APPENDIX B. Survey of Programs on Thermochemical Hydrogen Production

AEROJET GENERAL CORPORATION

Location: 9100 Flair Drive

El Monte, CA (213-572-6000)

Sponsor: In-house funding

Program Duration as

of January 1975: Unknown, now

discontinued

Principal Investigators: A. R. Miller and H. Jaffe

<u>Program Description:</u> To the best of our knowledge, there is no work on thermochemical hydrogen production currently under way at Aerojet General Corp. The only reference we have is to U.S. Patent No. 3,490,871 filed in October of 1965. Cognizant personnel at Aerojet could not be located for this survey.

Cycles Published or Disclosed:

200	+ 2H ₂ O →	3C - OTT	1 77	/70000
205	" LII2O "	4CSOM	T_{2}	(100°C)

$$2CsOH + {}^{3}/{}_{2}O_{2} \rightarrow 2CsO_{2} + H_{2}O$$
 (500°C)

$$2CsO_2 \rightarrow Cs_2O + \frac{3}{2}O_2$$
 (700°C)

$$Cs_2O \rightarrow 2Cs + \frac{1}{2}O_2$$
 (1200°C)

- 1. Carney, H. C., "Cesium-Water H₂ Production Process," <u>Aerojet-General Nucleonics Rep.</u> No. <u>AN-1377</u>, Defense Documentation Center Catalog No. <u>AD-4608412</u> (1965).
- Miller, A. R. and Jaffe, H., "Process for Producing Hydrogen From Water Using an Alkali Metal," U.S. Patent 3,490,871 (1965) October 19.

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AIR PRODUCTS AND CHEMICALS, INCORPORATED

Location: P.O. Box 538

Allentown, PA 18105 (215-395-4911)

Sponsor: In-house funding

Program Duration as

of January 1975: Unknown

Principal Investigator: P. Foust

Program Description: Air Products and Chemicals, Inc., is a large manufacturer of hydrogen via natural gas steam-reforming and off gases from oil refineries. Although they have no specific program dealing with thermochemical hydrogen production, they are keeping up to date on progress made in the field and expect to eventually apply thermochemical technology. A patent on a thermochemical-electrochemical process was granted to Air Products in 1965.

Cycles Published or Disclosed:

 $H_2O + Cl_2 \rightarrow 2HCl + \frac{1}{2}O_2$ (700°C)

 $2HC1 \rightarrow H_2 + Cl_2$ (electrolysis) (300°C)

Publications and Patents:

Hallet, N. C., "Study, Cost, and System Analysis of Liquid H₂ Production," NASA No. CR73-226. Allentown, Pa.: Air Products and Chemicals, Inc., June 1968.

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ARGONNE NATIONAL LABORATORIES

Location: Argonne, IL 60439 (312-739-7711-X 2206) Sponsor: ERDA

Program Duration as of January 1975: 1-1/2 years

Principal Investigators: B. M. Abraham and F. Schreiner

<u>Program Description:</u> Work at Argonne is geared towards the goal of demonstration of a viable, close-loop thermochemical cycle. Their efforts presently include cycle derivation, efficiency analysis, and laboratory experimentation on individual reactions. Several cycles derived at Argonne have been published.

Cycles Published or Disclosed:

$$LiNO_2 + I_2 + H_2O \rightarrow LiNO_3 + 2HI$$
 (300°K)

$$2HI \rightarrow I_2 + H_2$$
 (700 °K)

$$LiNO_3 \rightarrow LiNO_2 + \frac{1}{2}O_2$$
 (750°K)

$$2NH_3 + 2H_2O + 2CO_2 + 2NaBr \rightarrow 2NH_4Br + 2NaHCO_3$$

$$2NH_4Br + 2Ag \rightarrow 2AgBr + 2NH_3 + H_2$$

$$Na_2CO_3 + 2AgBr \rightarrow 2NaBr + 2Ag + CO_2 + \frac{1}{2}O_2$$

$$2NH_3 + 2H_2O + 2CO_2 + 2KI \rightarrow 2NH_4 I + 2KHCO_3$$

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$$

$$2NH_4 I \rightarrow 2NH_3 + I_2 + H_2$$

$$K_2 CO_3 + I_2 \rightarrow 2KI + CO_2 + 1/2O_2$$

ARGONNE NATIONAL LABORATORIES, Cont.

$$2KNO_3 + I_2 \rightarrow 2KI + 2NO_2 + O_2$$

 $2NO_2 + {}^1/{}_2 O_2 + H_2O \rightarrow 2HNO_3$
 $2HNO_3 + 2NH_3 \rightarrow 2NH_4NO_3$
 $2KI + 2NH_4NO_3 \rightarrow 2KNO_3 + 2NH_4I$
 $2NH_4I \rightarrow 2NH_3 + I_2 + H_2$

Publications and Patents:

- 1. Abraham, B. and Schreiner, F., "A Low-Temperature Thermal Process for the Decomposition of Water," Science 180, 959-60 (1973) June 1.
- 2. Abraham, B. and Schreiner, F., "Low Temperature Thermal Decomposition of Water," Science 182, 1372 (1973).
- 3. Abraham, B. and Schreiner, F., "General Principles Underlying Chemical Cycles Which Thermally Decompose Water Into the Elements," Ind. Eng. Chem. 13, 305-10 (1974).

G A S

ATOMIC ENERGY OF CANADA, LTD.

Location: Whiteshell Nuclear Research

Establishment Pinawa, Manitoba Sponsor: In-house funding

Program Duration as of January 1975: 1972-1973

Principal Investigators: G. G. Strathee and D. J. Cameron

Program Description: This program was a feasibility study comparing various methods of hydrogen production with projections on natural gas supplies and costs. The study was concerned with Canada's projected energy situation, with only a cursory examination of problems in the United States. Direct references to thermochemical hydrogen production are minimal.

Cycles Disclosed and Published: None

Publications and Patents:

Strathee, G. G. and Cameron, D. J., "Production of Hydrogen From a Nuclear Base," Rep. No. WNRE-131. Pinawa, Manitoba: Atomic Energy of Canada, Ltd., June 1973.

AVCO SYSTEMS DIVISION

Location: 201 Lowel

Wilmington, MA 01887

(617-657-5111)

Sponsor: Unknown

Program Duration as

of January 1975: Unknown

Principal Investigator: Dr. W. Gibson

<u>Program Description:</u> Avco was not willing to divulge any information concerning their program.

Cycles Published or Disclosed: None

EURATOM

- 1. Joint Nuclear Center Ispra, Italy
- 2. University of Aachen W. Germany

Location: 1. Joint Nuclear Research Center Ispra Establishment, Italy

Sponsor: In-house funding

2. University of Aachen Aachen, W. Germany

Program Duration as of January 1975: 4 years

Principal Investigator: G. De Beni

Program Description: This program is concerned with thermochemical cycle derivation, thermochemical efficiency analysis, laboratory trials of reaction steps (including some kinetic work), materials testing, flow-sheet evaluation, and nuclear reactor interface studies. The program is carried out at both Ispra and the University of Aachen. In addition, they may subcontract some of the program to KFA.

Cycles Published or Disclosed:

$$C + H_2O \rightarrow CO + H_2 \qquad (700 \,^{\circ}C)$$

$$CO + 2Fe_3O_4 \rightarrow C + 3Fe_2O_3 \qquad (250 \,^{\circ}C)$$

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + ^{1}/_{2} O_2 \qquad (1400 \,^{\circ}C)$$

$$(Marchetti)$$

$$2CrCl_2 + 2NC1 \rightarrow 2CrCl_3 + H_2 \qquad (200 \,^{\circ}C)$$

$$2CrCl_3 \rightarrow 2CrCl_2 + Cl_2 \qquad (1000 \,^{\circ}C)$$

$$H_2O + Cl_2 \rightarrow 2HC1 + ^{1}/_{2} O_2 \qquad (900 \,^{\circ}C)$$

$$3H_2O + 3Cl_2 \rightarrow 6HC1 + ^{3}/_{2} O_2 \qquad (800 \,^{\circ}C)$$

$$18HC1 + 3Fe_2O_3 \rightarrow 6FeCl_3 + 9H_2O \qquad (100 \,^{\circ}C)$$

$$6FeCl_3 \rightarrow 6FeCl_2 + 3Cl_2 \qquad (400 \,^{\circ}C)$$

$$6FeCl_2 + 8H_2O \rightarrow 2Fe_3O_4 + 12HC1 + 2H_2 \qquad (600 \,^{\circ}C)$$

$$2Fe_3O_4 + ^{1}/_{2} O_2 \rightarrow 3Fe_2O_3 \qquad (400 \,^{\circ}C)$$

$$(C. Hardy)$$

$$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$$
 (500°C)

$$Fe_3O_4 + \frac{9}{2}Cl_2 \rightarrow 3FeCl_3 + 2O_2$$
 (1000°C)

$$3FeCl_3 \rightarrow 3FeCl_2 + \frac{3}{2}Cl_2$$
 (350°C)

$$3\text{FeCl}_2 + 3\text{H}_2 \rightarrow 3\text{Fe} + 6\text{HCl}$$
 (1000°C)

$$6HC1 + {}^{3}/_{2} O_{2} \rightarrow 3H_{2}O + 3C1_{2}$$
 (500 °C)

$$SO_2 + H_2O + I_2 \rightarrow SO_3 + 2HI$$

 $SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$
 $2HI \rightarrow H_2 + I_2$

1. MARK 1

$$CaBr_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HBr$$
 (730°C)

$$2HBr + Hg \rightarrow HgBr_2 + H_2 \qquad (200 \,^{\circ}C)$$

$$HgBr_2 + Ca(OH)_2 \rightarrow CaBr_2 + HgO + H_2O$$
 (200°C)

$$HgO \rightarrow Hg + \frac{1}{2}O_2$$
 (600°C)

(G. De Beni)

2. MARK 1B

$$CaBr_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HBr$$
 (730 °C)

$$2HBr + Hg2Br2 - 2HgBr2 + H2$$
 (120°C)

$$HgBr_2 + Hg \rightarrow Hg_2Br_2$$
 (120°C)

$$HgBr_2 + Ca(OH)_2 \rightarrow CaBr_2 + HgO + H_2O$$
 (200°C)

$$HgO \rightarrow Hg + \frac{1}{2}O_2$$
 (600°C)

(G. De Beni and G. Schütz)

3. MARK 1C

$$2CaBr2 + 4H2O \rightarrow 2Ca(OH)2 + 4HBr (730 °C)$$

$$4HBr + Cu_2O \rightarrow 2CuBr_2 + H_2O + H_2$$
 (100°C)

$$2CuBr_2 + 2Ca(OH)_2 \rightarrow 2CuO + 2CaBr_2 + 2H_2O$$
 (100°C)

$$2CuO \rightarrow Cu_2O + \frac{1}{2}O_2$$
 (900 °C)

(G. De Beni)

4. MARK 1S

$$SrBr_2 + H_2O \rightarrow SrO + 2HBr$$
 (800°C)

$$2HBr + Hg \rightarrow HgBr_2 + H_2$$
 (200°C)

SrO + HgBr₂
$$\rightarrow$$
 SrBr₂ + Hg + 1 /₂ O₂ (500 °C)
(G. De Beni)

5. MARK 2

$$Mn_2O_3 + 4NaOH \rightarrow 2Na_2O. MnO_2 + H_2O + H_2$$
 (800°C)

$$2Na_2O. MnO_2 + nH_2O \rightarrow 4NaOH(acq.) + 2MnO_2$$
 (100°C)

$$2MnO_2 \rightarrow Mn_2O_3 + \frac{1}{2}O_2$$
 (600°C)
(G. De Beni)

6. MARK 2C

$$Mn_2O_3 + 2Na_2CO_3 \rightarrow 2Na_2O. MnO_2 + CO_2 + CO$$
 (850°C)

$$CO + H_2O \rightarrow H_2 + CO_2$$
 (500°C)

$$2NaO. MnO_2 + nH_2O + 2CO_2 \rightarrow 2Na_2CO_3(acq.) + 2MnO_2$$
 (100°C)

$$2MnO_2 \rightarrow Mn_2O_3 + \frac{1}{2}O_2$$
 (600°C)
(G. De Beni)

7. MARK 3

$$Cl_2 + H_2O \rightarrow 2HC1 + \frac{1}{2}O_2$$
 (800°C)

$$2HC1 + 2VOC1 \rightarrow 2VOC1_2 + H_2$$
 (170°C)

$$4VOCl_2 \rightarrow 2VOCl + 2VOCl_3 \tag{600 °C}$$

$$2VOCl_3 \rightarrow 2VOCl_2 + Cl_2$$
 (200°C)

(G. De Beni)

8. MARK 4

$$H_2O + Cl_2 \rightarrow 2HCl + \frac{1}{2}O_2$$
 (800°C)

$$2 \text{ HC1 +S} + 2 \text{FeCl}_2 \rightarrow \text{H}_2 \text{S} + 2 \text{ FeCl}_3$$
 (100°C)

$$H_2S \rightarrow H_2 + \frac{1}{2}S_2$$
 (800°C)

$$2 \text{ FeCl}_3 \rightarrow 2 \text{FeCl}_2 + \text{Cl}_2 \qquad (420 \,^{\circ}\text{C})$$

(C. Hardy)

9. MARK 5

$$CaBr2 + H2O + CO2 \rightarrow CaCO3 + 2HBr$$
 (600°C)

$$CaCO_3 \rightarrow CaO + CO_2$$
 (900°C)

$$2 HBr + Hg \rightarrow HgBr_2 + H_2$$
 (200°C)

$$HgBr_2 + CaO + nH_2O \rightarrow CaBr_2(acq.) + HgO$$
 (200°C)

$$HgO \rightarrow Hg + \frac{1}{2}O_2$$
 (600°C)

(G. De Beni)

10. MARK 6

$$Cl_2 + H_2O \rightarrow 2HC1 + \frac{1}{2}O_2$$
 (800°C)

$$2HC1 + 2CrCl2 \rightarrow 2CrCl3 + H2$$
 (170°C)

$$2CrCl3 + 2FeCl2 \rightarrow 2CrCl2 + 2FeCl3$$
 (700°C)

$$2FeCl3 \rightarrow 2FeCl2 + Cl2$$
 (350°C)

(G. De Beni)

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11. MARK 6C

$$Cl_2 + H_2O \rightarrow 2HC1 + ^1/_2 O_2$$
 (800°C)
 $2HC1 + 2CrCl_2 \rightarrow 2CrCl_3 + H_2$ (170°C)
 $2CrCl_3 + 2FeCl_2 \rightarrow 2CrCl_2 + 2FeCl_3$ (700°C)
 $2FeCl_3 + 2CuC1 \rightarrow 2FeCl_2 + 2CuCl_2$ (150°C)
 $2CuCl_2 \rightarrow 2CuC1 + Cl_2$ (500°C)
(G. De Beni)

12. MARK 7

$$6 \text{FeCl}_2 + 8 \text{ H}_2 \text{O} \rightarrow 2 \text{Fe}_3 \text{O}_4 + 12 \text{ HCl} + 2 \text{H}_2$$
 (650°C)
 $2 \text{ Fe}_3 \text{O}_4 + {}^1/{}_2 \text{ O}_2 \rightarrow 3 \text{Fe}_2 \text{O}_3$ (350°C)
 $3 \text{Fe}_2 \text{O}_3 + 18 \text{HCl} \rightarrow 6 \text{FeCl}_3 + 9 \text{H}_2 \text{O}$ (120°C)
 $6 \text{FeCl}_3 \rightarrow 6 \text{FeCl}_2 + 3 \text{Cl}_2$ (420°C)
 $3 \text{H}_2 \text{O} + 3 \text{Cl}_2 \rightarrow 6 \text{HCl} + {}^3/{}_2 \text{ O}_2$ (800°C)
(C. Hardy)

13. MARK 7A

$6FeCl_2 + 8H_2O \rightarrow 2Fe_3O_4 + 12HC1 + 2H_2$	(650°C)
$2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3$	(350°C)
$2\text{Fe}_2\text{O}_3 + 12\text{HC}1 \rightarrow 4\text{FeCl}_3 + 6\text{H}_2\text{O}$	(120°C)
$Fe_2O_3 + 3Cl_2 \rightarrow 2FeCl_3 + \frac{3}{2}O_2$	(1000°C)
$6FeCl_3 \rightarrow 6FeCl_2 + 3Cl_2$	(420°C)
(C. Hardw)	

14. MARK 7B

$$6\text{FeCl}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 12\text{HC1} + 2\text{H}_2$$
 (650°C)
 $2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3$ (350°C)
 $3\text{Fe}_2\text{O}_3 + 9\text{Cl}_2 \rightarrow 6\text{FeCl}_3 + \frac{9}{2}\text{O}_2$ (1000°C)

$$6FeCl_3 \rightarrow 6FeCl_2 + 3Cl_2 \qquad (420 °C)$$

15. MARK 8

$$6MnCl_2 + 8H_2O \rightarrow 2Mn_3O_4 + 12HC1 + 2H_2$$
 (700°C)

$$3Mn_3O_4 + 12HC1 \rightarrow 6MnCl_2 + 3MnO_2 + 6H_2O$$
 (100°C)

$$3MnO_2 \rightarrow Mn_3O_4 + O_2 \tag{900 °C}$$

(G. De Beni)

16. MARK 9

$$6\text{FeCl}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 12\text{HCl} + 2\text{H}_2$$
 (650°C)
 $2\text{Fe}_3\text{O}_4 + 3\text{Cl}_2 + 12\text{HCl} \rightarrow 6\text{FeCl}_3 + 6\text{H}_2\text{O} + \text{O}_2$ (150-200°C)
 $6\text{FeCl}_3 \rightarrow 6\text{FeCl}_2 + 3\text{Cl}_2$ (420°C)
(C. Hardy)

- 1. Beghi, G., Broggi, A. and De Beni, G., "Thermochemical Water-Splitting as a Method for Hydrogen Production," Paper presented at the BNS Conference, London, November 1974.
- 2. "Considerations on Iron-Chlorine-Oxygen Reactions in Relation to Thermochemical H₂O Splitting." Paper No. Euratom Sll-13 presented at the Miami THEME Conference, March 1974.
- 3. De Beni, G., "Hydrogen Production Cycle Process," Ger. Offen. 2,005,015 (C2.C.01b) (1970) September 10.

EURATOM, Concluded

- 4. De Beni, G., "Process for the Preparation of Hydrogen," U.S. Patent 3,594,124 (1971) July 20.
- 5. De Beni, G. and Marchetti, C., "A Chemical Process to Decompose H₂O Using Nuclear Heat." Paper presented to the Division of Fuel Chemistry of the ACS, Boston, April 1972.
- 6. EURATOM, Annu. Prog. Rep. No. 1-5, 1970-74.
- 7. Gremer, H., et al., "Water-Splitting Processes of the Iron-Chlorine Family." Paper presented at the BNS Conference, London, November, 1974.

GENERAL ELECTRIC COMPANY

Location: P. O. Box 8
Schenectady, NY 12304
(518-346-8771)

Sponsor: In-house funding

Program Duration as

of January 1975: 2 years (not ongoing)

Principal Investigator: R. E. Hanneman

Program Description: General Electric's program lasted from mid-1972 to mid-1974. This effort consisted of experimental and theoretical analysis of three derived cycles. Because GE does not work with high-temperature nuclear reactors, these cycles had an upper temperature limit of 700 °C. This program has been suspended, and GE is now working on open-loop cycles.

Cycles Published or Disclosed:

$3\text{FeCl}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$	(550°C)
$Fe_3O_4 + 8HC1 \rightarrow FeCl_2 + 2FeCl_3 + H_2O$	(110°C)
$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$	(300°C)
$Cl_2 + Mg(OH)_2 \rightarrow MgCl_2 + \frac{1}{2}O_2 + H_2O$	(800°C)
$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HC1$	(350°C)
ı	
2Cu + 2HCl → 2CuCl + H ₂	(100°C)
4CuCl → 2CuCl ₂ + 2Cu	(100°C)
2CuCl ₂ → 2CuCl + Cl ₂	(600°C)
$Cl_2 + Mg(OH)_2 \rightarrow MgCl_2 + H_2O + \frac{1}{2}O_2$	(80°C)

GENERAL ELECTRIC COMPANY, Cont.

$3I_2 + 6LiOH \rightarrow 5LiI + LiIO_3 + 3H_2O$	(140°C)
LiIO ₃ + KI → KIO ₃ + LiI	(0°C)
$KIO_3 \rightarrow KI + \frac{3}{2}O_2$	(-650°C)
6LiI + 6N ₂ O → 6HI + 6LiOH	(525°C)
$6HI + 3Ni \rightarrow 3NiI_2 + 3H_2$	(150°C)
3NiI ₂ → 3Ni + 3I ₂	(700°C)

- 1. Abstract No. 227 in Proc. 146th Electrochem. Soc. Meet. 74-2, October 1974.
- 2. "GE Progress Could Make Cheaper H₂," Chem. Eng. News 46, 48 (1968) November 4.
- 3. Hanneman, R. E., Vakil, H. and Wentorf, R. H., Jr., "Closed Loop Chemical Systems for Energy Transmission, Conversion, and Storage." Paper presented at the Ninth IECEC Conference, 1974.
- 4. Interrante, L. Y. and Wentorf, R. H., Jr., "Closed-Cycle Thermochemical Production of Hydrogen and Oxygen," U.S. Patent 3,821,358 (1973) February 1.
- 5. Wentorf, R. H., Jr., "Closed-Cycle Thermochemical Process for the Decomposition of Water," U.S. Patent 3,839,550 (1973) June 28.
- Wentorf, R. H., Jr., and Hanneman, R. E., "Thermochemical H₂ Generation. Paper presented at the ACS Meeting and Hydrogen Fuel Symposium, August 1973; published in Science 185, 311-19 (1974) July 26.

HOLIFIELD NATIONAL LABORATORIES (Formerly Oak Ridge National Laboratories)

Location: P.O. Box X

Oak Ridge, TN 37830 (615-483-8611)

Sponsor: ERDA

Program Duration as of January 1975: 2 years

Principal Investigator: C. Bamberger

Program Description: This program is geared towards deriving closed-loop thermochemical cycles. The exact nature of the cycles developed at Oak Ridge are considered proprietary and have not been published. Six or seven patents have been applied for thus far. In addition, experimental trials of individual reaction steps are included in this program.

Cycles Published or Disclosed: None

INSTITUTE OF GAS TECHNOLOGY

Location: 3424 South State St. Chicago, II, 60616

Chicago, IL 60616 (312-225-9600)

Sponsor: A.G.A.

Program Duration as of January 1975: 3-1/2 years

Principal Investigators: J. Pangborn and J. Sharer

Program Description: The program at IGT involves cycle derivation, laboratory testing, and thermodynamic efficiency analysis. A large number of potential cycles have been derived and screened by a sophisticated thermodynamic analysis and by laboratory trials of individual reaction steps and sequences of steps using recycled materials. Several cycles have been evaluated as both workable and efficient. Kinetic studies are under way for these processes.

Cycles Published or Disclosed:

 $2Cu + 2HC1 \rightarrow 2CuC1 + H_2$ $4CuC1 \rightarrow 2Cu + 2CuC1_2$ $2CuC1_2 \rightarrow 2CuC1 + C1_2$ $C1_2 + H_2O \rightarrow 2HC1 + \frac{1}{2}O_2$ $Cd + 2H_2O \rightarrow Cd(OH)_2 + H_2$ $Cd(OH)_2 \rightarrow CdO + H_2O$ $CdO \rightarrow Cd + \frac{1}{2}O_2$

Fe₃O₄ + 2H₂O + 3SO₂
$$\rightarrow$$
 3FeSO₄ + 2H₂
3FeSO₄ \rightarrow ³/₂Fe₂O₃ + ³/₂SO₂ + ³/₂SO₃
³/₂Fe₂O₃ + ¹/₂SO₃ \rightarrow Fe₃O₄ + ¹/₂SO₃
2SO₃ \rightarrow 2SO₂ + O₂

INSTITUTE OF GAS TECHNOLOGY, Cont.

$$H_2O + Cl_2 \rightarrow 2HC1 + \frac{1}{2}O_2$$

$$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$$

$$Fe_3O_4 + \frac{9}{2}Cl_2 \rightarrow 3FeCl_3 + 2O_2$$

$$3FeCl_3 \rightarrow 3FeCl_2 + \frac{3}{2}Cl_2$$

$$3FeCl_2 + 3H_2 \rightarrow 3Fe + 6HC1$$

$$6HC1 + \frac{3}{2}O_2 \rightarrow 3H_2O + 3Cl_2$$

Fe +
$$H_2O \rightarrow FeO + H_2$$

$$3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$

Chemonuclear Reactor

O₂ Separation

- 1. Gregory, D. P., "The Hydrogen Economy." Paper submitted to Sci. Am., March 1972.
- Gregory, D. P., "A Hydrogen-Energy System." Paper presented to the American Chemical Society Annual National Meeting - Symposium on Nonfossil Chemical Fuels, Boston, April 9-14, 1972; also in <u>Am. Chem. Soc.</u> <u>Div. Fuel Chem. Proc.</u> 16, 88-94 (1972) April.

INSTITUTE OF GAS TECHNOLOGY, Cont.

- 3. Gregory, D. P., "Status of R&D Related to the Production, Transportation, and Utilization of Hydrogen as a Fuel." Statement prepared for the U.S. House of Representative Committee on Science and Astronautics, Washington, D. C., June 1972.
- 4. Gregory, D. P., "Technical Problems Facing the Hydrogen Economy." Paper presented at The Hydrogen Economy Miami Energy (THEME) Conference, Miami, March 18-20, 1974.
- 5. Gregory, D. P., "Hydrogen A Gaseous Fuel From Nuclear Energy." Testimony presented before the Federal Energy Administration Project Independence Public Hearings on Nuclear Energy and Advanced Energy Systems in U.S. Energy Developments, Chicago, Sept. 9-13, 1974.
- 6. Pangborn, J. B., "Thermochemical Cracking of Water." Remarks to the Cornell University Symposium and Workshop on "The Hydrogen Economy," August 21, 1973.
- 7. Pangborn, J. B., "Thermo-Electrochemical Process for Producing Hydrogen and Oxygen From Water," U.S. Patent 3,907,980 (1975) September 23.
- 8. Pangborn, J. B., and Sharer, J. C. "Analysis of Thermochemical Water-Splitting Cycles." Paper presented at The Hydrogen Economy (THEME) Conference, Miami, March 18-20, 1974.
- 9. Pangborn, J. B., and Gregory, D. P., "Nuclear Energy Requirements for Hydrogen Production From Water." Paper presented at the Ninth IECEC, San Francisco, August 26-30, 1974.
- 10. Pangborn, J. B., and Gregory, D. P., "Evaluation of Thermochemical Hydrogen and Oxygen Formation From Water." Paper presented at the BNES International Conference on the HTR and Process Applications, London, November 26-28, 1974.
- 11. Von Fredersdorff, C. G., "Non-Fossil Fuel Process for Production of Hydrogen and Oxygen," U.S. Patent 3,802,993 (1971) December 27.

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8/75

IOWA STATE UNIVERSITY

Location: Ames Laboratory USAEC

Iowa State University Ames, Iowa 50010 (515-294-4111) Sponsor: ERDA

Program Duration as of January 1975: 6 months

Principal Investigator: D. L. Ulrichson

<u>Program Description:</u> This program is deriving potential thermochemical cycles and evaluating them on thermodynamic and kinetic bases. Some experimental work on reaction kinetics is also under way. Details of this program are currently unavailable.

Cycles Published or Disclosed:

$$12H_2O + 2EuCl_2 + 2HC1 \rightarrow 2EuCl_3 \cdot 6H_2O + H_2$$

$$2EuCl_3 \rightarrow 2EuCl_2 + Cl_2$$

$$Cl_2 + H_2O \rightarrow 2HC1 + \frac{1}{2}O_2$$

K.F.A. (NUCLEAR RESEARCH CENTER) - JÜLICH

Location: Jülich Nuclear Research Center Sponsor: West German Gov-Jülich, W. Germany ernment

Program Duration as of January 1975: Unknown

Principal Investigator: H. Barnert

Program Description: This program is concentrated on problems associated with the chemical process — nuclear reactor interface. In addition, they also have derived and evaluated the efficiency of some close-loop thermochemical cycles. Most of this latter work seems to be done in connection with the EURATOM efforts at Ispra, Italy, and at the University at Aachen, W. Germany. Cycles and laboratory work have not been published.

Cycles Published or Disclosed: None

- 1. Barnert, H., "Fundamentals of Thermochemical Cyclic Processes,"

 NRC Rep. No. JUL-967-RG. Jülich, W. Germany: Institute for Reactor Development, KFA, June 1973.
- 2. Barnert, H., "Thermochemical and Nuclear Technology for Nuclear Water-Splitting." Paper presented at the Cornell International Symposium and Workshop on the Hydrogen Economy, Cornell University, Itranco, August 1973.
- 3. Barnert, H., "Nuclear Water-Splitting," Atomwietschaft, 408-10 (1973) August September.
- 4. Barnert, H., and Schulten, R., "Nuclear H₂O Splitting and High Temperature Reactors." Paper No. <u>53-1</u> presented at the THEME Conference, Miami, March 1974.
- 5. Schulten, R., Von der Decken, C. and Barnert, H., "Nuclear Water Splitting by Heat From the Pebble Bed HTR." Paper presented at the BNS Conference, London, November 1974.

KMS FUSION, INCORPORATED

Location: P.O. Box 1467

Ann Arbor, MI 48106 (313-769-8500)

Sponsor: Texas Gas Transmission Co.

Program Duration as

of January 1975: Unknown

Principal Investigator: K. Siegal

<u>Program Description</u>: This program deals with the production of hydrogen and oxygen from water via a series of chemical reactions. This process is proprietary, and little information could be obtained. A "chemical mist" is bombarded with neutrons and radiation from a fusion reactor. All chemicals are recycled within the process.

Cycles Published or Disclosed: None

Publications and Patents:

Siegel, K. M., "Laser Fusion, Inflation and Project Independence," testimony at FEA Public Hearings, September 1974.

LAWRENCE LIVERMORE LABORATORIES (University of California)

Location: P.O. Box 808

Livermore, CA 94550

Sponsor: ERDA

(415-447-1100)

Program Duration as of January 1975: 1/2 year

Principal Investigator: O. H. Kirkorian

Program Description: Lawrence Livermore Labs is concentrating on the derivation and laboratory testing of several low-temperature (<700°C) cycles. Although thermodynamic analysis of their cycles is lacking, an attempt at purely chemical descriptions of individual reaction steps is in progress.

Cycles Published or Disclosed:

$K_2Se(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2Se(g)$	(100°C)
$H_2Se(g) \rightarrow N_2(g) + Se(s)$	(200°C)
$^{3}/_{2}Se(l) + 2KOH(l) \rightarrow K_{2}Se(s) + ^{1}/_{2}SeO_{2}(g) + H_{2}O(g)$	(700°C)
$V_2O_4(s) + \frac{1}{2} SeO_2(l) \rightarrow V_2O_5(s) + \frac{1}{2} Se(l)$	(327°C)
$V_2O_5(s) \rightarrow V_2O_4(s) + \frac{1}{2}O_2(g)$	(500°C)
·	
$2CsOH(l) + (x+1) O_2(g) \rightarrow CsOx + H_2O(g)$	(410°C)
$CsOx(s) + (x + y) Hg(l) \rightarrow Cs Hg(l) + x HgO(s)$	(300°C)
$HgO(s) \rightarrow Hg(g) + \frac{1}{2}O_2(g)$	(477°C)
$CsHgy(l) + H_2O(g) \rightarrow yHg(l) + CsOH(l) + I_2H_2(g)$	(320°C)
$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$	(700°C)
$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$	(230°C)
$CH_2OH(g) + As_2O_4(s) \rightarrow CH_4(g) + As_2O_5(s)$	(227°C)
$^{1}/_{2} \text{As}_{2}\text{O}_{5}(g) \rightarrow ^{1}/_{2} \text{As}_{2}\text{O}_{3}(g) + ^{1}/_{2} \text{O}_{2}(g)$	(700°C)
$^{1}/_{2} As_{2}O_{5}(g) + ^{1}/_{2} As_{2}O_{3}(l) \rightarrow As_{2}O_{4}(g)$	(450°C)

LAWRENCE LIVERMORE LABORATORIES, Cont.

- 1. Dreyfuss, R. and Krikorian, O. H., "Exploration of Selium-Based Cycles for the Thermochemical Production of Hydrogen From Water," LLL Rep. No. USRL-51741, February 1975.
- 2. Hechman, R. G., Krikorian, O. H. and Ramsey, W. J., "Thermochemical Hydrogen Production at Lawrence Livermore Laboratory." Paper presented at THEME Conference, Miami, March 1974.

LOS ALAMOS SCIENTIFIC LABORATORY

Location: University of California

P.O. Box 1663

Sponsor: ERDA

Los Alamos, NM 87544 (505-667-6014)

Program Duration as

of January 1975: Started November

1973

Principal Investigators: M. G. Bowman and J. D. Farr

Program Description: The Program at LASL incorporates a balance between theoretical and experimental work on a variety of closed-loop thermochemical cycles. The chemical reaction steps of two cycles are reported to have been demonstrated experimentally. Additional cycles are being developed, and they are starting an engineering study on one of these cycles. LASL has one of the few programs also studying the feasibility of hybrid thermochemical - electrochemical cycles.

Cycles Published or Disclosed:

1. Oxide-Sulfate Cycles

$$SO_2(g) + H_2O(l) + MO \rightarrow MSO_4 + H_2(g)$$

$$MSO_4 \rightarrow MO + SO_2(g) + \frac{1}{2}O_2(g)$$
(where $M = a \text{ metal}$)

2. Complex Oxide-Sulfate Cycles

$$SO_2 + xH_2O + BaMoO_4 \rightarrow BaSO_3 + MoO_3 *xH_2O$$

$$BaSO_3 + H_2O \rightarrow BaSO_4 + H_2$$

$$BaSO_4 + MoO_3 \rightarrow BaMoO_4 + SO_2 + \frac{1}{2}O_2$$

3. Bromide-Sulfate Cycles

$$SO_2(g) + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr$$
 (70-100°C)
 $H_2SO_4 \rightarrow H_2O + SO_2 + {}^1/{}_2 O_2$ (~800°C)
 $2RBr_x + 2HBr \rightarrow 2RBr_{(x+1)} + H_2$ (low temp.)
 $2RBr_{(x+1)} \rightarrow 2RBr_x + Br_2$ (high temp.)

LOS ALAMOS SCIENTIFIC LABORATORY, Cont.

4. Oxide-Carbonate Cycles

$$U_3O_8 + H_2O + 3CO_2 \rightarrow 3UO_2CO_3 + H_2$$
 (at low temperature)
 $3UO_2CO_3 \rightarrow 3UO_3 + 3CO_2$ (at intermediate temperature)
 $3UO_3 \rightarrow U_3O_8 + \frac{1}{2}O_2$ (at high temperature)

5. Complex Oxide Cycles

$$6NaOH(l) + 2Mn3O4 + 6NaMnO2 + 2H2O + H2$$
 (800-1000 K)

$$6NaMnO2 + 3H2O(l) + 6NaOH(aq.) + 3Mn2O3$$
 (300-400 K)

$$6NaOH(aq.) + 6NaOH(c)$$
 (400-450 K)

$$3Mn2O3 + 2Mn3O4 + 1/2 O2$$
 (1100-1300 K)

In this category are 2 cycles they have demonstrated experimentally:

$$3\text{Li}_2\text{CO}_3 + \text{H}_2\text{O} + 2\text{Mn}_3\text{O}_4 \rightarrow 6\text{LiMnO}_2 + \text{H}_2 + 3\text{CO}_2$$

 $6\text{LiMnO}_2 + 6\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow 6\text{LiHCO}_3(\text{aq.}) + 3\text{Mn}_2\text{O}_3$
 $6\text{LiHCO}_3(\text{aq.}) \rightarrow \text{Li}_2\text{CO}_3(\text{s}) + 3\text{CO}_2 + 3\text{H}_2\text{O}$
 $3\text{Mn}_2\text{O}_3 \rightarrow 2\text{Mn}_3\text{O}_4 + \frac{1}{2}\text{O}_2$

$$Sr_2UO_4 + 2Sr(OH)_2 \stackrel{550}{=}^{\circ} (SrO)_3$$
 · $SrUO_4 + H_2O + H_2$
 $(SrO)_3$ · $SrUO_4 \stackrel{leach}{=}^{\circ} SrO$ · $SrUO_4 + 2Sr(OH)_2$
 $SrO \cdot SrUO_4 \stackrel{600}{=}^{\circ} C Sr_2UO_4 + \frac{1}{2}O_2$ ·

6. Combined Work Plus Heat Cycles

$$SO_2 + 2H_2O(l) \rightarrow H_2SO_4(aq) + H_2(g)$$

 $H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2}O_2$ Electrolysis, thermal

or

$$SO_2(g) + Br_2(g) + 2H_2O(l \text{ or } g) \rightarrow H_2SO_4 + 2HBr$$
 (70°-100°C)
 $H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2}O_2$ Electrolysis, thermal
 $2HBr \rightarrow H_2 + Br_2$

LOS ALAMOS SCIENTIFIC LABORATORY, Cont.

$$2Cu + 2HBr \rightarrow 2CuBr + H_{2}$$

$$4CuBr + 2A \rightarrow 2Cu + 2CuABr_{2}$$

$$2CuABr_{2} + SO_{2} + SO_{2} + 2H_{2}O \rightarrow 2CuBr + A. (HBr)_{2} + A. H_{2}SO_{4}$$

$$A. (HBr)_{2} + H_{2}SO_{4} \rightarrow A. H_{2}SO_{4} + 2HBr$$

$$2A. H_{2}SO_{4} + MgO \rightarrow 2A + 2MgSO_{4} + 2H_{2}O$$

$$2MgSO_{4} \rightarrow 2MgO + SO_{2} + SO_{3} + \frac{1}{2}O_{2}$$

$$SO_{3} + H_{2}O \rightarrow H_{2}SO_{4}$$

A chemical complexing agent

7. Electrolysis With Cu as Anodic Depolarizer

$$2CuSO_{4}^{1100} \stackrel{K}{\sim} 2CuO + 2SO_{3}$$

$$2CuO^{1350} \stackrel{K}{\sim} Cu_{2}O + {}^{1}/_{2} O_{2}$$

$$2SO_{3} + 2H_{2}O^{365} \stackrel{K}{\sim} 2H_{2}SO_{4}$$

$$Cu_{2}O + H_{2}SO_{4}^{365} \stackrel{K}{\sim} CuSO_{4} + Cu + H_{2}O$$

$$Cu + 4HBr^{365} \stackrel{K}{\sim} H_{2}CuBr_{4} + H_{2}$$

$$H_{2}CuBr_{4} + H_{2}SO_{4}^{500} \stackrel{K}{\sim} CuSO_{4} + 4HBr$$

- 1. Balcomb, J. D., "Hydrogen Production Economics." Paper presented at the Cornell International Symposium on the Hydrogen Economy, Ithaca August 1973.
- 2. Balcomb, J. D. and Booth, L. A., "High Temperature Nuclear Reactors as an Energy Source for H₂ Production." Paper No. S3-15 presented at THEME Conference, Miami, March 1974.
- 3. Bowman, M. G., "Thermochemical Production of Hydrogen From Water," Q. Rep. No. <u>LA-5731-PR</u>. Los Alamos, N. M.; Los Alamos Scientific Laboratories, April 1-June 30, 1974.
- 4. Bowman, M. G., "Fundamental Aspects of Systems for the Thermochemical Production of Hydrogen From Water." Paper presented at the First National Topical Meeting on Nuclear Process Heat Applications, Los Alamos, N. M., October 1974.
- 5. "Hydrogen Production by Low Voltage Electrolysis in Combined Thermochemical and Electrochemical Cycles." Paper presented at the 146th Meeting of the Electrochemical Society, New York, October 1974.

PECHINEY UGINE KUHLMANN

Location: Paris, France

Sponsor: In-house funding

Program Duration as of January 1975: Unknown

Principal Investigator: F. Foley

Program Description: We have very little indication as to of what this program consists. Their presentation at the Miami THEME Conference in March 1974 indicates an effort to develop economic criteria for various thermochemical cycles proposed by others.

Cycles Published or Disclosed: None

Publications and Patents:

Joley, F., "Economic Criteria of Selection for Closed-Cycle Thermochemical H₂O Splitting Processes." Paper presented at the THEME Conference, Miami, March 1974.

STEVENS INSTITUTE OF TECHNOLOGY

Location: Castle Point Station Hoboken, N.J.

Hoboken, N.J. (201-792-2700)

Sponsor: U.S. Navy

Program Duration as

of January 1975: 9 months — not ongoing

Principal Investigator: R. F. Mc Chevely III

<u>Program Description:</u> This program is an engineering study of the technical problems expected with the large-scale introduction of hydrogen as a fuel. Included in the study is an evaluation prepared by R. S. Magee, of the potential of hydrogen production by thermochemical processes employing nuclear heat sources.

Cycles Published or Disclosed: None

Publications and Patents:

"Hydrogen as a Fuel," Semiannual technical report, Contract No. N00014-67-A-0202-0046. Hoboken, N.J.: Stevens Institute, January-June 1974.

"SUNSHINE" PROGRAM - JAPAN

Location: c/o Dr. Ohta

University of Tokyo Tokyo, Japan Sponsor: Japanese Ministry of

International Trade and

Industry

Program Duration as

of January 1974: Started 1974

Principal Investigator: Dr. Ohta

Program Description: The Japanese have started what appears to be a major effort on thermochemical hydrogen production as part of a comprehensive "Sunshine" energy research program. Specific details on this program are currently unavailable, but our best estimate is that most of their effort is concerned with methods of cycle derivation and evaluation.

Cycles Published or Disclosed:

 $H_2O + Cl_2 \rightarrow 2HCl + \frac{1}{2}O_2$ $2HCl + 2 TaCl_2 \rightarrow 2 TaCl_5 + H_2$ $2TaCl_5 \rightarrow 2TaCl_2 + Cl_2$

 $H_2O + Cl_2 \rightarrow 2HCl + \frac{1}{2}O_2$ $2HCl + 2CrCl_2 \rightarrow 2CrCl_3 + H_2$ $2CrCl_3 \rightarrow 2CrCl_2 + Cl_2$

- 1. Fueri, K., "Application of Free Energy Diagrams to Thermochemical Processes,"
- 2. Kameyama, H., Yoshida, K. and Kunii, D. S., "First Judgement of Thermochemical Decomposition Processes of H₂O Based on the ΔC° Diagram." Paper presented at the 39th Annual Meeting of the Chemical Engineering Society of Japan, 1974.

UNIVERSITY OF KENTUCKY

Location: Dean, College of Engineering

Sponsor: NASA - Lewis

University of Kentucky Lexington, KY. 40506 (606-257-1688)

Program Duration as of January 1975: 2 years

Principal Investigator: J. E. Funk

<u>Program Description</u>: The program sponsored by NASA-Lewis involves the development of a computer program to assess energy efficiencies of thermochemical cycles. This computer program (HYDRN) is currently on-line. Publications have also included the results of cycle derivation efforts at the University of Kentucky.

Laboratory work is planned for their 1975 program. Also in progress is work on a subcontract for Westinghouse to investigate and evaluate the system —

1. Mg(A)

$MgO(s) + SO_2 + H_2O + S(1) \rightarrow MgSO_4(s) + H_2S$	(500°K)
$MgSO_4(s) \rightarrow MgO(s) + SO_2 + 0.5 O_2$	(1400°K)
$H_2S \rightarrow H_2 + S$	(1300°K)

2. Mg(B)

3. Zn-Ba

0. 25BaS(s) +
$$H_2O \rightarrow 0.25BaSO_4(s) + H_2$$
 (500°K)
0. 25BaSO₄(s) + 0.5S \rightarrow 0. 25BaS(s) + 0.5SO₂ (1400°K)
 $ZnO(s) + 1.5SO_2 \rightarrow ZnSO_4(s) + 0.5S(1)$ (500°K)
 $ZnSO_4(s) \rightarrow ZnO(s) + SO_2 + 0.5O_2$ (1300°K)

(1300°K)

4. Zn-Ca(A)

0.
$$25CaS(s) + S(1) + H_2O \rightarrow 0.25CaSO_4(s) + H_2S$$
 (500 °K)
0. $25CaSO_4(s) + 0.5S \rightarrow 0.25CaS(s) + 0.5SO_2$ (1400 °K)
 $H_2S + 0.67Bi(s) \rightarrow 0.33Bi_2S_3(s) + H_2$ (500 °K)
0. $33Bi_2S_3(s) \rightarrow 0.67Bi(1) + S$ (1000 °K)

$$ZnO(s) + 1.5SO_2 \rightarrow ZnSO_4(s) + 0.5S(1)$$
 (500°K)

$$ZnSO_4(s) \rightarrow ZnO(s) + SO_2 + 0.5O_2$$

5. Zn(A)

$$H_2O + 1.5S \rightarrow H_2S + 0.5SO_2$$
 (850°K)
 $H_2S \rightarrow H_2 + S$ (1300°K)
 $ZnO(s) + 1.5SO_2 \rightarrow ZnSO_4(s) + 0.5S(1)$ (550°K)
 $ZnSO_4(s) \rightarrow ZnO(s) + SO_2 + 0.5O_2$ (1300°K)

6. Zn-Ca(B)

7. Zn(B)

$$2H_2O + 3S \rightarrow 2H_2S + SO_2$$
 (850°K)
 $H_2S \rightarrow H_2 + S$ (1300°K)
 $ZnS(s) + 2SO_2 \rightarrow ZnSO_4(s) + 2S(1)$ (500°K)
 $ZnSO_4(s) \rightarrow ZnO(s) + SO_2 + 0.5O_2$ (1100°K)
 $ZnO(s) + H_2S \rightarrow ZnS(s) + H_2O$ (600°K)

8. Fe-Ba

0.
$$25BaS(s) + H_2O \rightarrow 0.25BaSO_4(s) + H_2$$
 (500°K)
0. $25BaSO_4(s) + 0.5S \rightarrow 0.25BaS(s) + 0.5SO_2$ (1400°K)
 $Fe_2O_3(s) + 2.5SO_2 \rightarrow 2FeSO_4(s) + 0.5S(1)$ (600°K)
 $2FeSO_4(s) \rightarrow Fe_2O_3(s) + SO_2 + SO_3$ (1000°K)
 $SO_3 \rightarrow SO_2 + 0.5O_2$ (1300°K)

9. Fe-Ca

$0.25CaS(s) + S(1) + H_2O \rightarrow 0.25CaSO_4(s) + H_2S$	(500°K)
$0.25CaSO_4(s) + 0.5S \rightarrow 0.25CaS(s) + 0.5SO_2$	(1400°K)
$Fe_2O_3(s) + 2.5SO_2 \rightarrow 2FeSO_4(s) + 0.5S(1)$	(600°K)
$2\text{FeSO}_4(s) \rightarrow \text{Fe}_2\text{O}_3(s) + \text{SO}_2 + \text{SO}_3$	(1000°K)
$H_2S + 0.667 Bi(s) \rightarrow 0.333 Bi_2S_3(s) + H_2$	(500°K)
$0.333 \text{Bi}_2 \text{S}_3(s) \rightarrow 0.667 \text{Bi}(1) + \text{S}$	(1000°K)
$SO_2 \rightarrow SO_2 + 0.5O_2$	(1300°K)

10. Fe(A)

$$H_2O + 1.5S \rightarrow H_2S + 0.5SO_2$$
 (800°K)
 $H_2S \rightarrow H_2 + S$ (1300°K)
 $Fe_2O_3(s) + 2.5SO_2 \rightarrow 2FeSO_4(s) + 0.5S(1)$ (400°K)
 $2FeSO_4(s) \rightarrow Fe_2O_3(s) + SO_2 + SO_3$ (940°K)
 $SO_3 \rightarrow SO_2 + 0.5O_2$ (1300°K)

11. Fe(B)

$$4H_2O + 6S \rightarrow 4H_2S + 2SO_2$$
 (850°K)

$$Fe_2O_3(s) + 4H_2S \rightarrow 2FeS_2(s) + 3H_2O + H_2$$
 (600°K)

$$2FeS_2(s) + 4SO_2 \rightarrow 2FeSO_4(s) + 6S(1)$$
 (500°K)

$$2FeSO_4(s) \rightarrow F2_2O_3(s) + SO_3 + SO_2$$
 (1000°K)

$$SO_3 \rightarrow SO_2 + 0.5O_2$$
 (1300°K)

12. Cd

$$H_2O + 1.5S \rightarrow H_2S + 0.5SO_2$$
 (850°K)
 $H_2S + Cd$) s) $\rightarrow CdS(s) + H_2$ (500°K)
0. 33 $CdO(s) + 0.67CdS(s) + 1.83SO_2$
 $\rightarrow CdSO_4(s) + 1.5S(1)$ (500°K)
 $CdSO_4(s) \rightarrow CdO(s) + SO_2 + 0.5O_2$ (1300°K)
0. 67CdO(s) + 0.33Cd) s) $\rightarrow Cd + 0.33SO_2$ (1300°K)

13. Cd(B)

$$H_2O + Cd(s) \rightarrow CdO(s) + H_2$$
 (400 °K)
1.33 CdO(s) + 1.33 SO₂ \rightarrow CdSO₄(s) + 0.33CdS(s) (500 °K)
CdSO₄(s) \rightarrow CdO(s) + SO₂ + 0.5O₂ (1300 °K)
0.67CdO(s) + 0.33CdS(s) \rightarrow Cd + 0.33SO₂ (1300 °K)

14. Vanadium Chloride Process

$H_2O + Cl_2 \rightarrow 2HCl + \frac{1}{2}O_2$	(1340°F)
$2HC1 + 2VC1_2 \rightarrow 2VC1_3 + H_2$	(77°F)
$4\text{VCl}_3 \rightarrow 2\text{VCl}_2 + 2\text{VCl}_4$	(1340°F)
$2VCl_4 \rightarrow 2VCl_3 + Cl_2$	(77°F)

- 1. Funk, J. E., "Thermodynamics of Multi-Step H₂O Decomposition Processes," Research Report. G. M.'s Allison Division, Indianapolis, Ind., July 1966.
- 2. Funk, J. E., "Evaluation of Multi-Step Thermochemical Processes for the Production of H₂ From H₂O." Paper No. S11-1 presented at THEME Conference, Miami, March 26-30, 1974.
- 3. Funk, J. E., University of Kentucky, letter of October, 1974.
- 4. Funk, J. E., "The Generation of H₂ by the Thermal Decomposition of H₂O." Paper presented at the Ninth IECEC, San Francisco, 1974.
- 5. Funk, J. E., Congar, D. L., Carty, R. H. and Barker, R. E., "Thermochemical Production of H₂ From Water." Paper presented at the BNS Conference, London, November 1974.
- 6. Soliman, M. A., Carty, R. H., Congar, W. L. and Funk, J. E., "New Thermochemical Cycles for Hydrogen Production," to be published in Can. J. Chem. Eng.

UNIVERSITY OF NEW MEXICO

Location: Energy Information Center

University of New Mexico Albuquerque, New Mexico Sponsor: NASA

87131

<u>of January 1975:</u> Program ended January 1974.

Principal Investigator: K. E. Cox.

Program Description: The objective of this program was to compile a complete bibliography (1953 to 1973) with abstracts on hydrogen production, utilization, transmission, storage, distribution, and safety. Actual compilation was done by the Technology Application Center for the Energy Information Center at the University of New Mexico. Also, Dr. Cox has written on the topic of cycle analysis and evaluation.

Cycles Published or Disclosed: None

- 1. Cox, K. and Chao, R. E., "An Analysis of Hydrogen Production Via Closed-Cycle Schemes." Paper presented at THEME Conference, Miami, March 1974.
- 2. Hydrogen Energy, Cox, K., Ed. University of New Mexico, Albuquerque, January 1974.

UNIVERSITY OF PUERTO RICO

Location: Dept. of Chemical Engineering

University of Puerto Rico Mayaguez, Puerto Rico 00708 Sponsor: NASA

Program Duration as of January 1975: 2 years

Principal Investigator: R. E. Chao

Program Description: This program consisted of a survey of various thermochemical schemes presented by other sources up to 1973. The program was begun while Dr. Chao was under contract to NASA at Johnson Space Center in Houston. A theoretical analysis of thermal efficiencies for proposed thermochemical processes is included in the survey and compared with water electrolysis.

Cycles Published or Disclosed: None

- 1. Chao, R. E., "Thermochemical Water Decomposition Processes," Ind. Eng. Chem. Prod. Res. Dev., 13, 94-101 (1974).
- 2. Chao, R. E. and Cox, K. E., "An Analysis of Hydrogen Production Via Closed-Cycle Schemes." Paper presented at THEME Conference, Miami, March 26-30, 1974.

WESTINGHOUSE ELECTRIC CORPORATION

Location: Beulah Road, Churchill Boro

Pittsburg, PA 15235

(412-256-7000, ext. 5039)

Sponsor: In-house,

Now NASA-Lewis

Program Duration as

of January 1975: Unknown

Principal Investigator: L. E. Brecher

Program Description: This program with NASA is getting under way, and no specific information has yet been generated. The work at Westinghouse is designed to evaluate one cycle. The program is to include laboratory trials and an engineering flowsheeting in order to eventually generate a complete economic analysis of this process.

Cycles Published or Disclosed:

$$2H_2O + SO_2 \rightarrow H_2SO_4 + H_2$$
 (electrolysis)
 $H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2}O_2$ (875°C)

(Cycle was detailed in a private communication with J. Sharer, January 1975.)

GAZ de FRANCE

Location: Paris, France

Sponsor: In-house funding

Program Duration as of January 1975: Unknown

Principal Investigators: J. Pottier and D. Souriau

Program Description: Gaz de France and Electricité de France have started a comprehensive program to research a hydrogen aconomy. Gaz de France's tasks include thermochemical water splitting. Subcontracts to study such reactions have already been awarded to three universities. Present efforts include cycle derivation, thermodynamic analysis, experimental reaction trials, corrosion problems, and hydrogen energy system economics. This is a relatively new effort.

Cycles Published or Disclosed:

$Sn + 2H_2O \rightarrow 2H_2 + SnO_2$	(400°C)
$2SnO_2 \rightarrow 2SnO + O_2$	(1700°C)
$2SnO \rightarrow SnO_2 + Sn$	(700°C)
$K_2O_2 + H_2O \rightarrow 2KOH + \frac{1}{2}O_2$	(400°C)
$2KOH + 2K \rightarrow 2K_2O + H_2$	(700°C)
$2K_2O \rightarrow K_2O_2 \div 2K$	(1000°C)

- 1. Pottier, J. and Souriau, D., "Chemical Cycles Studied by Gaz de France for Production of Nuclear Hydrogen as a Future Energy Vector." Paper presented at the BNS Conference, London, November 1974.
- 2. Souriau, D., "Method and Device for the use of High Temperature and Heat Energy, in Particular of Nuclear Origin," U.S. Patent 3, 761, 352 (1972) May.

GENERAL ATOMIC COMPANY

Location: P. O. Box 81608
San Diego, CA 92138
(714-455-2903)

Sponsor: NASA-Lewis, N.E. Utilities
Service Co., So. Cal. Edison Co.
Co.

Program Duration as of January 1975: 2-1/2 years

Principal Investigator: J. L. Russell

Program Description: The main effort at General Atomic (sponsored by N.E. Utilities Service Co., and So. Cal. Edison Co.) has been the derivation of potential thermochemical cycles via a computer program. Manual sorting of 3 X 10⁶ cycles has left them with 4 cycles (unpublished) that they consider most promising. Some experimental work and engineering studies are under way. In addition, NASA-Lewis has contracted a short assessment of thermochemical feasibility to General Atomic.

Cycles Published or Disclosed: None

- 1. Quade, R. N. and McMain, A. J., Jr., "H₂ Production With an HTGR." Paper No. S3-21 presented at the THEME Conference, Miami, March 1974.
- 2. Russel, J. L., Jr., and Porter, J. T., "A Search for Thermochemical H₂O-Splitting Cycles." Paper No. <u>Sll-49</u> presented at the THEME Conference, Miami, March 1974.