightarrow Bi_2O_2SO_4 + (1-x)SO_3 + xSO_2 + x/2\ O_2$$

AT 1125K: x = 0.66, TOTAL P = 4.2 ATM

FOR DECOMPOSITION OF 1.14 MOLES OF $Bi_2O(SO_4)_2$ TO $Bi_2O_2SO_4$ AND EQUILIBRIUM GAS MIXTURE AT 1125K (4.2 ATM) THE HEAT REQUIREMENT IS 270.4 kJ. HEATING THE GAS AND OBTAINING EQUILIBRIUM WOULD REQUIRE HEAT (NET) AS FOLLOWS:

TEMPERATURE	HEAT NEEDED	ACCUM. HEAT
AT 1125K	270.4 kJ	270.4 kJ
1125 - 1200	12.8	283.2
1200 - 1300	10.7	293.9

HEAT REQUIREMENTS COULD BE MET BY COOLING 81 MOLES OF He 175 DEGREES (1325 - 1150K)?

FIG. XII. BISMUTH SULFATE DECOMPOSITION.

$Bi_2O(SO_4)_2 \rightarrow Bi_2O_2SO_4 + (1-x)\ SO_3 + xSO_2 + x/2\ O_2$ (1)

AT 1125K: $x = 0.66$, TOTAL P = 4.2 ATM.

FOR CASES AT 1300K AND 4.2 ATM. $x = 0.88$ AND MIXTURE CONTAINING 1 MOLE OF SO_2 AND 1/2 MOLE OF O_2 WOULD CONTAIN 0.14 MOLE OF SO_3. THUS, 1.14 MOLE OF $Bi_2O(SO_4)_2$ DECOMPOSED IN REACTION 1 WOULD YIELD 1 MOLE OF SO_2 AFTER GASES HEATED TO BOOK.

IF GAS MIXTURE CONTAINING 7.0 MOLES OF SO_2, 3.5 MOLES OF O_2 AND 0.95 MOLES OF SO_3 IS BROUGHT IN CONTACT WITH 1.14 MOLES OF $Bi_2O(SO_4)_2$ AT 1125K, THE HEAT CONTENT OF COOLING GASES PLUS HEAT EVOLVED IN SHIFTING EQUILIBRIUM IS JUST SUFFICIENT TO DECOMPOSE THE SULFATE AND YIELD OVERALL EQUILIBRIUM AT 1125K. (~ 270 kJ)

THUS: 11.5 MOLES OF GAS WOULD BE CYCLED IN THE HEAT PIPE SYSTEM.